RADIJACIJSKA OBRADA STARENIH MODELNIH UZORAKA TEKSTILA

RADIATION TREATMENT OF ARTIFICIALLY AGED MODEL TEXTILES

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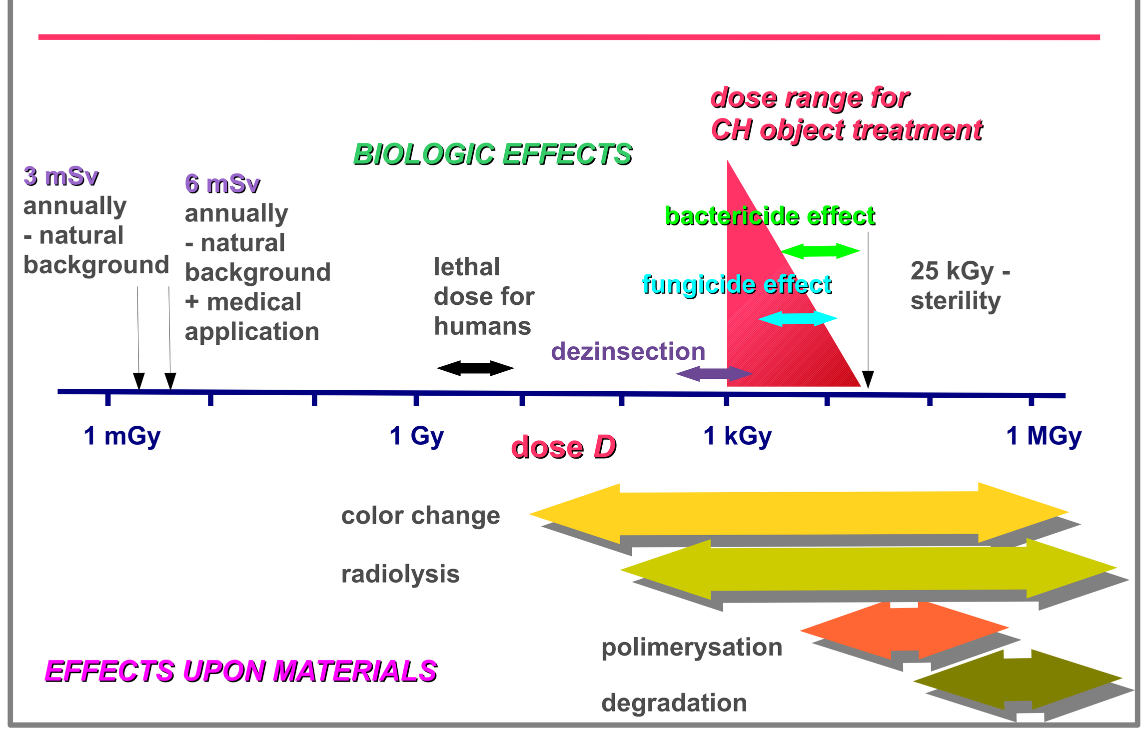
Tekstilni objekti kulturne baštine posebno su podložni biološkim oštećenjima izazvanim insektima, gljivicama, plijesnima i bakterijama koje ih nastanjuju i uzrokuju kemijske promjene. Može doći do promjene oksidacijskih stanja i depolimerizacija prirodnih polimera od kojih se sastoje tekstilni materijali. Posljedice mogu biti promjene boja, pogoršanja mehaničkih svojstava pa čak i potpuno propadanje tekstila [1]. Većina postupaka zaštite samo djelomično rješava problem često uz primjenu toksičnih spojeva.

Iskustva sterilizacije medicinskih pomagala i farmaceutika osnova su radijacijske obrade baštinskih predmeta. Za uklanjanje insekata primjenjuju se doze do 0,5 kGy, 4-10 kGy za gljivice dok 5-20 kGy osigurava mikrobiološku dekontaminaciju. Prednosti radijaciijske obrade su:

- visoka pouzdanost, djeluje po cijelom volumenu objekta
- istovremeno djeluje na sve štetne organizme u svim fazama njihova razvoja
- bez neželjenih promjena u skoro svim materijalima
- netoksična, ozračeni objekti ne postaju radioaktivni
- prodire kroz ambalažu
- ovisi o samo apsorbiranoj dozi koju je lako kontrolirati
- postupak relativno brz i veći broj objekata se može tretirati istovremeno
- provodi se na sobnoj temperaturi a po potrebi na povišenoj temperaturi (radi povećanja osjetljivost zagađivača) ili u smrznutom stanju
- uz konzervaciju moguća i konsolidacija

