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# Monitoring of a drying process in polymer water solutions by dynamic speckle detection

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Observation of speed of processes by dynamic speckle analysis has been applied to different samples of industrial or biological nature. The method allows for indicating regions of lower or higher activity on the sample surface through statistical processing of the speckle patterns formed on this surface under laser illumination. The aim of the paper is to check applicability of dynamic speckle technique for detection of the drying process in polymer water solutions. For the purpose, we recorded several sets of 256 correlated in time speckle patterns of a transparent drop of PAZO water solution on a glass plate illuminated by a He-Ne laser. The sets were separated by intervals of 5 minutes, and the last set was recorded 75 minutes after the start of the experiment. For statistical description of activity on the observed sample we chose evaluation of a temporal structure function. The obtained two-dimensional maps of the structure function at different time lags demonstrated efficiency of dynamic speckle analysis for monitoring of drying processes in polymer water solutions.

**Keywords:** polymer, drying, dynamic speckle analysis

## INTRODUCTION

Non-destructive detection of physical or biological activity through statistical processing of speckle patterns on the surface of diffusely reflecting objects is gaining popularity in optical metrology. Known as dynamic laser speckle analysis, this method is sensitive to microscopic changes of the surface over time and needs simple optical means for implementation [1,2]. This technique has been applied to study blood flow perfusion in human tissues [3], bacterial response [4], plant growing processes [5], seeds viability [6], animal reproduction [7], drying of paints and coatings [8], fruits quality [9] and bread cooling [10]. Advances in two-dimensional (2D) optical sensors and computers make possible development of pointwise algorithms, which rely on acquisition of a temporal sequence of correlated speckle patterns and show activity as a 2D spatial contour map of the estimate of a given statistical measure. The most widely used pointwise estimates are the intensity-based estimates. The map entry at each point for such an estimate is composed from a time sequence of intensity values taken at one and the same pixel in the acquired speckle patterns. By building such activity maps at different moments, one may follow the undergoing processes in time.

The aim of the paper is to check applicability of dynamic speckle technique for detection of the drying process in polymer water solutions. For the purpose, we recorded several sets of 256 correlated in time speckle patterns of a transparent drop of PAZO water solution on a glass plate. Processing was performed by intensity based pointwise algorithms [11]. For statistical description of activity on the observed sample we chose evaluation of a temporal structure function [12].

## EXPERIMENTAL

In the present study, we use the azopolymer Poly[1-[4-(3-carboxy-4-hydroxyphenylazo) benzenesulfonamido]-1,2-ethanediyl, sodium salt] or shortly PAZO. The azopolymer is commercially available from Sigma Aldrich. Its chemical structure is shown in Fig. 1. An important advantage of this polymer is that it is water soluble. For our experiments water solution of PAZO with concentration C = 50 mg/ml was used. The average molecular weight of the azopolymer is Mw = 50 000−65 000 g/mol and glass transition temperature is Tg = 95 ± 5°C [13]. The parameters of the photoinduced birefringence (Δn) in thin films of PAZO and PAZO based nanocomposites have

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already been studied by our group [14, 15]. The observed high values of Δn and its very high thermal stability attracted our attention to the process of thin film formation by drying of azopolymer water solution casted on a glass substrate. This was the reason to evaluate the potential of the dynamic speckle technique to study this drying process. To the best of our knowledge, this is the first time to monitor a polymer water solution by dynamic speckle technique.

