Radiation Physics and Chemistry 182 (2021) 109395

Contents lists available at ScienceDirect

Radiation Physics and Chemistry

journal homepage: www.elsevier.com/locate/radphyschem

Gamma and electron beam irradiation effects for conservation treatment of cellulose triacetate photographic and cinematographic films

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ARTICLE INFO

Keywords:
Tangible cultural heritage preservation
Ionizing radiation processing
Cellulose triacetate films
Disinfection
Crosslinking

ABSTRACT

Photographic and cinematographic films of cellulose triacetate safeguarded in historical and cultural institutions are often contaminated by fungi when stored in inadequate conditions of humidity and temperature. The presence of fungi affects the image contained in the films, accelerates the process of biodeterioration and represents a risk to the health of people working with contaminated materials. In addition, another common physicochemical degradation affecting cellulose triacetate films causing deacetylation of polymer chain is called "vinegar syndrome". Considering the dose interval established for the disinfection of cultural heritage materials, in this work the effects of irradiation with gamma rays and electron beam on photographic and cinematographic films of cellulose triacetate were evaluated. Additionally, the thermal stability behavior of the films and the feasibility of crosslinking of CTA films were investigated. Film samples were selected and characterized by FTIR-ATR spectroscopy. Irradiated samples by gamma rays and electron beam with radiation absorbed doses between 6 kGy and 200 kGy were examined by FEGSEM microscopy, UV–Vis spectrophotometry and differential scanning calorimetry (DSC). The results showed that disinfection by gamma and electron beam irradiation, in the dose range of 6 kGy–10 kGy, does not change or modification of main properties of the constitutive materials of photographic and cinematographic films. The applied dose of 50 kGy, both gamma rays and electron beam, indicated a crosslinking effect on the films and can be considered a possibility for the treatment of films affected by the "vinegar syndrome".

1. Introduction

Safeguarding photographic and cinematographic films collections has been a challenge to conservators due to materials structure used as film support and the storage conditions with inadequate levels of temperature and humidity for conservation. Majority of black-and-white photographic and cinematographic films on libraries, museums and historical archives collections are made on cellulose triacetate (CTA) base. CTA is a semisynthetic polymer of the cellulose esters and also was widely used as a photographic film support in the mid-1920s until 1990s (Ahmad et al., 2020; Nobukawa et al., 2015). CTA properties include toughness, clarity, low permeability, good chemical resistance and flexibility. CTA base is obtained from a blend made of cotton linters, acetic acid, acetic anhydride and sulfuric acid as a catalyst (Reac. 1) (Martuscelli, 2010).

$$[C_6H_7O_2(OH)_3]_n + 3n(CH_3CO)_2O \rightarrow C_6H_7O_2(OCOCH_3)_3 + 3n(CH_3COOH) \quad \text{(Reac. 1)}$$

Often plasticizers like triphenyl phosphate (TPP) and diethyl phthalate (DEP), for instance, are added to improve flexibility, toughness and moisture resistance. Layers are applied in the case of black-and-white photographic and cinematographic films namely an adhesive layer to adhere the gelatin emulsion to the CTA base, an anti-halation layer to protect the film and other surface coatings to provide static protection (Nunes et al., 2020). The polymer base is approximately 90% of the films composition (Carter et al., 2020). The photographic and cinematographic emulsion contains about 60–70% gelatin as a binder for suspended light-sensitive silver halide salts (Gaspard et al., 2007).

The physical and chemical stability of CTA films are affected by temperature and humidity and depends on the storage conditions in which films are kept. In the presence of moisture and heat, detachment of acetyl groups can occur and free acetic acid released and diffuses to

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https://doi.org/10.1016/j.radphyschem.2021.109395
Received 5 July 2020; Received in revised form 21 October 2020; Accepted 7 February 2021
Available online 10 February 2021

the surface, giving rise to an intense odor of vinegar. The deacetylation process and breakdown of CTA films known as "vinegar syndrome". As a result of the hydrolysis of the ester bonds, the acetate ions interact with moisture to yield acetic acid (Reac. 2) (Blanton et al., 2014).

$[C_6H_7O_2(OCOCH_3)_3]_n + 3n(H_20) \rightarrow [C_6H_7O_2(OCOCH_3)_s(OH)_3]_n + 3n(CH_3COOH)$ (Reac. 2)

In this case, as a consequence, the "vinegar syndrome" makes the support of CTA films shrunken, fragile and brittle (Ahmad et al., 2020; Blanton et al., 2014). In addition, image stability is affected because the effects of acetic acid liberate leading to softening of gelatin emulsion and image loss. A leading cause of biodeterioration of photographic and cinematographic films is the fungi attack under storage conditions in environments with humidity above 70% (Mazzoli et al., 2018; Rakotonirainy et al., 2016; Tomšová et al., 2016). Gelatin emulsion and CTA base from films are the food source for fungi growth. Damage from enzymes produced by fungi includes softening of gelatin and permanent stains on the image. There are no satisfactory corrective treatments in the affected films for "vinegar syndrome" and fungi damage, prevention is the only practical method. Once deterioration is detected, the recommendation is to isolate the affected films and take actions to stop the deterioration, including freezing (Reilly, 1993). Traditional disinfection treatments, for instance, ethylene oxide fumigation was largely used in museums, although is nowadays considered an obsolete practice for its cancerogenic properties. Besides, ethylene oxide damages gelatin emulsions and is ineffective in eliminating spores (Nitterus, 2000). The application of a 70% ethanol solution is a common option to stop the active growth of fungi, however it also has no biocidal effect on spores (Zervos and Alexopoulou, 2015). In this way, the development of new technologies are useful tools for the preservation of photographic and cinematographic materials in historical and cultural collections.

