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MASS LOSS BY SU-8 POLYMER UNDER X-RAY IRRADIATION

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The principal volatile products forming in air degradation of SU-8 polymer under influence of synchrotron radiation in the wavelength range of 2.5–0.25 Å have been studied. The material degradation products such as hydrogen, acrolein, acetone, allyl alcohol, benzene, and methyl formate have been identified, as well as atmospheric products. However, the most often products of outgassing are water and carbon oxide molecules, which contribute to the mass loss of the polymer irradiated.

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1. INTRODUCTION

In the last decade, photoresist SU-8, which is based on cured diglycidyl ether of bisphenol-A (DGE-BA), has been widely used in basic investigations and industrial manufacturing. Its cross-linked structure, exhibiting a three-dimensional molecular network, allows SU-8 application as a thermosetting resin with favorable material properties, such as low shrinkage, high strength, good chemical resistance, and high electrical insulation [1, 2]. Due to its excellent stability against ionizing radiation [3], namely X-rays, cured epoxy resin has been employed for manufacturing of magnets and insertion devices at synchrotron sources, and later, due to its photosensitivity, SU-8 photoresist has been applied to manufacturing of X-ray masks [4], X-ray lenses [5], and X-ray gratings, which are used in the Talbot interferometer [6]. Nevertheless, SU-8 specimens exposed to X-rays generate volatile fragments leaving the polymer and causing slow degradation of the material [3]. This degradation results in geometrical distortions of the patterned microstructures and deterioration of their physical properties [4, 7, 8].

In this study, actual degradation conditions are reproduced, i.e. the aforementioned X-ray polymer optics are used in air atmosphere under both high X-ray power and high X-ray dose deposited, for mass-spectrometry, which is often applied to identification of volatile degradation products [7–12].

2. EXPERIMENTAL

2.1. Materials

The SU-8 specimens of 4 inches in diameter were prepared by casting of the SU-8(10) photoresist (produced by MicroChemCorp) onto a Kapton foil and

dried at 95°C for several hours until the residual solvent (γ -butyrolactone) concentration achieved approx. 3.5 weight percent. Then, a scanning X-ray beam irradiated the dried SU-8 layer through an improvised X-ray mask at the X-ray lithography station LITHO-III at the ANKA synchrotron source. The X-ray mask consists of several copper wires of 1 mm in diameter, which are non-transparent to the radiation and separated from each other by a space of 12 mm, making slit-like openings. With the spectrum of the incoming X-ray beam, set by the varying number of aluminium foils, the dose deposited was 44 and 40 J/cm³ at the top and at the bottom of the resist layer, respectively. After the post-exposure baking at 95°C for 10 hours and development with 1-Methoxy-2-propyl acetate (PGMEA), the Kapton foil was removed, releasing free standing SU-8 foils of 12 mm in width and several centimeters in length.

The degradation was analysed using two different techniques described below.

2.2. Mass Spectra Analysis

The mass spectrometry technique was employed at the TOPO-TOMO beamline (ANKA synchrotron source), where white X-ray beam was delivered to the measurement point from a bending magnet in 30 m from it.

A stack of free standing SU-8 foils of different thickness from 50 μ m to 490 μ m was placed into a measurement cell with two windows on the front and the back sides, through which the X-ray beam crossed the cell. The X-ray beam dimensions on the specimen are 25 mm (hor.) \times 15 mm (vert.).

To avoid X-ray power attenuation, which might result in heating of the specimens, we inserted a stack of aluminium foils into the beam. Nevertheless, the temperature of the specimens as calculated in a hypothesis of heat losses via conduction, convection in the gas phase, and radiation [13, 14] was in the range between 65 and 92°C.