IRRADIATION EFFECTS AND THE ABSORBED DOSE



Textile cultural heritage (CH) objects are especailly susceptible to biological damage by insects, fungi, molds and bacteria that inhabit those objects and produce chemical changes. Changes in oxidation states and/or depolymerization of natural polymers that textiles consist of occurr resulting in discoloration, detrioration of mechanical properties and even full decomposition [1]. Most treatment methods include application of toxic compounds while only partially solving the problem.

Irradiation treatment is based on the experience gathered in sterilization of medical devices and pharmacuticals. Doses of 0.5 kGy provide desinsection, 4-10 kGyare applied for fungi control and up to 5-20 kGy if complete microbiological decontamination is needed. The advantages of radiation treatment are:

- highly efficient throught the volume of the object
- simultaneous treatment of all biodetriorants at every development stage
- almost no unwanted chages in treated materails
- nontoxic, objects do not become radioactive
- penetrates the packaging
- depends soleyly on absrobed dose taht is easily controlled
- several objects can be treated simulatenously
- usually performed at room temperature, but temperature may be higher (to increase sesnsitivity of biodetriorants) or object may be frozen
- provides conservation, might be used for consolidation

U ^{60}Co izvoru gama zračenja u Laboratoriju za radijacijsku kemiju i dozimetriju Instituta "Ruđer Bošković" u Zagrebu više od 20 godina se provodi obrada objekata kulturne baštine od drva, papira, tekstila, kože itd. [2]. U tom periodu efikasno su dezinficirani brojni tekstilni artefakti dozom manjom od 2 kGy. Neštetnost viših doza potrebnih za kontrolu kontaminacije gljivicama potrebno je potvrditi ispitivanjima djelovanja zračenja na tekstilna vlakna i pokazati da li takva obrada zadovoljava visoke standarde konzervatora obzirom na neželjene promijene. Stoga su u prikazanom istraživanju **ispitivani modelni uzorci tekstilnih materijala koji se najčešće javljaju u objektima kulturna baštine – svile, pamuka, lana i vune. Ti modelni uzorci ozračeni su visokom dozom gama zračenja, D=120 kGy u kontaktu s zrakom. Tako visoka doza izabrana je kako bi se osiguralo da se mogu detektirati sve promjene izazvane zračenjem kako bi ih se moglo prepoznati ukoliko se javljaju kod primjene skoro 20 puta manjih doza potrebnih za kontrolu gljivica.** Dio uzoraka je bio umjetno staren 25 dana u Vötsch Climatic Chamber, VC 0020 pri 80 °C i 65 % RH. Termička svojstva i stabilnost uzoraka mjerena su pretražnim kalorimetrom Perkin Elemer Diamond DSC-om i termogravietrijski na Shimadzu TGA. Promjene na vlaknima promatrane su pretražnim elektronskim mikroskopom SEM, JEOL JSM-6060LV.

[1] K. Kavkler, A. Demšar, Polym. Degrad. Stab. 97 (2012), 5; 786-792.
[2] B. Katušin-Ražem, D. Ražem, M. Braun, Radiat. Phys. Chem. 78 (2009), 7/8; 729-731.

^{60}Co gamma irradiation facility at Laboratory for Radiation Chemistry and dosimetry of the Ruđer Bošković Institute in Zagreb, Croatia provides treatment of cultural heritage (CH) objects made of wood, paper, textile, leather etc for more than 20 years [2]. During that period numerous textile artifacts were efficiently disinfected by irradiation to dose of less than 2 kGy. However, the application of higher doses for the control of fungi needs to be justified by investigating the effects of irradiation on textile fibers and to determine whether the treatment complies to the high standards of conservator specialists considering undesirable changes. Because of that **the most common textile materials in CH artifacts - silk, cotton, linen and wool were selected as model samples. The samples were γ-irradiated to a high dose, D=120 kGy, in contact with air. Such high dose was chosen to ensure that all radiation effects can be detected and recognized if appear in samples irradiated to almost 20 times lower doses needed for fungi control.** A part of the samples was artificially aged using Vötsch Climatic Chamber, Type VC 0020 at 80 °C and 65 % RH.for 25 days. Thermal properties and stability of the samples were determnined using differential calorimetry, Perkin Elemer Diamond DSC, and termogravietry, Shimadzu TGA. Fiber changes were observed by a scanning electron microscope JEOL JSM-606OLV.