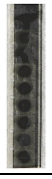
Radiation processing technology currently is widely applied worldwide. Gamma and electron beam-sterilized products have a wide range of applications. In recent years, the processing by ionizing radiation of cultural heritage materials, such as books, parchments, canvas, paintings, textiles, leather, sculptures, furniture, among others, have been enhanced and intensified. Ionizing radiation with gamma rays, X-rays, and electron beam has helped to eliminate insects and fungi contamination (Baccaro and Cemmi, 2017; Borgognoni et al., 2017; Chmielewska-Śmietanko et al., 2018; Cortella et al., 2020; International Atomic Energy Agency, 2017; Vadrucci et al., 2020). Fungal contamination in photographic and cinematographic collections had been extensively studied and stablished (Abrusci et al, 2005, 2006; Bingley and Verran, 2013; Borrego et al., 2010; Bučková et al., 2014; Lucas et al., 2017; Rakotonirainy et al., 2016; Vivar et al., 2013). Several studies have been conducted to determine the recommended dose to eliminate fungi contamination in cultural heritage materials and doses between 6 kGy and 10 kGy have been found to be effective in eradicating fungal contamination and their spores in cellulose-based materials (Area et al., 2014; International Atomic Energy Agency, 2017; Kantoğlu et al., 2018; Marušić et al., 2020; Moise et al., 2019). If the treated materials are placed in an inappropriate environment for their conservation, fungal contamination can occur again. Thus, it is important to compromise that the storage environment after irradiation is free from biological contamination and with appropriate parameters for the conservation of materials. Nevertheless, in the specific case of photographic and cinematographic films based on cellulose triacetate, it has not been assessed whether the recommended absorbed dose range for disinfection, which is sufficient to eradicate most fungi, would be reliable not to affect the films properties. For the conservation of audiovisual materials, it is essential to certify the absence of secondary effects that would compromise the legibility of the images. Exposure to ionizing radiation can lead to structural changes in polymers and breakdown of molecular chains. However, according to the dose applied, ionizing radiation is capable of producing a crosslinking effect, promoting the branching of polymer chains and increasing the molar mass. In this sense, crosslinking, as an effect of ionizing radiation, can enable the support to be reconstituted, increasing the mechanical resistance. The crosslinking effect of ionizing radiation would lead to the interruption of the "vinegar syndrome", which affects cellulose triacetate films, and would facilitate the migration of the support to preserve information. While natural polymers, especially purified cellulose materials, are susceptible to degradation by irradiation (International Atomic Energy Agency, 2016), cellulose ethers and esters also undergo degradation, but to a lesser extent. The presence of aromatic groups in cellulose favors the reduction of degradation yield. The acetyl groups in cellulose diacetate have a high protective effect against the polymer chain scission prompted by ionizing radiation (Ershov, 1998). Studies to evaluate the effects of ionizing radiation on cellulosic materials, paper samples and cotton linters (Baccaro et al., 2013; Baccaro and Cemmi, 2017; Bouchard et al., 2006; Kovalev and Bugaenko, 2003; Moise et al., 2019), have indicated processes of crosslinking at low doses (up to 10 kGy) and degradation at doses above 10 kGy. Degradation by ionizing radiation increases the mobility of macrochains and at the same time, mobility has been restricted by the crosslinking process. Macrochains that split off become short fragments of macro chains that undergo crosslinking (Baccaro and Cemmi, 2017; Bouchard et al., 2006; Kovalev and Bugaenko, 2003; Moise et al., 2019). The presence of plasticizer additives from aromatic compounds in photographic and cinematographic films, as well as the higher percentage of acetyl groups in cellulose triacetate, would enhance the resistance of these films to degradation by interaction with ionizing radiation. The aim of this study is to obtain information on the interaction of deteriorated CTA photographic and cinematographic films with the treatment for irradiation disinfection and to verify the feasibility of improving its resistance for the recovery of the images contained in the films through the irradiation crosslinking effect. This work presents an unprecedented investigation of the use of irradiation as an alternative treatment of "vinegar syndrome" with the possibility of strengthening the physical properties of the material. In this study, samples were characterized by FTIR-ATR spectroscopy to know their compositions. FEGSEM microscopy was used to analyze the surface morphology of non-irradiated and the effective disinfected (10 kGy) films samples. The samples were irradiated between 6 kGy and 200 kGy to evaluated the stability of the films to irradiation with gamma rays and electron beam and to obtain a detailed study of the chemical reaction processes in low and high doses. The non-irradiated and irradiated samples were investigated by UV–Vis absorption to verify the effective dose range to eliminate fungal contamination and preserve the material properties of the photographic and cinematographic films. Possible crosslinking effects promoted by ionizing radiation were examined by DSC for the treatment of films affected by "vinegar syndrome".

2. Experimental

2.1. Films samples selection and preparation

For this study, two black-and-white photographic and cinematographic films samples were selected from collections of libraries at the University of São Paulo. Representative samples were obtained from separate materials for disposal due to the advanced state of deterioration, which allowed the performance of destructive analyzes. Precisely because of the type of material and its peculiar conditions, data on the date of manufacture of the films were not available. Table 1 shows the main characteristics of the selected materials. The Mitutoyo micrometer (Mexico) 0–25 mm ± 0.001 mm was used to thickness measurements. These two film samples, Neg-F and Cine-K, exhibited evident deteriorations by "vinegar syndrome" with physical losses of the support, embrittlement, shrinkage, channeling, exudation of plasticizer additives and strong characteristic vinegar odor. For each photographic negative and cinematographic film, 65 samples cut in the approximate size of 3.5 cm x 1.0 cm were prepared to fit in different equipment samples holders

Table 1
Films samples properties.

	Sample code	Film type	Manufacturer	Frame size (mm)	Thickness (mm)
	Neg-F	Photographic negative	Kodak	170x125	0.242 ± 0.001
	Cine-K	Cinematographic film	Kodak	16	0.124 ± 0.001
					

for characterization.

2.2. Irradiation by gamma rays from cobalt-60 sources and in the electron beam accelerator

The gamma rays irradiation of the samples was carried out in air, at room temperature, at the Multipurpose Gamma Irradiation Facility of the Nuclear and Energy Research Institute – IPEN-CNEN/SP, Brazil, located inside the University of São Paulo campus. The installed current activity is around 13.0 PBq (350 kCi).