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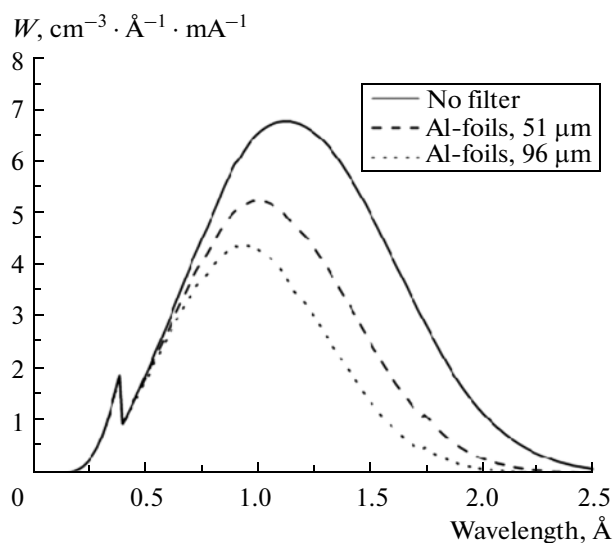


Fig. 1. Spectral distribution of X-ray beam power absorbed in the surfaces of free standing SU-8 foils at an electron energy of 2.5 GeV and an electron current of 150 mA, including a 120 cm long path of transmission in air.

Because of the hardness of the filtered X-ray beam (Fig. 1) the difference between the doses deposited on the front and back sides of the SU-8 foils did not exceed 40%.

The cell, which was connected to vacuum meter V1 from one side and a coupling chamber (Fig. 2) from the other side, was evacuated to a residual air pressure of about 5 mbar, at which the mean free path of molecules of air did not exceed the inner diameter of the cell. The residual air in the cell played a role of a precursor gas imitating the atmospheric conditions, on the one hand, and a carrier gas delivering the volatile fragments to the mass spectrometer, on the other hand. However, the base pressure in the coupling chamber connected to the mass spectrometer was as high as of the order of 10^{-7} mbar, because of the direct connection to the vacuum pump.

The gas analysis was executed using a commercial quadrupole mass spectrometer (model QMS 200 F2, Prisma™, Pfeiffer Vacuum) capable of measuring ion masses of 1 to 200 Da. The ionizing chamber of the mass spectrometer was placed in approx. 140 cm from the specimens.

First of all, the cell was irradiated through the side-wall windows without specimens what resulted in outgassing of the cell and allowed us study the volatile fragments inside as the background spectrum for further measurements. In this case, the gases typical of the air atmosphere, like H^+ ions, H_2O , CO , CO_2 , N_2 , and NO^+ were recorded. Additionally, the mass spectra of PGMEA and isopropyl alcohol irradiated with X-rays were recorded, because these substances, when used in manufacturing of the specimens, can add some

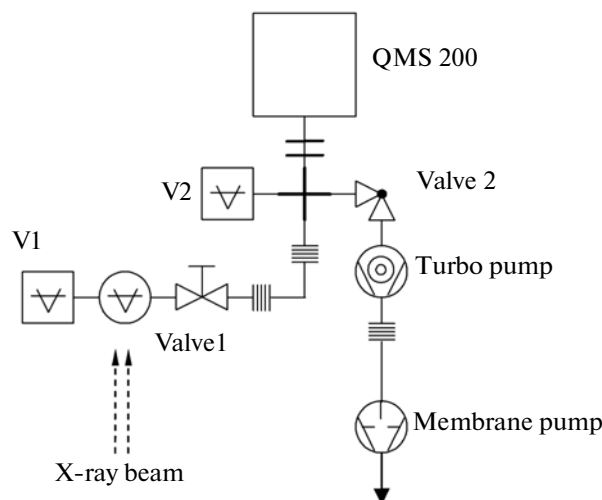


Fig. 2. Schematic experimental setup. Vacuum meter V1 (produced by “Balzers”) is based on the thermal conductivity of gases; Penning vacuum meter V2 (produced by “Pfeiffer Vacuum”) employs ionization of residual gas molecules; turbo pump model 150HT Macro-Torr by Varian.

fragments to the spectrum of the polymer during their degradation in the X-ray beam.