[2] B. Katušin-Ražem, D. Ražem, M. Braun, Radiat. Phys. Chem. 78 (2009), 7/8; 729-731.
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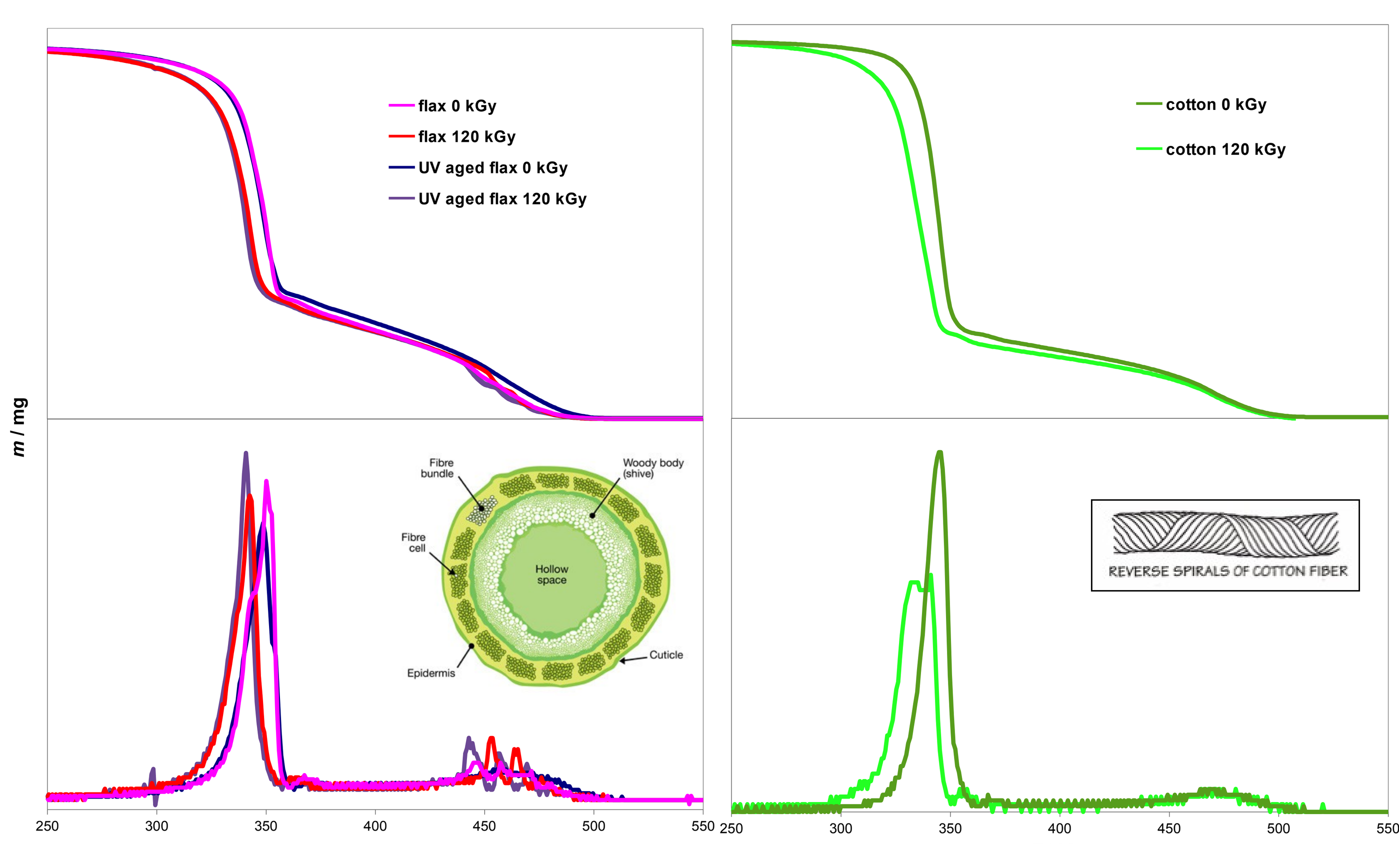
CELLULOSE-BASED TEXTILE / TEKSTIL CELULOZNE OSNOVE