For electron beam irradiation, the samples were processed in the Dynamitron® Industrial Electron Beam Accelerator at the IPEN/CNEN-SP. The Dynamitron® accelerator, manufactured by RDI – Radiation Dynamics Inc, model DC1500/25/4, JOB 188 series, operates with energy of 1.5 MeV, current of 25 mA and power of 37.5 kW, with beam sweeping that varies from 60 cm to 120 cm.

Samples were irradiated with radiation absorbed doses of 6, 10, 15, 25, 50, 100 and 200 kGy at a dose rate 5–6 kGy h^{-1}, for gamma rays, and 500 kGy h^{-1}, for electron beam. The PMMA-Harwell dosimetry system (Harwell, United Kingdom) was used to estimate the absorbed dose in the irradiated samples.

2.3. Attenuated total reflection fourier-transform infrared spectroscopy (FTIR-ATR)

The non-irradiated samples were investigated by FTIR-ATR to the characterize the organic compounds of the materials and identify the type of polymeric support of the films. FTIR-ATR as non-destructive analysis technique is commonly used for the basic characterization of tangible cultural heritage materials (Derrick et al., 2015; Picollo et al., 2014). The spectra were collected on the emulsion side of the films using a Thermo Scientific Nicolet FTIR-ATR 6700 (Thermo Fisher Scientific, United States of America), with range from 4000 to 500 wavenumber (cm^{-1}).

2.4. Field-emission gun scanning electron microscopy (FEGSEM)

Scanning electron microscopy has been widely used to analyze the surface of materials and surface deterioration processes for materials conservation (Stuart, 2007). FEGSEM was used to examine the non-irradiated (0 kGy) and the effective disinfected (10 kGy) films samples. The surface topographies of the films were accomplished in an area where the emulsion was present using a Jeol JSM-6701F (Jeol, USA) electron microscope with a field emission gun operating at 1 kV and 6 kV. A piece of each sample was cut and fixed with a double-sided conducting carbon tape. The images were taken with the "raw" samples at an accelerating voltage of 1 kV.

2.5. Ultraviolet–visible spectroscopy (UV–Vis)

Changes in the perceived color of materials irradiated by gamma rays and electron beam can occur due to the excitation of the electrons depending of the absorbed dose (International Atomic Energy Agency, 2017). For this reason, the UV–Visible spectroscopy has been chosen to ensure that the effective disinfection dose does not induce undesired secondary effects in the constituent materials of the films. The absorption spectra were carried out using Thermo Scientific Genesys, model UV–Visible spectrophotometer, with scan range of 325 nm–1100 nm. The absorbance values were normalized to the thickness of the films samples to find the relative absorbance and to withdraw the thickness variations between samples. Samples thickness were measured three times with a digital micrometer Mitutoyo code nº 156-101, Mexico, and was calculated the average values of each sample.

2.6. Differential scanning calorimetry (DSC)

DSC have been used to measure the properties of materials used in cultural heritage objects, especially because of the sensitivity in detecting subtle phase transitions and reactions in amorphous, organic and polymeric materials (Artioli, 2010). The DSC characterization was performed in a Mettler-Toledo DSC822e heat flow device. The film samples, of approximately 5 mg each, were subjected to heating at a speed of 10 °C.min^{-1}, from 25 °C to 400 °C, in an N_2 atmosphere. The melting temperatures (T_m) of all samples were determined. The % degree crystallinity variation ($\Delta\tau$), to verify effects of ionizing radiation, was calculated in accordance with the Eq. (1) (Fintzou et al., 2007).

$$\Delta\tau = \frac{\Delta H_m - \Delta H_m^*}{\Delta H_m} \text{x} \ \ 100\% \quad (1)$$

where, ΔH_m^* is the melting enthalpy of irradiated samples and ΔH_m is the melting enthalpy of the non-irradiated sample (0 kGy).

3. Results and discussion

3.1. FTIR-ATR spectroscopy analysis

In view of the lack of data on the date of the film samples, besides the variation of properties of the materials used over the years in the film supports (Carter et al., 2020; Nunes et al., 2020; Valverde, 2005), it was necessary to identify and confirm the type of polymeric support and binder used in the films. FTIR-ATR spectroscopy has been a suitable method of characterization for unknown commonly polymers found in heritage collections (Mitchell et al., 2013; Picollo et al., 2014). This technique was applied to identify the non-irradiated samples (0 kGy). For the interpretation of FTIR-ATR spectra has been resorted a database of materials used in cultural heritage (Vahur et al., 2016) and references from photographic and cinematographic materials studies (Carter et al., 2020; Ciliberto et al., 2013; Knotek et al., 2018; Nunes et al., 2020; Stulik and Kaplan, 2018; Vivar et al., 2013). The infrared spectra of two samples are similar and revealed peaks of cellulose triacetate (CTA), gelatin, and diethyl phthalate (DEP) and triphenyl phosphate (TPP) plasticizers, Fig. 1.

CTA was characterized in FTIR spectrum by the methyl asymmetric stretching at 2972 cm^{-1} and the methyl symmetric stretching at 2868 cm^{-1} and 2865 cm^{-1}, carbonyl stretching at 1725 cm^{-1} and 1727 cm^{-1}, the methyl bending at 1369 cm^{-1} and 1371 cm^{-1}, and the ester stretching at 1222 cm^{-1} and 1221 cm^{-1}. The degradation state, which is the case of the study samples, leads to a process of deacetylation of CTA that decrease the carbonyl group band intensity (C═O), at 1725 cm^{-1} and 1727 cm^{-1} (Vivar et al., 2013). Gelatin, which is the binder medium of the photographic and cinematographic emulsion, is a protein of animal origin and in the FTIR spectra is identified in the bands corresponding to amide II at 1531 cm^{-1} and 1527 cm^{-1}, the methylene bending at 1447 cm^{-1}, the methylene wagging at 1339 cm^{-1} and the ester carbonyl groups stretching at 1091, 1082 and 994 cm^{-1}, and the methyne bending at 925 cm^{-1} and 914 cm^{-1}. Phosphorous as P-OR esters of DEP and TPP, plasticizer additive commonly found in CTA films for improving the resistance to moisture and as a flame retardant (Ciliberto et al., 2013), showed absorbance peaks at 1599 cm^{-1}, 863 cm^{-1}, 858 cm^{-1}, 769 cm^{-1} and 786 cm^{-1}. The assignment of characteristic groups to the ATR-FTIR spectrum of the samples and references have been described in Table 2.