The interpretation of the arising spectra was carried out based on the following information: the data base with distribution of fragments of certain gases, the characteristic spectra library, the distribution of isotopes, the nitrogen rule, and the probability data for the specific ionization, and multiple ionization for a fixed filament bias [15–17].

The aforementioned data are applicable because of no any charged volatile fragments generated by direct irradiation, reach the detector of mass spectrometer, causing absence of contribution to the observed intensities. We checked this fact, switching off the filament bias. On the other hand, the recharging process and the deposition of charged fragments onto the sidewall of the transport pipe, taking into account the high collision rate under the rough vacuum condition, can suppress the flow of the charged fragments on their way toward the mass spectrometer [18].

2.3. Mass Loss Analysis

Firstly, the free-standing foils, which had been held in the evacuated cell for 12 h, were weighed on a microbalance (Mettler MT5) with an accuracy of 5 μ g. A mass loss of about 1.2% of the initial mass, ranging from 30 mg up to 350 mg, was found and ascribed to the water and γ -butyrolactone evaporation from the specimens. After that, the free-standing foils were exposed to radiation and weighed periodically during the experiment.

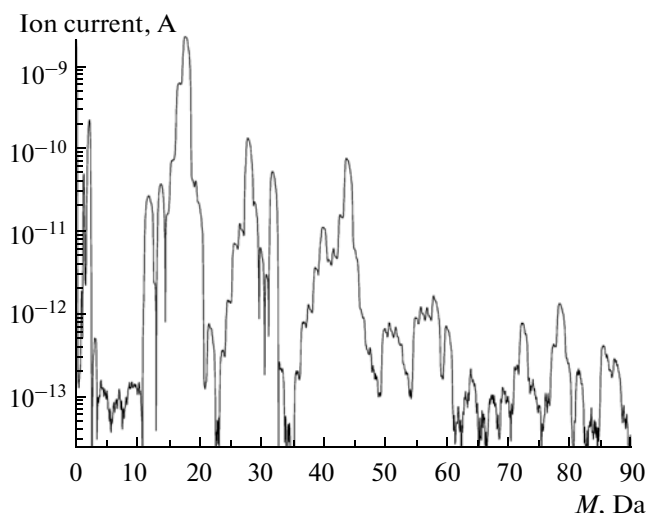


Fig. 3. Ion current depending on fragment masses released from SU-8 foils irradiated by white X-ray beam from the ANKA storage ring.

3. RESULTS AND DISCUSSION

3.1. Identification of Fragments

During the irradiation with X-rays, volatile products in the mass range between 1 Da and 89 Da are observed. A corresponding mass spectrum is shown in Fig. 3, but no mass peaks in the range between 90 Da and 200 Da appeared.

In general, the volatile fragments registered are products of direct interaction with the X-rays and electrons emitted by the filament under a voltage of 90 V. But, the charged fragments produced due to the electron impact only reach the detector. Mathematically, the mass spectra observed are a convolution of the mass spectrum of the volatile products stimulated by X-rays with the proper mass spectrum of each volatile product caused by the electron impact. Therefore, one can calculate the spectrum of the volatile fragments released by synchrotron radiation, deconvolving the resulting spectra and the proper spectra of the products to be recognized. These products, compounded of atoms of precursor molecules, were modelled with due account of the limited number of the products and the probability of their appearance [17].