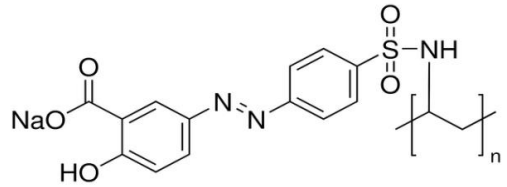


**Fig. 1**. Chemical structure of the PAZO azopolymer.

For the experiment, a drop of PAZO water solution was deposited on a glass plate. A specific feature of this sample was its transparency at the used wavelength. The plate was placed in a Petri dish. A CMOS camera with a pixel interval Δ = 7 μm was adjusted to focus the sample with its optical axis normal to the glass surface. The set-up was positioned on a vibration-insulated table. We used a He-Ne laser. The camera recorded successively a sequence of $N$ = 256 correlated images of size $N_x \times N_y = 500\,\mathrm{x}\,780$ pixels for time $T$ at a sampling rate $1/\Delta t = N/T$ with the time interval $\Delta t$ = 250 ms between the frames. Exposure time was 10 ms. A time sequence of 8-bit encoded intensities $I_{kl,n} \equiv I(k\Delta, l\Delta, n\Delta t), n = 1..N$ was formed at each pixel $(k\Delta, l\Delta), k = 1..N_x, l = 1..N_y$ of the acquired images. This data were used to build a point wise estimate of a given statistical measure over $T$. One of the captured speckle patterns is shown as a bitmap image in Fig.2. The borders of the drop and the glass plate are clearly seen. We put also a marker on the glass plate. We captured 6 sets of 256 correlated images with time offset from the start of the experiment 0, 5, 10, 15, 20 and 75 minutes.

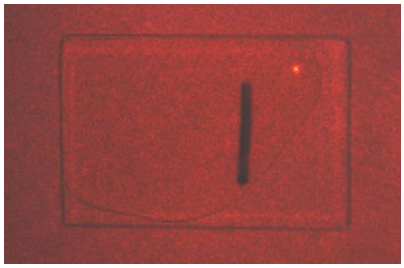

**Fig. 2.** Speckle pattern of a glass plate with PAZO water solution.

## RESULTS AND DISCUSSIONS

In order to choose a proper processing, we calculated the two-dimensional (2D) distributions of the mean value and the variance of intensity fluctuations at each point. The estimates of these two parameters were obtained from the algorithms:

$$\hat{I}_{kl} = \frac{1}{N}\sum_{i=1}^{N} I_{kl,i}\,,\ \hat{\upsilon}_{kl} = \frac{1}{(N-1)}\sum_{i=1}^{N}\left(I_{kl,i} - \hat{I}_{kl}\right)^2, \qquad (1)$$

where averaging was done for the time sequences formed from the captured images. The 2D maps of the average value at time offsets 0 and 75 minutes are shown in Fig.3. The observed distributions are not strictly uniform because of slightly non-uniform intensity distribution within the illuminating laser beam. The same is valid at all time offsets.

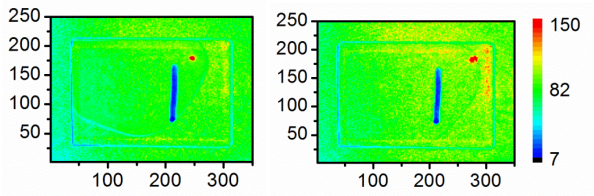


**Fig. 3.** 2D distribution of the mean value at time offsets 0 minutes (left) and 75 minutes.

Nevertheless, we chose for this first experiment a non-normalized estimate as providing better contrast of the activity map. We applied a temporal structure function. Its estimate at a time lag $\tau = m\Delta t$, where $m \geq 0$ takes integer values, is determined by

$$\hat{S}(k,l,m) = \frac{1}{N-m}\sum_{i=1}^{N-m}\left(I_{kl,i} - I_{kl,i+m}\right)^2 \qquad (2)$$

As it can be seen from Eq.(2), the structure function is zero at zero activity and full correlation. It increases with the time lag and theoretically should reach the value of the variance multiplied by 2 when there is no correlation between images. The higher the value of the structure function, the lower is the correlation and the higher is the activity within the sample. The results of applying Eq.(2) to the acquired sets of correlated images are given in Fig.4 which depicts 2D maps of the structure function at time lags $\tau = 10\Delta t$ and $\tau = 50\Delta t$. We processed all sets, but Fig.4 presents only the data corresponding to three time offsets. Several conclusions can be made from the obtained distributions. The most important result is that the dynamic speckle techniques allows for detecting the process of drying. To be sure that the observed result was due to evaporation from the drop surface, we recorded a set of 256 speckle images of a glass plate without the drop.