Table 2
FTIR frequencies results and sample characterization.

Wavenumber (cm^{-1})		Functional group assignment	References	Origin
Neg-F	Cine-K			
2972	2972	CH_3 asymmetric stretch	Knotek et al., Vahur et al., Stulik et al.	CTA
2868	2865	CH_3 symmetric stretch	Knotek et al., Vahur et al., Stulik et al.	CTA
1725	1727	C=O stretching	Vivar et al., Ciliberto et al., Knotek et al., Vahur et al.	CTA
1599	1599	C=C stretching aromatic ring (phthalate)	Vivar et al., Knotek et al., Carter et al., Nunes et al.	TPP
1531	1527	N–H bending	Ciliberto et al., Vivar et al., Vahur et al., Stulik et al.	Gelatin
1447	1447	CH_2 bending	Ciliberto et al., Vahur et al. Carter et al., Stulik et al.	Gelatin
1369	1371	CH_3 bending	Ciliberto et al., Vivar et al., Carter et al., Nunes et al.	CTA
1339	1339	CH_2 wagging	Vahur et al., Stulik et al.	Gelatin
1222	1221	C–O–C stretching	Ciliberto et al., Vivar et al., Knotek et al., Nunes et al.	CTA
1091	1082	C–O stretching	Vahur et al., Stulik et al.	Gelatin
994	994	C–O–C stretching	Vahur et al.	Gelatin
925	914	CH bending	Vahur et al.	Gelatin
863	858	C–H bending aromatic ring (phthalate)	Nunes et al.	DEP
769	786	C–H bending aromatic ring (phthalate)	Vivar et al., Knotek et al., Nunes et al.	TPP

3.2. Field emission gun scanning electron microscopy, FEGSEM, micrographs

FEGSEM was employed in order to evaluate possible surface changes in the samples irradiated with 10 kGy. FEGSEM micrographs of non-irradiated samples indicated different morphologies for Neg-F and Cine-K films. The micrographs of Neg-F samples revealed agglomeration of light spots that are related to the silver particles present in the photographic emulsion. The Cine-K sample exhibited a darker surface because some layers are different from photographic films. The layers of

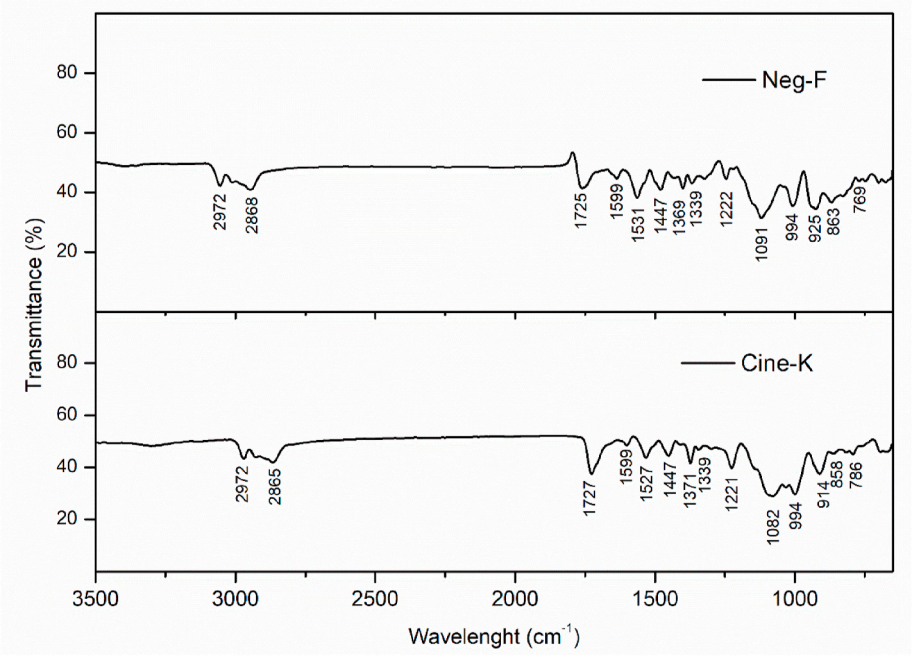


Fig. 1. FTIR spectra (4000-500 cm^{-1}) for samples Neg-F and Cine-K.

cinematographic films are designed to protect the film emulsion from scratches and abrasion, in addition to make the film slide smoothly through the camera and image projection equipment (Eastman Kodak Company, 2007).

No degradation effect of irradiation on the surface topology of the samples was indicated in the FEGSEM micrographs of non-irradiated and gamma and electron beam irradiated samples as shown in Fig. 2. The images displayed different morphologies for Neg-F and Cine-K films. Marks and particles from abrasion and dirt particles were all found to be related to the advanced deterioration of the samples and are not associated with irradiation. Therefore, the micrographs evidenced that the supra-molecular structure was not affected by the ionizing radiation with the absorbed dose of 10 kGy. Considering that the recommended dose of 6–10 kGy (Cortella et al., 2020; International Atomic Energy Agency, 2017; Moise et al., 2017) for disinfecting objects of cultural heritage includes the elimination of fungi most commonly found in historical and cultural collections (Borrego et al., 2010; Bučková et al., 2014; Ciliberto et al., 2013; Mazzoli et al., 2018; Vivar et al., 2013) is possible to be regarded the dose of 10 kGy to eradicate fungi contamination in CTA films without compromising the image of photographic and cinematographic films.