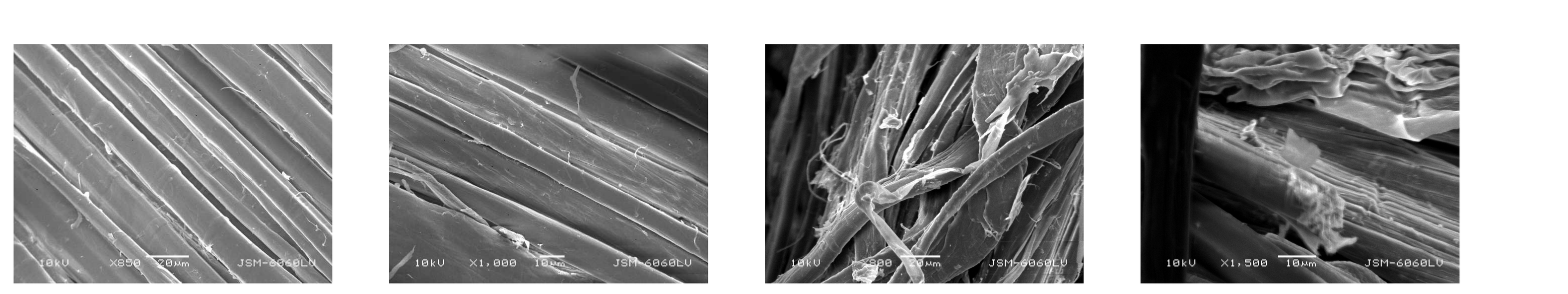
Poznato je da celuloza degradira pod djelovanjem zračenja pa su promjene toplinskih svojstava i stabilnosti lanenog platna i pamuka bile očekivane. Unatoč relativno visokoj dozi od 120 kGy temperatura maksimuma gubitka mase u TGA je samo malo niža nego kod neozračenog uzorka. U DSC termogramima (nisu prikazani) zračenih kao i starenih uzoraka pamuka i lanenog platna pojavljuje se visokotemperaturni maksimum kojeg nema u neozračenom nestarenom uzorku. Kod starenih uzoraka lanenog platna taj maksimum pomiče se prema nižoj temperaturi a toplina mu raste. SEM mikrografije pokazuju oštećenja strukture vlakna u ozračenim uzorcima, najviše kutikule ali i mjestimično pucanje cijelih vlakana. Slične promjene iako manje izražene vidljive su i u neozračenom starenom uzorku pa se kod skoro 20 puta manje doze potrebne za kontrolu gljivica mogu očekivati promjene manje onih koje uzrokuje samo starenje.



	neozračeni / unirradiated			120 kGy		
	linen	aged linen	cotton	lan	stareni lan	pamuk
	lan	stareni lan	pamuk	linen	aged linen	cotton
DSC Peak T/ °C		370		302	303	298
DSC ΔH / J/g		-3,83		-23,26	-290,74	-342,43
diff TGA Peak T/ °C	350	349	345	343	341	341

Cellulose is known to be prone to radiation degradation so the changes in thermal properties of irradiated linen and cotton. Although 120 kGy is relatively high dose temperature of maximum rate of mass decrease in TGA is only slightly lower than in unirradiated sample. In DSC thermograms (not shown) of both aged and irradiated samples of cotton and linen a high temperature peak appears that is not present in unirradiated fresh sample. In aged linen samples that peak shifts to lower temperature and its heat significantly increases. On the other hand damage to fiber strucuture, primarily to cuticule, and even some destruciton of complete fiber is obvious in SEM micrographs. Since about 20 times lower dose is needed for fungi control it can safely be proposed that the change to textile would not be greater than that caused by ageing itself.