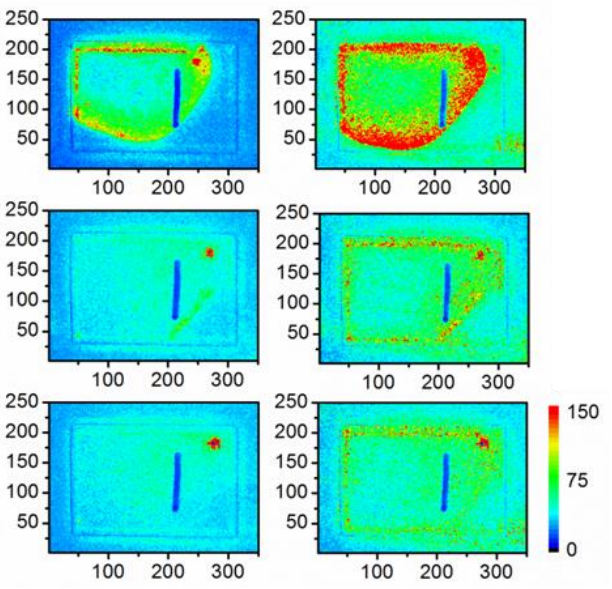


**Fig. 4.** 2D distribution of the temporal structure function at time offsets 0 minutes (top), 20 minutes (middle) and 75 minutes (bottom); left - $\tau = 10\Delta t$, right - $\tau = 50\Delta t$.

Processing of this set of images confirmed that the activity on the plate surface was the same as for the surrounding Petri dish and the values of the variance of intensity fluctuations in time were much lower. We see the change of the drop in time and much higher activity at its borders. As it should be expected, with increase in time elapsing from the start of the drying process activity within the sample is decreasing. Furthermore, the contrast of the speckle, given by the ratio between the square root of the variance and the average value of intensity fluctuations, is also decreasing. Evaporation of the drop caused also rise of activity around the glass plate. Strong variation of activity within the drop is detected at the beginning of the drying process whereas at larger time offsets activity equalizes within the drop and increases only on the borders.

To evaluate the time scale of the drying process, we found the dependence of the structure function on the time lag for the spatial region around the approximate center of the drop. For the purpose, we averaged the estimate (2) within a spatial window of 30×30 pixels. The size of the window was so chosen as to ensure relatively large number of points corresponding to uniform intensity. Speckle nature of the raw data leads to a very low spatial correlation of the estimate within the window and makes possible to obtain practically smooth curves by averaging over 900 points. The uniform intensity within the window is necessary to guarantee correct average value. The functions evaluated at three different time offsets are depicted in Fig.5. The fall of the variance is clearly seen at large time lags. For the elapsed 75 minutes it decreases more than two times. To find the time scales we normalized the obtained functions to the variance estimates (1). The result is shown in Fig.6. Judging from the normalized curves activity remains very high within the drop even after 75 minute, so the drying process is not completed yet. Actually, the steepest normalized structure function is observed at time offset 75 minutes due to decrease of the water solution in the drop and faster evaporation. We can determine the correlation radii from the formula $S_{norm}(\tau) = 2[1 - R_{norm}(\tau)]$ relating the normalized structure and correlation functions of intensity fluctuations in time [12]. If we adopt a widely used negative exponential model $R_{norm}(\tau) = \exp(-\tau/\tau_c)$ to approximate $S_{norm}(\tau)$, the correlation radii determined at level $1/e$ from for the offsets 0, 20 and 75 minutes are approximately 2 s, 3 s and 1.25 s respectively.

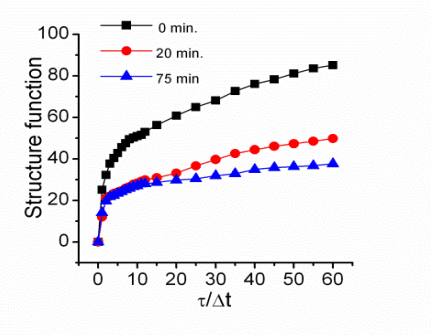


**Fig. 5** Structure function of intensity fluctuations in the center of the drop pf PAZO water solution at three time offsets.).

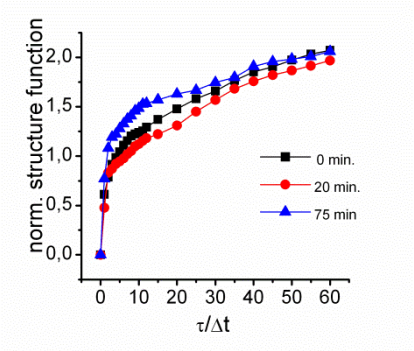


**Fig. 6.** Normalized structure function of intensity fluctuations in the center of the drop pf PAZO water solution at three time offsets.