3.3. UV–vis spectroscopy analysis

The UV–visible spectrophotometry technique has often been applied to objects of cultural heritage, since it supports the analysis of colors and the quantification of visible effects related to the production, use and degradation of materials (Artioli, 2010). The interaction of photons from ionizing radiation with matter has the effect of producing secondary electrons and can give rise to excited and ionized species and radicals which will cause chemical changes such as the generation of color centers, main chain scission, and new double bonds (Rai et al., 2017). The chemical changes stem from ionizing radiation act according to the applied dose and can influence the absorption spectra depending on the compounds formed during irradiation. For this reason and considering the nature of the studied films, which have transparency to light, UV–vis spectrophotometry was chosen to define the effective absorbed dose for disinfection and to certify the absence of undesired side effects on the properties of the treated materials.

Upon visual examination, the samples presented a slight yellowish and emitted a noticeable odor after irradiation at doses of 50 kGy, 100 kGy and 200 kGy. Both samples showed peaks in the region ranging from 405 nm to 450 nm which are related to quinone specimens, chromophores originating from carbohydrates (Tribulová et al., 2016). The absorption band at about 650 nm in Cine-K samples are also assigned to quinone structures (das Neves and De Paoli, 1998). Chromophoric compounds of quinone possibly arise in cellulose materials deteriorated on account of aging or oxidative process (Korntner et al., 2015). The advanced state of deterioration of photographic and cinematographic films samples could conceivably have contributed to the production of chromophores, in addition to the effect of the doses applied for samples irradiation.

UV–visible absorption spectra of samples Neg-F and Cine-K non-irradiated and irradiated with gamma radiation doses from 6 kGy up to 200 kGy are indicated in Fig. 3. In spectra Neg-F samples, the absorbance did not rise up to 10 kGy. The doses of 15 kGy and 200 kGy intensified the absorption peak around 405 nm. UV–visible spectra of Cine-K samples revealed an intensification in absorbance after approximately 450 nm and in the absorption bands around 650 nm attributed to the polaron formation (Ebrahim et al., 2007). The doses of 15 kGy, 25 kGy and 200 kGy indicated a hyperchromic effect of absorption intensity at 450 nm, while the dose of 100 kGy promoted a hypochromic effect on the absorption intensity.

For samples irradiated with electron beam, in the range of 6 kGy–200 kGy, Fig. 4, a hyperchromic effect was noticed in the peak intensity at 404 nm, in the Neg-F sample at a dose of 200 kGy, which indicated the increment in chromophore groups activated by compounds formed during the irradiation. The Cine-K sample revealed a hyperchromic effect at peak intensity around 450 nm at doses of 15 kGy and 25 kGy.

The modifications in the optical properties of the CTA films, verified from gamma and electron beam irradiation, take place mainly as a result of the unsaturation and the addition of hydroxyl and carbonyl compounds resulting from the irradiation process in the presence of oxygen (Moura et al., 2004). Secondary effects caused by the interaction of ionizing radiation can induce defects and new sub-levels of energy in molecular orbitals. The increase in optical absorption can be attributed to the enlarge in the number of dipoles (C–O and C═O) due to irradiation. Therefore, C–C bond breakage and dehydrogenation of polymer chains occur with the escape of hydrogen atoms (Raghu et al., 2015). The enhancement in the amount of free radicals triggered by higher radiation ionizing doses is a destructive effect that intensifies and widens the peaks and become the film samples fragile and easily damaged (El-Fiki et al., 1996; Emmi et al., 2000).

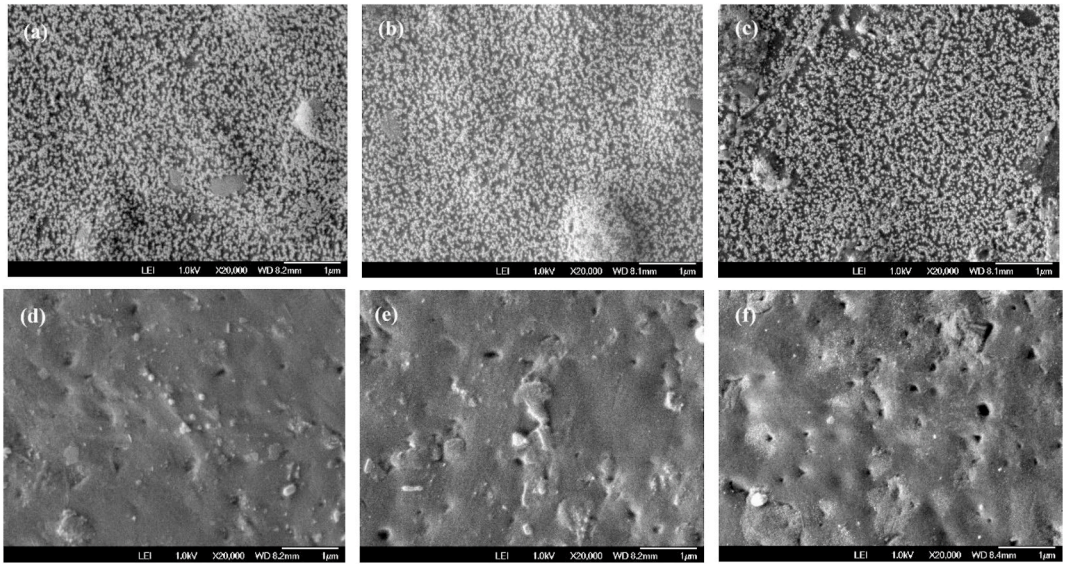


Fig. 2. FEGSEM micrographs, magnification 20.000 x: Neg-F **(a)** non–irradiated (0 kGy), **(b)** gamma irradiated 10 kGy and **(c)** e-beam irradiated 10 kGy, Cine-K **(d)** non-irradiated (0 kGy), **(e)** gamma irradiated 10 kGy and **(f)** e-beam irradiated 10 kGy.