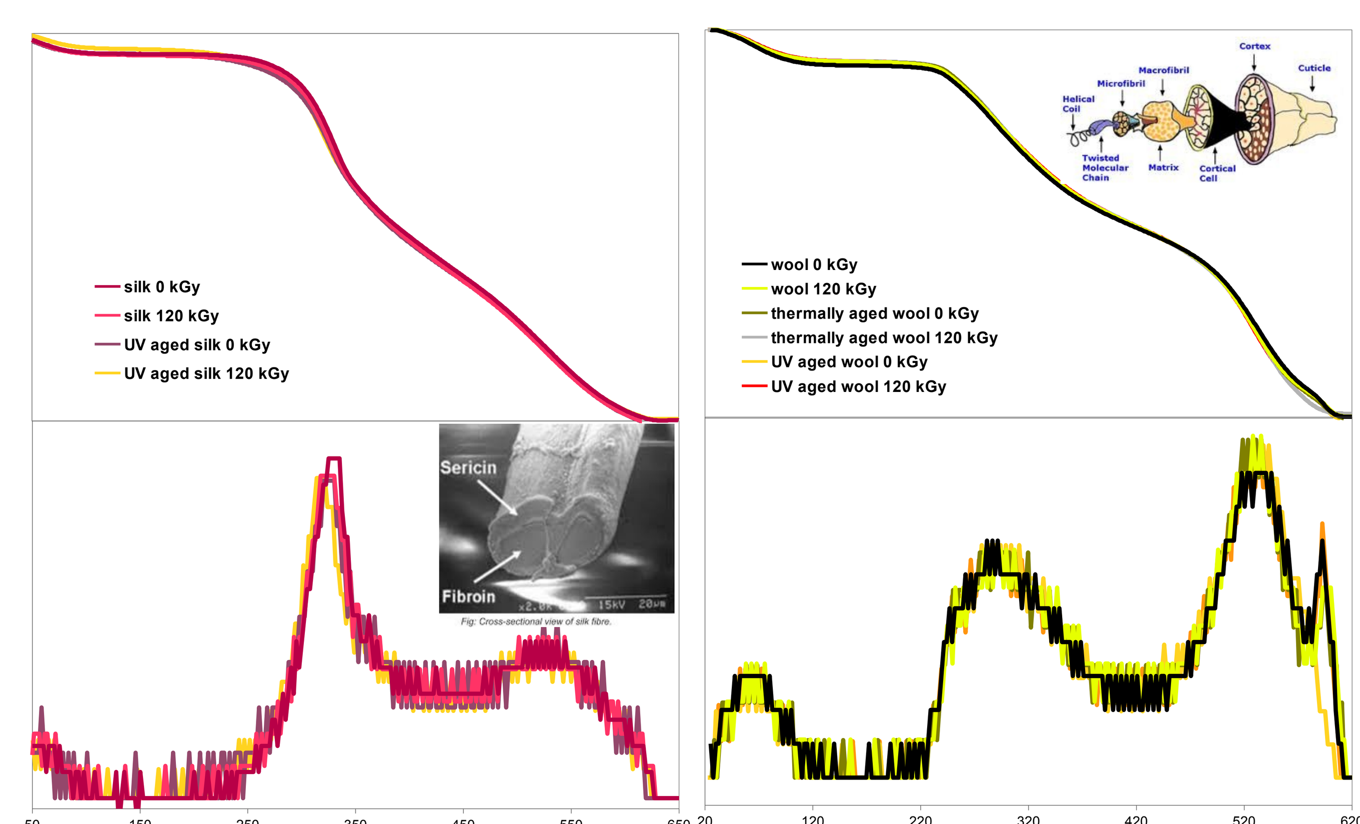
SEM micrograps of linen samples: unaged and unirradiated (left), aged and unirradiated (center left), unaged and irradiated 120 kGy (center right) and aged and irradiated 120 kGy (right). Damaged cuticule and some destroyed fibers are visible in irradiated samples.



SEM mikrografije uzoraka lana: nestaren i neozračen (lijevo), staren i neozračen (sredina lijevo), nestaren i ozračen s 120 kGy (sredina desno) te staren i ozračen s 120 kGy (desno). Na ozračenim uzorcima vidljiva su oštećenja kutikule a i oštećenja vlakna.