Analysis of the appearing volatile fragments reveals three precursor types, namely the destroyed polymer, the residual gas, and water molecules dissolved in the polymer. The water photodissociation produces H^+ , O^+ , OH^+ , H_2^+ , and O_2^+ ions, which are recorded in the mass spectra. They cause formation of carbon monoxide and carbon dioxide, whose mass peaks increase after the irradiation was on. Besides, the total pressure and the ion current of the water molecules increase synchronously, reaching a steady state. After that, the

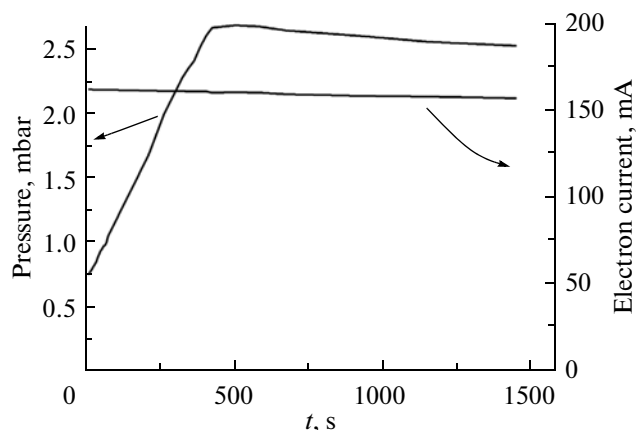


Fig. 4. Temporal pressure in the cell under synchrotron radiation and electron current in the storage ring.

pressure decreases simultaneously with the electron current in the storage ring, as shown in Fig. 4. In contrast to that, the temporal current of CO and CO₂ is increasing permanently (see Fig. 5), due to the high concentration of oxygen ions released during the water molecules dissociate.

It should be noted that no antimony-containing volatile fragments were observed.

3.2. X-Ray Induced Mass Loss

The irradiation makes all the specimens studied brownish hue and causes a loss of mass, which was measured and shown in Fig. 6. Only some of the arising volatile fragments reach the mass spectrometer, the rest depositing on the sidewalls of the vacuum pipe. The later part was studied after removal of the speci-

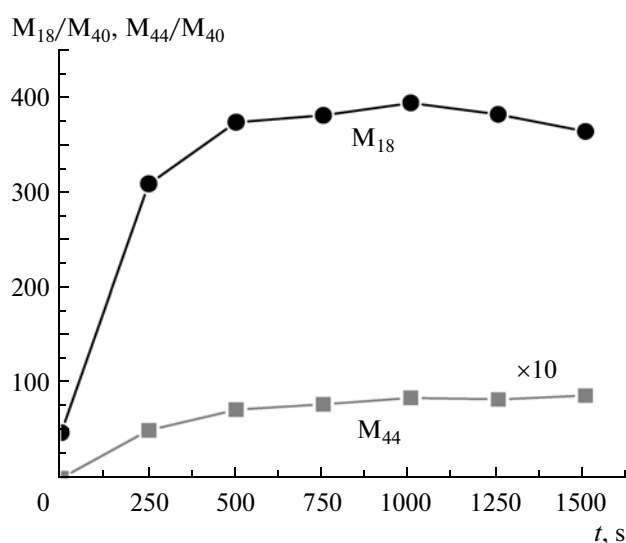


Fig. 5. Temporal ion current of M₁₈ (water) and M₄₄ (CO₂) normalized to argon ion current, vs. time.

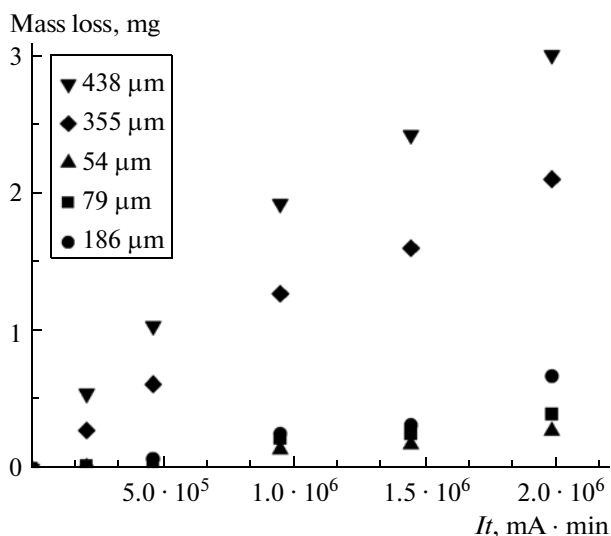


Fig. 6. Measured mass loss of SU-8 specimens of different thickness vs. exposure dose.