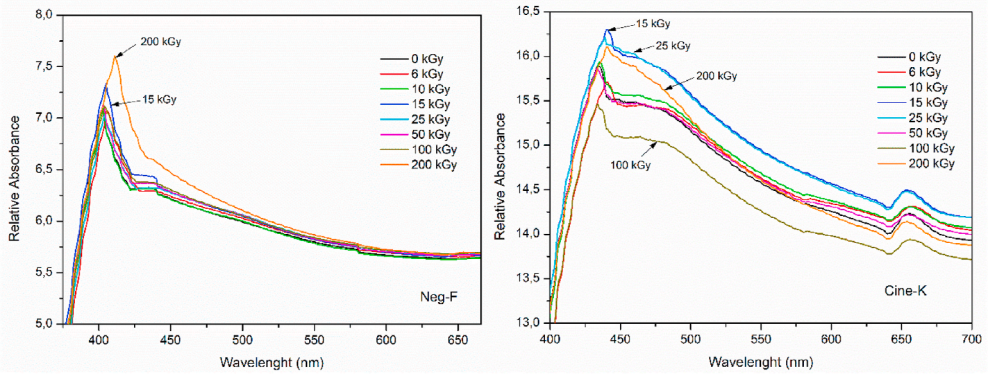


Fig. 3. UV–Vis absorption spectra of non-irradiated and gamma irradiated samples Neg-F and Cine-K.

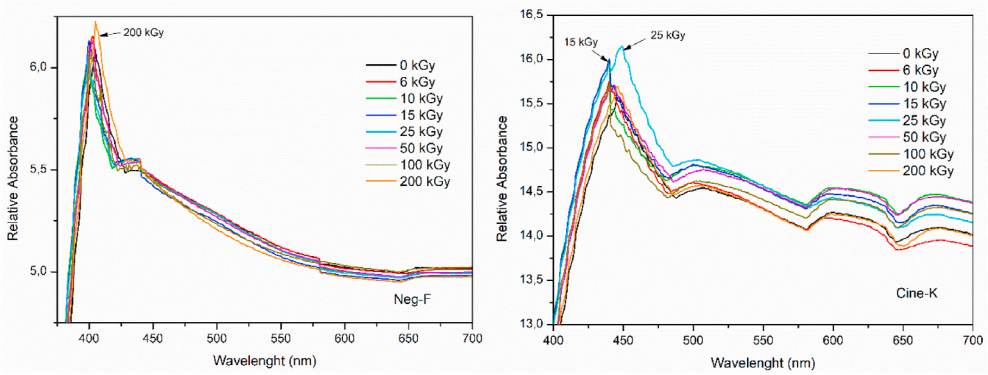


Fig. 4. UV–Vis absorption spectra of non-irradiated and electron beam irradiated samples Neg-F and Cine-K.

From the UV–Vis results obtained, the changes in absorption prompted by the action of ionizing radiation in the studied CTA films become evident from 15 kGy. Since photographic and cinematographic films depend on the passage of light for image reproduction, it is important to ensure that optical properties are not affected by irradiation. The outcomes of the UV–visible spectrophotometric analysis technique indicated the safe dose of gamma and electron beam irradiation to be applied for disinfection treatment in these materials should remain within 10 kGy to avoid changes in optical properties. The intensity of the effect of ionizing radiation might be accentuated regarding to the state of samples conservation. Furthermore, deterioration in advanced stages in the films compromises the treatment for recovering the images.

3.4. Differential scanning calorimetry (DSC)

Thermal analysis techniques are useful tools for characterizing polymers and produce useful information that complements chemical analysis data and provide parameters such as thermal stability, oxidative stability and melting point (Schilling et al., 2010). The DSC curves and their modifications depending on the absorbed doses of irradiation with gamma rays and electron beam are presented in Figs. 5 and 6. The melting temperature of cellulose triacetate is characterized in DSC thermograms reported from literature at endothermic peaks of 245 °C–315 °C (An et al., 2019; Krasovskii et al., 2011b; Nabili et al., 2017). In the results obtained the melting temperatures for the samples irradiated with gamma rays and electron beam ranged from 235.2 °C to 268.2 °C, Tables 3 and 4. A slight yellowish coloration and an unpleasant off-odor were noted after irradiation doses above 50 kGy. The intensity

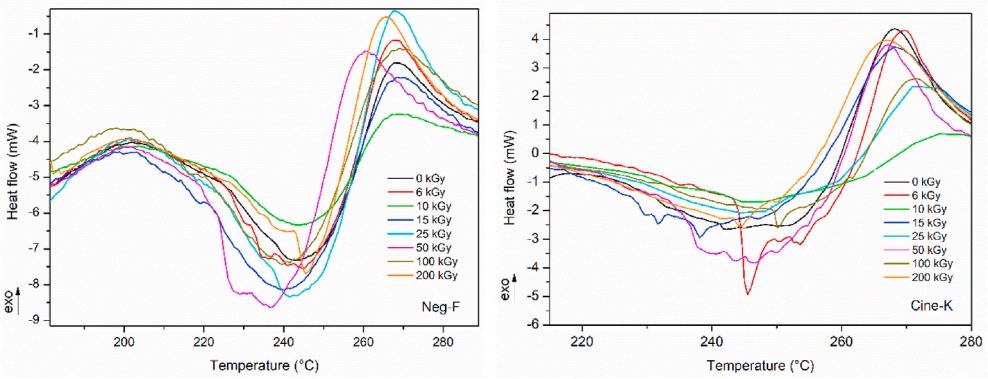


Fig. 5. DSC thermograms of non-irradiated and gamma irradiated samples Neg-F and Cine-K.

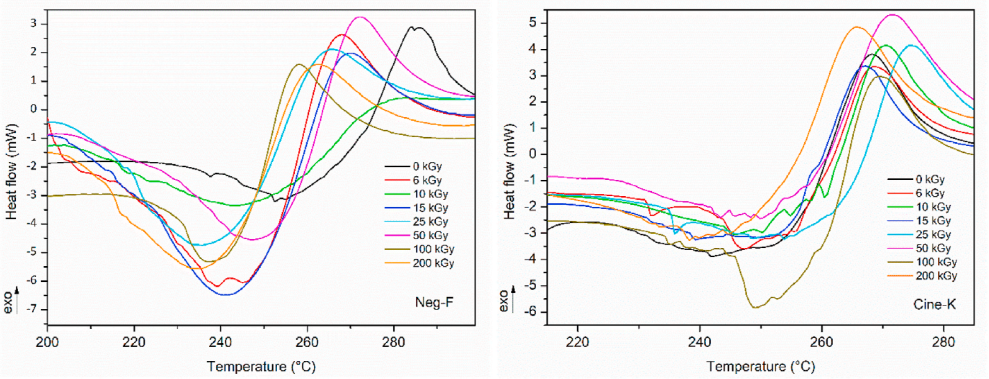


Fig. 6. DSC thermograms of non-irradiated and electron beam irradiated samples Neg-F and Cine-K.

