Ionizing Radiation for the Preservation and Conservation of Photographic and Cinematographic Films

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Context

- Brazilian weather conditions affect directly tangible materials causing deterioration notably getting worse by insects and fungi attack.
- Contamination by fungi is one of leading causes of problem in photographic and cinematographic collections.
- Ionizing radiation recovery to treat materials affected by fungi and insects has been used effectively in cultural heritage artifacts.

Goal of the study

- Characterization of the films.
- Evaluate gamma and electron beam radiation effects for the disinfection of photographic and cinematographic films.
- Check the effect of ionizing radiation-induced crosslinking (vinegar syndrome)

Research Model

Film samples selection → Caracterization **FTIR-ATR** **FEGSEM-EDS** → Gamma rays/electron beam irradiation **2-200 kGy** → Irradiation effects evaluation **UV-Vis/FEGS EM/TG/DSC**

Materials and Method

Films Samples

Figure 1. Samples of photographic negative (N5) and cinematographic film (F1) selected from University of Sao Paulo libraries.

Methodology

- Samples were irradiated by gamma rays and electron beam with following absorbed dose 2, 6, 10, 15, 20, 25, 50, 100 and 200 kGy. Dose rate was 5-6kGy/h.
- Samples were analyzed by FTIR-ATR to characterization organic compounds of the materials.
- Measures by UV-Visible spectroscopy were undertaken to verify changes in the absorption of eletromagnetic radiation due to the properties of the films induced by gamma radiation.
- Scanning electron microscopy (FEG-SEM) and EDS spectroscopy was used to analyze and characterize the non-irradiated (0kGy) and the effective disinfected (10kGy) films samples.
- Thermal analyzes by thermogravimetry (TG) and differencial scanning calorimetry (DSC) were performed to verify for possible crosslinking effects to treat vinegar syndrome films.

Results

FTIR-ATR samples characterization

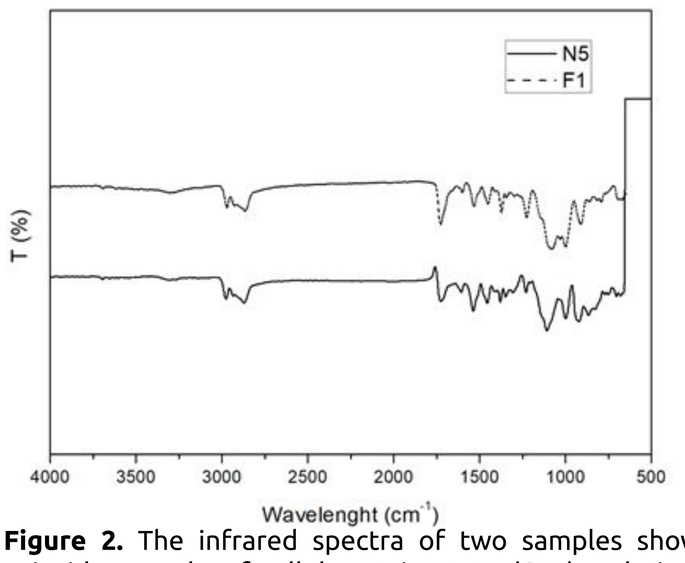
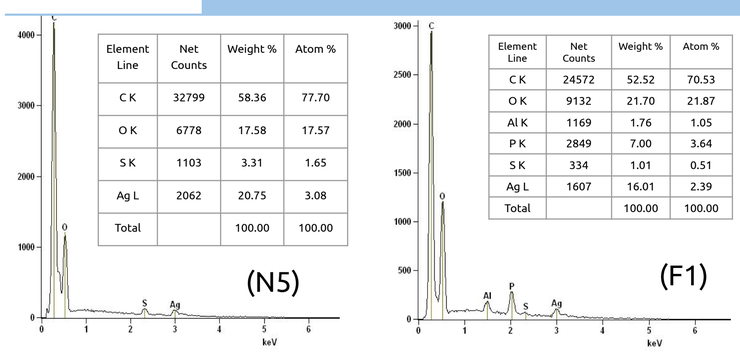


Figure 2. The infrared spectra of two samples showed coincident peaks of cellulose triacetate (CTA), gelatin and triphenyl phosphate (TPP).