mens from the cell. The spectra recorded show a similar ratio of water concentration to other volatile fragments. Thus, the mass loss can be considered to be proportional to the mass volatile fragments taking into account the mass transport conductivity of the vacuum pipe and the relative ionization probabilities for different molecules [19, 20]. Generally, the mass loss rate depends on the specimen temperature T which can be increased due to irradiation.

The temperature dependence of the water diffusion in an epoxy polymer is presented by the Arrhenius factor as $\exp\left(-\frac{E_a}{RT}\right)$, where R is the universal gas constant and $E_a = 61$ kJ/mol [21] for the non-irradiated polymer. With the calculated temperature induced by the irradiation in the specimens of different thickness and the contribution of water to the total mass loss taken into account, the activation energy of water diffusion is determined as $E_a = 18.3 \pm 2$ kJ/mol (Fig. 7), which is less than the latent heat of water evaporation (45 kJ/mol) at the aforementioned pressure.

CONCLUSIONS

Mass spectrometry and measurement of mass losses have been applied, characterizing the release of gaseous species from solid SU-8 layers exposed to a white beam of hard X-ray synchrotron radiation. The mass loss rate and the formation of volatile products depend, in part, on the dose deposited and on the power of the X-ray beam. Possible polymer modifications towards for instance increased stability to ionizing radiation, realized for example via hard baking process

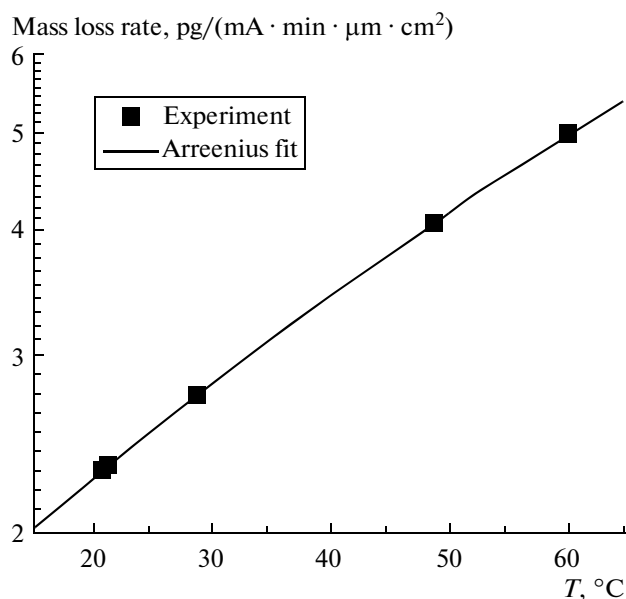


Fig. 7. Measured mass lost rate vs. temperature of specimens.

could also be studied by means of mass spectrometry of released volatile products.