Table 3
Effect of gamma irradiation on thermal properties of Neg-F and Cine-K samples.

	NEG-F			CINE-K		
DOSE (KGY)	T_m (°C)	ΔH_m (J. g^{-1})	$\Delta\tau$ (%)	T_m (°C)	ΔH_m (J. g^{-1})	$\Delta\tau$ (%)
0	244.9 ± 0.06	24.3 ± 0.5	0,0	246.8 ± 0.05	24.4 ± 0.6	0,0
6	241.6 ± 0.06	23.5 ± 0.6	-3,3	246.2 ± 0.06	16.5 ± 0.5	-32,4
10	240.2 ± 0.07	20.4 ± 0.7	-16,2	244.4 ± 0.06	15.7 ± 0.7	-35,7
15	239.6 ± 0.07	19.0 ± 0.7	-22,0	243.4 ± 0.07	15.0 ± 0.7	-38,5
25	236.7 ± 0.08	18.5 ± 0.8	-23,9	238.0 ± 0.09	12.4 ± 0.9	-49,2
50	245.0 ± 0.10	26.6 ± 1.0	9,5	247.0 ± 0.11	31.3 ± 1.1	28,3
100	245.5 ± 0.14	31.7 ± 1.2	30,6	250.3 ± 0.15	37.1 ± 1.1	52,0
200	246.0 ± 0.24	32.5 ± 1.4	33,7	268.2 ± 0.22	40.6 ± 1.3	66,4

Table 4
Effect of electron beam irradiation on thermal properties of Neg-F and Cine-K samples.

	NEG-F			CINE-K		
DOSE (KGY)	T_m (°C)	ΔH_m (J.g^{-1})	$\Delta\tau$ (%)	T_m (°C)	ΔH_m (J.g^{-1})	$\Delta\tau$ (%)
0	246.7 ± 0.05	24.4 ± 0.5	0,0	250.0 ± 0.06	24.0 ± 0.6	0,0
6	241.6 ± 0.06	23.0 ± 0.7	-5,7	247.3 ± 0.06	23.5 ± 0.6	-2,1
10	237.4 ± 0.07	23.0 ± 0.6	-5,7	245.5 ± 0.07	23.5 ± 0.7	-2,1
15	235.7 ± 0.07	22.5 ± 0.7	-7,8	239.3 ± 0.07	20.9 ± 0.8	-12,9
25	235.2 ± 0.08	13.5 ± 0.9	-44,7	238.3 ± 0.08	17.4 ± 0.9	-27,5
50	241.9 ± 0.11	25.9 ± 1.1	6,1	253.8 ± 0.12	24.1 ± 1.0	0,4
100	244.0 ± 0.16	29.0 ± 1.2	18,9	257.8 ± 0.17	24.2 ± 1.3	0,8
200	247.1 ± 0.27	32.5 ± 1.2	33,2	268.2 ± 0.26	36.7 ± 1.4	52,9

of such alterations was accentuated with irradiation doses up to 200 kGy. The photographic and cinematographic film samples remain stable after irradiation even with the higher doses for both irradiation methods.

A relevant issue to be considered for the interpretation of the DSC outcomes would be the specificity of the selected samples. These were samples of archived photographic and cinematographic films with fixed images and signs of deterioration by "vinegar syndrome", which affected parts of the same sample differently. Considering thermal analysis as a destructive technique, several samples of the same type of film were required, which implied obtaining samples with different degradation states and distinct parts of the image, therefore, with unlike proportions of sensitized and revealed silver.

The values of melting temperature (T_m) and enthalpy of melting (ΔH_m) obtained from DSC are indicated in Tables 3 and 4. The values of % variation in the degree of crystallinity ($\Delta\tau$) were calculated considering non-irradiated samples (0 kGy) as reference control samples.

The values of T_m, ΔH_m and $\Delta\tau$ reduced with the addition in the applied dose of ionizing radiation up to 25 kGy, and starting at 50 kGy increased with the absorbed dose up to 200 kGy. The values of $\Delta\tau$ indicated an enlargement of the crystallinity degree of the irradiated samples with high doses (above 50 kGy) compared to control samples (0 kGy), as seen in Fig. 7. For higher doses, between 50 kGy and 200 kGy the DSC findings evidenced an enhancement in thermal stability attributed to both irradiations, with gamma rays and electron beam, in the film samples.

Polysaccharides when exposed to ionizing radiation are susceptible to reactions of molecular chain branching, crosslinking and molecular degradation or scissioning. Such effects coexist and the prevalence of these phenomena depends on factors, namely, initial molecular structure, polymer morphology and irradiation environment (Spadaro et al.,

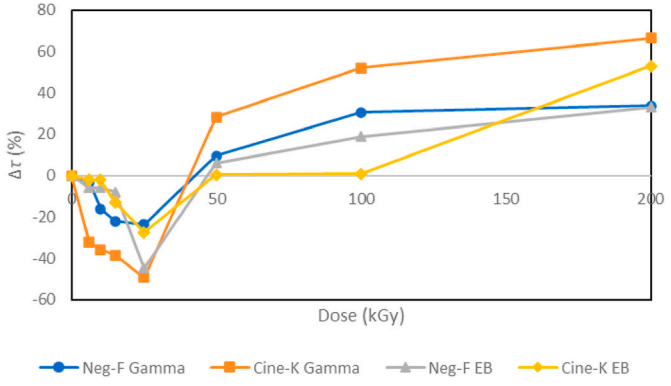


Fig. 7. Variation in degree of crystallinity ($\Delta\tau$) of samples in function of the absorbed dose for gamma and electron beam (EB).