FEG-SEM



Element Line	Net Counts	Weight %	Atom %
C K	32799	58.36	77.70
O K	6778	17.58	17.57
S K	1103	3.31	1.65
Ag L	2062	20.75	3.08
Total		100.00	100.00

Element Line	Net Counts	Weight %	Atom %
C K	24572	52.52	70.53
O K	9132	21.70	21.87
Al K	1169	1.76	1.05
P K	2849	7.00	3.64
S K	334	1.01	0.51
Ag L	1607	16.01	2.39
Total		100.00	100.00

Figure 3. Spectrum of the elements distribution non irradiation samples. All samples show carbon and oxygen as majority elements due to the organic compounds of film materials. Coating samples with carbon enhances the carbon peak of the EDS spectrum. Silver are the photosensitizing element. Phosphorus from TPP plasticizer can be observed in sample F1. Sulfur came from the fixing solution of thiosulfate. Aluminum can be attributed to the sample-holder material.

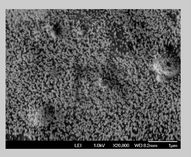
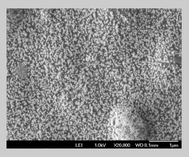
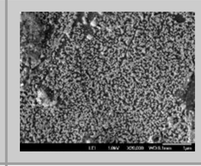
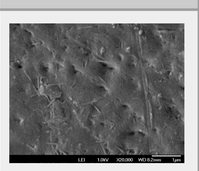
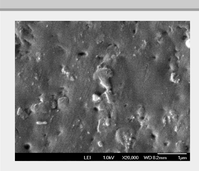
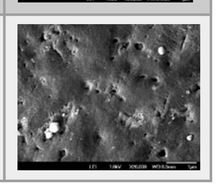
Sample	non-irradiated	10 kGy gamma irradiated	10 kGy e-beam irradiated
N5			
F1			

Table 1. Micrographs of the non–irradiated (0kGy) and irradiated samples (10kGy). Different kind of intensities and variations of white and black contrast can be associated with specific elements or with impurities and superficial contamination.

UV-Vis spectroscopy

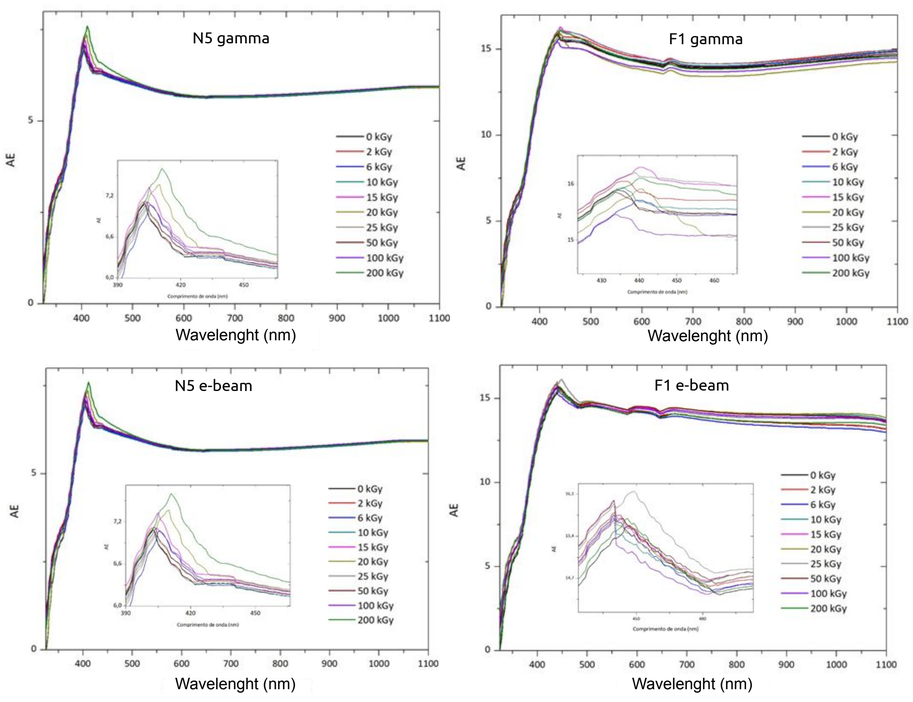
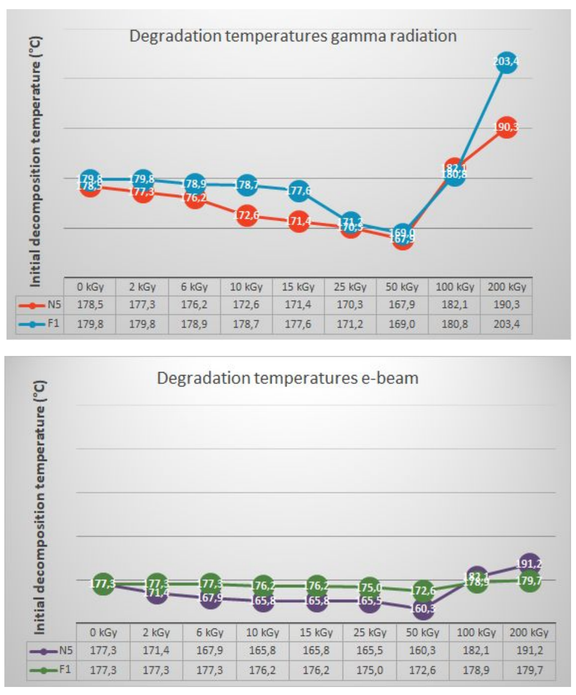