REFERENCES

1. *Bruins P.F., Editor.* Epoxy resin technology, New York: Interscience, 1968.
2. *Potter W.G.* Epoxide resins. Bristol: J.W. Arrowsmith Ltd.; 1970.
3. *Morita Y., Udagawa A.* Ultra-high radiation-resistant polymer materials. Polymer Materials under Severe Radiation Environment, (in Japanese) Genshiryoku eye, 1998; 44 (5): 40–45.
4. *Cabrini S., Perennes F., Marmioli B., Olivo A., Carpentiero A., Kumar R., Candeloro P., Fabrizio E.D.* Low cost transparent SU-8 membrane mask for deep X-ray lithography. *Microsystem Technologies* 2005;11(4–5): 370–373.
5. *Nazmov V., Reznikova E., Mohr J., Saile V., Vincze L., Vekemans B., Bohic S., Somogyi A.* Parabolic crossed planar polymeric x-ray lenses, *J. Micromech Microeng* 2011;21(1):015020–015030.
6. *Weitkamp T., Zanette I., Schulz G., Bech M., Rutishauser S., Lang S., Donath T., Tapfer A., Deyhle H., Bernard P., Valade J.-P., Reznikova E., Kenntner J., Mohr J., Müller B., Pfeiffer F., David C., Baruchel J.* X-ray grating interferometry at ESRF: applications and recent technical developments. *AIP Conf Proc* 2011; 1365:28–31.
7. *Snigireva I., Snigirev A., Drakopoulos M., Kohn V., Nazmov V., Reznikova E., Mohr J., Saile V.* Near-diffraction limited coherent x-ray focusing using planar refractive lenses made of epoxy SU-8 resist, *Proceedings of the SPIE* 2004; 5539: 20–30.
8. *Takahashi N., Tujii H., Katori M., Yamashita K., Noda D., Hattori T.* Fabrication of X-rays mask with carbon mem-

- brane for diffraction gratings Microsyst Technol 2010 16:1303–1307.
9. *Creasy W.R.* Epoxy resin analysis by Fourier transform mass spectrometry: a comparison of pyrolysis and laser ablation. *Polymer* 1992;33(21):4486–4492.
 10. *Rattana A., Abel M.-L., Watts J.F.* ToF-SIMS studies of the adsorption of epoxy resin molecules on organosilane-treated aluminium: Adsorption kinetics and adsorption isotherms. *Int. Journ. of Adhesion & Adhesives* 2006; 26(1–2):28–39.
 11. *Fuchslueger U., Rissler K., Stephan H., Grether H.-J., Grasserbauer M.* High-performance liquid chromatography-mass spectrometry of epoxy resins. *Journ of Appl Polym Sci* 1999; 72(7):913–925.
 12. *Sakamoto R., Takahashi Y., Ozawa T.* Mass spectrometric thermal analysis of impurities in epoxy resins, *Journ of Appl Polym Sci* 1972;16:1047–1051.
 13. *Blazso M.* Pyrolysis/mass spectrometry and pyrolysis/gas chromatography/mass spectrometry analysis of polymers. *Rapid communications in mass spectrometry* 1991; 5:507–511.
 14. *Grassie N., Guy M.I., Tennent N.H.* Degradation of epoxy polymers: 3 – photo-degradation of bisphenol-A diglycidyl ether. *Polymer degradation and stability* 1985;13:249–259.
 15. *Nazmov V.P., Pindyurin V.F.* Investigation of radiation-induced surface temperature of thick polymer layers under influence of synchrotron radiation. *Nucl Instr Meth Phys Res* 2000; B170(3–4):369–374.
 16. *Nazimek D., Czech B.* Artificial photosynthesis - CO₂ towards methanol. *IOP Conf. Series: Materials Science and Engineering* 2011;19: 012010.
 17. *Watson J.T., Sparkman O.D.* *Mass Spectrometry: Instructions, Applications, and Strategies for Data Interpretation*, Chichester: John Wiley & Sons, 2007.
 18. *Gross J.H.* *Mass spectrometry: A Textbook*, Berlin / Heidelberg: Springer-Verlag, 2011.
 19. *Robertson A.J.B.* *Mass Spectrometry* Methuen & Co, Ltd., London, 1954
 20. *Cornu A., Massot R.* *Compilation of Mass Spectral Data* Heyden and Son Ltd., London, 1966.
 21. *Aniskevich A., Jansons J., Plushchik O.* Moisture sorption and its effect on mechanical properties of polymer materials in Water transport in synthetic polymers Ed. By Iordansky, Startsev and Zaikov, p. 105–177, New York: NovaScience Publishers, 2003.