2017). Traditionally, ionizing radiation in natural polymers is mainly applied to degraded large molecules into smaller sizes, in terms of oligomers (International Atomic Energy Agency, 2016). On account of main-chain scission of the polymer, shorter chains are formed. Nevertheless, the macroradicals decay by interaction of ionizing radiation can be induced to combination reactions. In this way, during the irradiation process, long chain polymeric might be converted to short-chain crosslinked by the combination of macroradicals (Kovalev and Bugaenko, 2003). Chains that have been fractured present better mobility, are realigned in a more orderly way and compact more easily, facilitating the crystallization process and leading to raise the degree of crystallinity (Nakka et al., 2015).

The interpretation of the DSC analysis outcomes indicated degradation effect by chain scission and crosslinking process according to the irradiation doses. At low doses, between 6 kGy and 25 kGy, scission was initially predominant, reduced the polymer length, and favored the mobility of the chains, which contributed to shift of T_m towards lower temperatures. At the dose range of 50 kGy–200 kGy, the increase in T_m values suggests the probability of the free radicals formed being used in the chemical reactions and result in the crosslinking mechanism in CTA-based samples (Nouh et al., 2008). In the same way, the variation in crystallinity degree ($\Delta\tau$), on account of chain scissions and free radicals yield, is observed up to 25 kGy, with negative values of $\Delta\tau$. The higher values of $\Delta\tau$ at absorbed doses above 50 kGy–200 kGy, for both gamma and electron beam irradiation, are related to the melting enthalpy which are higher in these irradiated samples and surpassed the melting enthalpy of the control samples (0 kGy) due to the gain in the degree of crystallinity and, therefore, recovery of the thermal stability of the irradiated samples. The observed effects on irradiated CTA films at doses up to 25 kGy, could be assigned degradation of carbonyl group associated with development of C–O bonds and free radicals yield which take down the thermal stability. On the other hand, the improvement in thermal stability with higher doses would be related to the formation of C═O bonds, crosslinking process, as a function of the chemical bond reactions promoted by free radicals produced during irradiation (El-Fiki et al., 1996; Keriem, 2015; Nouh et al., 2008).

The thermal analysis findings presented are in accordance with Nouh et al. (2008) who reported an enlargement in thermal stability in electron beam irradiated CTA films at higher doses of 80 kGy–200 kGy. The study of Keriem (2015) reported in CTA film samples an improvement in the thermal stability attributed to the crosslinking process by gamma radiation. These findings also are in agreement with the study by Krasovskii et al. (2011a), which investigated the behavior of cellulose triacetate with photographic gelatin emulsion at different doses of electron beam radiation. According to the Krasovskii et al., the absorbed dose of 50 kGy was the one most successful in enhancement the adhesion strength of the gelatin emulsion with cellulose triacetate. In the case of the study, the dose of 50 kGy produced a formation of a strong bond between the amine groups of gelatin and the carbonyl groups of cellulose triacetate. The increase in gelatin viscosity in the absorbed dose of up to 50 kGy of gamma radiation and electron beam was corroborated by the work of Vieira and Del Mastro (2002) and thus complement the verification of the effect with the absorbed dose of 50 kGy of radiation ionizing to upgrade the mechanical and chemical properties in photographic and cinematographic films of cellulose triacetate.

Although the data obtained confirm the improvement in thermal resistance at doses above 50 kGy, it is necessary to consider that higher doses favor the interaction of free radicals in the polymer chains for a longer time. Thus, the oxidative effects accumulate, as well as the formation of chromophore groups and the consequent yellowing of the samples. In addition, photographic and cinematographic films require the maintenance of the flexibility property, which could be compromised with a more intense crosslinking in doses above 100 kGy. In view of the peculiarity and handling of the films, it is recommended to use the dose of 50 kGy for applications with gamma and electron beam irradiation for crosslinking purposes, which are useful for treating cases of "vinegar syndrome" in films in initial phase of deterioration whose images are not affected.

4. Conclusion

FTIR-ATR spectroscopy analysis characterized photographic and cinematographic samples with cellulose triacetate base, gelatin emulsion, diethyl phthalate and triphenyl phosphate plasticizers. The FEG-SEM micrographs of the 10 kGy irradiated samples with gamma rays and electron beam did not showed significant differences in the surface morphology of the films. The UV–Vis spectra revealed changes for gamma and electron beam irradiated samples from 15 kGy dose.

The proposal of this work was to contribute to supply the lack of studies to understand the behavior of photographic and cinematographic films from historical and cultural collections when treated to gamma ray and electron beam irradiation. Hence, the present study demonstrated that the recommended dose established for biocidal effect in cultural heritage materials, in the range of 6 kGy–10 kGy, is safe to be applied to photographic and cinematographic films of cellulose triacetate, without compromise or modify the main properties of the constitutive materials.

The DSC analysis findings demonstrated the potential of irradiation with gamma rays and electron beam as alternatives for the cases of films affected by the "vinegar syndrome". Irradiation with the absorbed dose of 50 kGy could be considered as a possibility to promote the thermal stability improvement and the crosslinking of polymeric chains of the deteriorated CTA films in order to strengthen their weakened support. Because of the fragility of the treated materials, it is highly recommended to continue checking periodically the possible changes that may be induced by ionizing radiation, in order to guarantee the absence of side effects and the stability of the materials. It is important to note that the recommended dose range for disinfection should not exceed 10 kGy as justified by several studies.

CRediT authorship contribution statement

Maria Luiza E. Nagai: Conceptualization, Data Curation, Methodology, Validation, Formal Analysis, Investigation, Writing – Original Draft preparation, Writing- Reviewing and Editing, Visualization. **Paulo de Souza Santos:** Data Curation, Validation, Investigation, Resources. **Larissa Otubo:** Data Curation, Validation, Investigation, Resources. **Maria José A. Oliveira:** Data Curation, Validation, Investigation, Resources. **Pablo A.S. Vasquez:** Conceptualization, Methodology, Formal Analysis, Supervision, Project Administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

The authors are grateful for financial support from the International Agency of Atomic Energy - IAEA.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.radphyschem.2021.109395.

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