PROTEIN-BASED TEXTILE / TEKSTIL PROTEINSKE OSNOVE

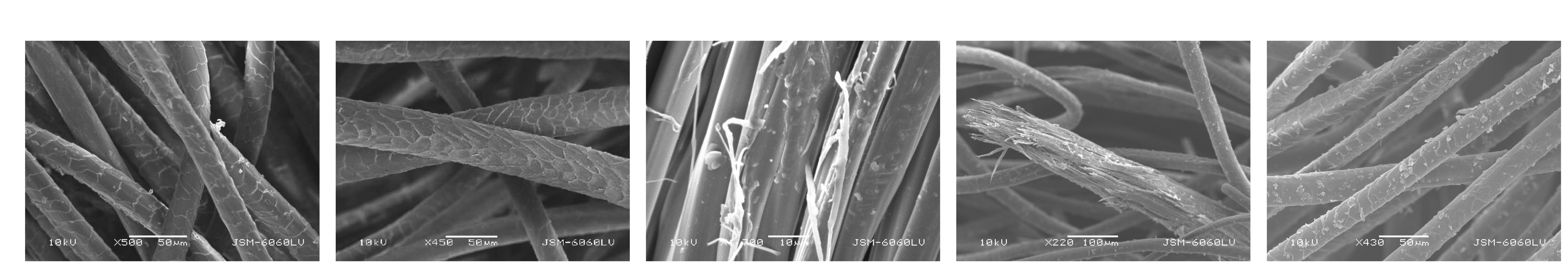
Thermal stability of silk and especially wool seems to be unaffected by irradiation to 120 kGy. This is somewhat unexpected because the corresponding proteins – sericin and fibroin in silk and keratin in wool - are by themselves sensitive to irradiation although less than cellulose. Temperatures and heats determined by DSC indicate that transformation of silk and wool are slightly influenced by irradiation. Those changes are not neccesary related to degradation because complex structure of animal fibers obviously offers significant protection to protein component. SEM micrographs of wool show only slight damage. It is interesting that UV-aged wool sample shows no damage despite high dose.



	neozračeni / unirradiated				120 kGy			
	silk	aged silk	wool	UV-aged wool	svila	starena svila	vuna	UV-starena vuna
	svila	starena svila	vuna	UV-starena vuna	silk	aged silk	wool	UV-aged wool
DSC Peak T/ °C	58	63	96	88	77	75	96	94
DSC ΔH / J/g	52,29	21,64	89,67	142,45	128,74	146,09	69,29	47,06
DSC Peak T/ °C			251	256			251	255
DSC ΔH / J/g			6,43	10,04			5,93	5,94
DSC Peak T/ °C	362	364	332	327	370	365	339	331
DSC ΔH / J/g	-2,54	-37,38	-32,3	-8,99	-17,76	-25,46	-8,02	-10,89
diff TGA Peak T/ °C	325-333	320-331	529-536	525-538	317-331	314-321	529-536	525-538

Zračenje do 120 kGy nema utjecaja na toplinsku stabilnost svile a naročito vune. To je pomalo neočekivano jer su proteini njihove osnove, sericin i fibroin kod svile te keratin kod vune, osjetljivi prema zračenju iako manje od celuloze. Iako temperature i topline određene DSC-om pokazuju da zračenje utječe na transformacije u svili i vuni to ne mora nužno rezultirati oštećenjima jer kompleksna struktura animalnih vlakana očito pruža znatnu zaštitu proteinskoj komponenti. Na SEM mikrografijama ozračene vune uočavaju se samo manja oštećenja. Zanimljivo je da UV-stareni uzorak vune nema oštećenja unatoč visokoj dozi.

SEM mikrografije uzoraka vune: nestarena i neozračena (lijevo), starena i neozračena (sredina lijevo), nestarena i ozračena s 120 kGy (sredina), starena i ozračena s 120 kGy (sredina desno) te UV-starena i ozračena s 120 kGy (desno). Na ozračenim uzorcima vidljiva su manja oštećenja kutikule osim kod uzorka koji je bio UV-staren.



SEM micrograps of wool samples: unaged and unirradiated (left), aged and unirradiated (center left), unaged and irradiated 120 kGy (center), aged and irradiated 120 kGy (center right), UV-aged and irradiated 120 kGy (center right). Slight damage of cuticule is visible in irradiated samples except the UV-aged one.

CONCLUSIONS:

- the changes in even the most senstitive materials were slight although the applied dose was relativiely high;
- cellulose - based textiles (linen and cotton) are more sensitive to irradiation than protein-based ones (silk, wool);
- irradaition of CH textiles to doses needed for fungi control should be safe.

ZAKLJUČCI:

- promjene u materijaliam uzoraka bile su neznatne iako je primjenjena doza bila relativno visoka;
- tekstili s celuloznom osnovom (lan i pamuk) osjetljiviji su prema zračenju u odnosu na one s proteinskom osnovom (svila, vuna);
- ozračivanje baštinskog tekstila dozama potrebnim za kontrolu gljivica može se smatrati sigurnim.