Figure 4. UV-visible absorption spectra of samples N5 and F1 irradiated with different gamma rays and electron beam irradiation doses. The changes induced by the action of ionizing radiation become evident from 15 kGy.

TG

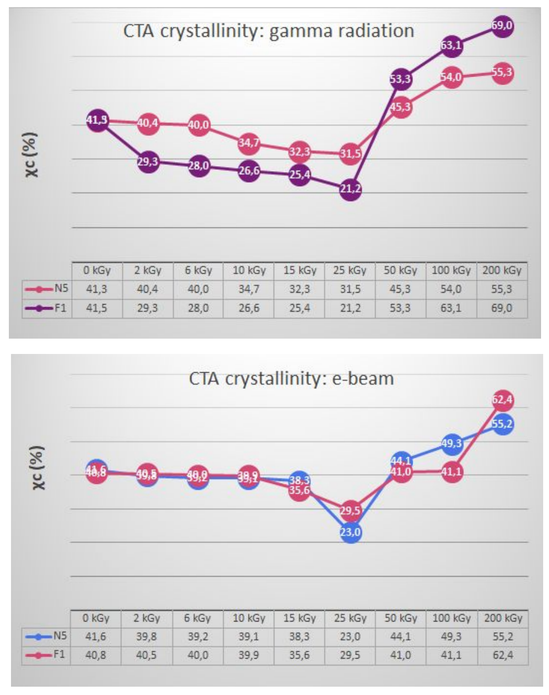


	0 kGy	2 kGy	6 kGy	10 kGy	15 kGy	25 kGy	50 kGy	100 kGy	200 kGy
N5	178,5	177,3	176,2	172,6	171,4	170,3	167,9	182,1	190,3
F1	179,8	179,8	178,9	178,7	177,6	171,2	169,0	180,8	203,4

	0 kGy	2 kGy	6 kGy	10 kGy	15 kGy	25 kGy	50 kGy	100 kGy	200 kGy
N5	177,3	171,4	167,9	165,8	165,8	165,5	160,3	182,1	191,2
F1	177,3	177,3	177,3	176,2	176,2	175,0	172,6	178,9	179,7

Figure 5. TG results of samples N5 and F1 irradiated with different gamma radiation irradiation doses. Both gamma radiation and electron beam were found to promote crosslinking at doses strating at 50 kGy.

DSC



	0 kGy	2 kGy	6 kGy	10 kGy	15 kGy	25 kGy	50 kGy	100 kGy	200 kGy
N5	41,3	40,4	40,0	34,7	32,3	31,5	45,3	54,0	55,3
F1	41,5	29,3	28,0	26,6	25,4	21,2	53,3	63,1	69,0

	0 kGy	2 kGy	6 kGy	10 kGy	15 kGy	25 kGy	50 kGy	100 kGy	200 kGy
N5	41,6	39,8	39,2	39,1	38,3	23,0	44,1	49,3	55,2
F1	40,8	40,5	40,0	39,9	35,6	29,5	41,0	41,1	62,4

Figure 6. DSC results of samples N5 and F1 irradiated with different gamma radiation irradiation doses. Higher degrees of crystallinity (indicative of crosslinking) were identified at doses starting at 50 kGy.

Conclusion

- Results showed that **disinfection** by gamma rays and electron beam radiation can be achieved safely applying radiation absorbed doses between **6 kGy to 10 kGy** with no significant change or modification of main properties of the constitutive polymeric materials.
- Gamma rays and electron beam irradiation, due to the effect of **crosslinking** is presented as an alternative to treat films affected by “vinegar syndrome” applying absorbed dose of **50 kGy** in order to increase shelf life of cultural heritage materials.

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