## CONCLUSIONS

In summary, we proved by experiment that the dynamic speckle analysis could be applied for monitoring of the drying process of polymers water solutions. The method is capable to demonstrate

changes in different size drops of such solutions in time by building 2D maps of a given statistical measure that includes the tested polymer water solution sample. By following time variation of the correlation radius of intensity fluctuations within speckle patterns formed on the sample surface it is possible to determine the time scales of the drying process. Since the aim of this preliminary study was to prove applicability of dynamic speckle analysis for observing the drying process of transparent polymers, we did not record sequences of speckle images till the end of this process, when practically full correlation should be observed.

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REFERENCES

1. H. Rabal, R. Braga, Dynamic laser speckle and applications, CRC Press, Boca Raton, 2009.
2. J. Goodman, Statistical Optics, Wiley – Interscience, 2000.
3. V. Rajan, B. Varghese, T. Leeuwen, W. Steenbergen, *Opt. Lett.*, **31**, 468 (2006).
4. S. Murialdo, G. Sendra, L. Passoni, R. Arizaga, J. Gonzalez, H. Rabal, M. Trivi, *J. Biomed. Opt.*, **14**, 064015 (2009).
5. R. Braga, L. Dupuy, M. Pasqual, R. Cardoso, *Eur. Biophys. J.*,**38**, 679 (2009).
6. R. Braga, G. Rabelo, L. Granato, E. Santos, J. Machado, R. Arizaga, H. Rabal, M. Trivi, *Biosystems Eng.*, **91**, 465 (2005).
7. R. Macedo, J. Filho, R. Braga, G. Rabelo, *Reprod. Fertil. Dev.*, **22**, 170 (2009).
8. M. Limia, A. Núñez, H. Rabal, M. Trivi, *Appl. Opt.*, **41**, 6745 (2002).
9. C. Mulone, N. Budini, F.Vincitorio, C. Freyre, A. Díaz, A. Rego, *Proc. SPIE* **8785**, 87851X (2013).
10. T. Lyubenova, E. Stoykova, E. Nacheva, B. Ivanov, I. Panchev, V. Sainov, *Proc. SPIE* **8770**, 87700S (2013).
11. E. Stoykova, D. Nazarova, N. Berberova, A. Gotchev, *Opt. Expres,s* **23**, 25128 (2015).
12. E. Stoykova, B. Ivanov, T. Nikova, *Opt. Lett.*, **39**, 115 (2014).
13. Q.Ferreira, P. Ribeiro, O. Oliveira, M.Raposo, *ACS Appl. Mater. Interfaces*, **4**, 1470 (2012).
14. L. Nedelchev, D. Nazarova, G. Mateev, N. Berberova, *Proc. of SPIE*, **9447**, 1I-1-7 (2015).
15. N. Berberova, D. Nazarova, L. Nedelchev, B. Blagoeva, D. Kostadinova, V. Marinova, E. Stoykova, *J. Phys.: Conf. Ser.*, **700**, 012032 (2016).

## МОНИТОРИНГ НА ПРОЦЕСА НА СЪХНЕНЕ НА ВОДНИ РАЗТВОРИ ОТ ПОЛИМЕРИ ЧРЕЗ ДЕТЕКТИРАНЕ НА ДИНАМИЧЕН СПЕКЪЛ

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(Резюме)

Наблюдаването на скоростта на протичане на процеси с помощта на динамичен спекъл анализ е прилагано към различни образци от индустриално или биологично естество. Методът позволява да се посочат областите с по-ниска и по-висока активност върху повърхността на образеца чрез статистическа обработка на спекъл картините, формирани върху тази повърхност при осветяване с лазер. Целта на настоящата работа е да се провери приложимостта на техниката на динамичния спекъл за детектиране на процеса на съхнене на водни разтвори на полимери. За осъществяване на проверката са записани няколко серии от 256 корелирани във времето спекъл картини на прозрачна капка на воден разтвор на PAZO полимер върху стъклена подложка, осветена с He-Ne лазер. Сериите бяха разделени с пет минутни интервали, като последната серия е записана 75 минути след капването на капката. Статистическото описание на активността в наблюдавания образец е проведено чрез пресмятане на времева структурна функция. Получените двумерни разпределения на тази функция за различни времеви лагове потвърдиха ефективността на динамичния спекъл анализ за наблюдаване на процеси във водни разтвори на полимери.