

Fourier Transform Infrared Spectra of Drying Oils Treated by Irradiation

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Drying oils, such as linseed oil and tung oil, have the potential as coating materials to improve barrier properties of biobased packaging films. Oil drying is a chemical reaction in which polyunsaturated fatty acids undergo autoxidation. During drying, oils polymerize and form water-resistant films. However, drying rates tend to be too slow for practical applications. Metal driers are used in the paint industry to accelerate drying, but often driers are not safe for food contact. The objective of this work was to investigate the effect of ionizing radiation on the oxidation or drying rate of drying oils. The effect of irradiation dose on the drying rate of linseed and tung oils was monitored by FTIR spectroscopy. The peak at 3010 cm^{-1} was found to be a useful index of oxidation rate. The decrease in peak intensity with time was fitted with exponential functions of the form $\text{Abs} = \text{Abs}_0 \exp(-t/k)$, where Abs_0 is the initial absorbance and $1/k$ is the rate constant for the oxidation process. Values for k were 9.91 ($R^2 = 0.98$), 6.59 ($R^2 = 0.95$) and 6.44 ($R^2 = 0.97$) for radiation levels of 0, 50, and 100 kGy, respectively. The k values suggested that the oxidation rate increased as the radiation dose increased from 0 to 50 kGy. A further increase to 100 kGy had only a limited effect.

KEYWORDS: FTIR; irradiation; drying oils; oil oxidation; biobased

INTRODUCTION

Environmental concerns have contributed to an increased interest in the production of biobased biodegradable packaging films. Due to the general hydrophilic nature of biobased polymers, nearly all biobased films have poor water barrier properties (1). Drying oils are widely used as coatings and varnishes in industrial and artistic applications (1–6). Drying oils are natural fatty oils that harden to a tough, solid film after exposure to air for a period of time. The common fatty acids in drying oils are saturated fatty acids with 12, 14, 16, or 18 carbon atoms and C_{18} polyunsaturated fatty acids with 1, 2, or 3 double bonds (7, 8). Oil drying is a chemical reaction wherein the unsaturated fatty acids in oils undergo autoxidation. During drying, the oil polymerizes into long-chain molecules and forms a film. When drying oils are applied as coatings, they impart water resistance properties and reduce air/oxygen transmission to the underlying materials (1). Linseed and tung oils are two examples of common drying oils. Linseed oil is widely used in industry because it forms continuous films with good optical and mechanical properties (1, 8–10). Linseed oil has a faster drying rate than most other common oils due to its high content of linolenic acid (7, 8, 11, 12). Tung oil is used as a drying agent in paints.

Drying rate is important in oil applications. Metallic catalysts or driers have been used for decades to increase

the rate of drying (3, 13–16). The energy of activation for oxygen uptake by the oil is reduced by an order of magnitude in the presence of a drier (17, 18). However, due to their toxicity, many metal drying catalysts are not safe for food contact uses. Poor through-dry is another drawback for the use of driers (19). The oxidative polymerization mechanism of drying oils follows the three classic steps: initiation, propagation, and termination. During initiation, the proton on a methylene group adjacent to a double bond is removed, producing a free alkyl radical. The next reaction, termed propagation, occurs when the alkyl radical combines with molecular oxygen to form a peroxy radical. Peroxy radicals will react with other methylene groups adjacent to double bonds, removing the proton and forming hydroperoxides. After proton removal, alkyl radicals remain as the product, and the propagation reaction is continued. Hydroperoxides can decompose and produce a highly reactive hydroxyl radical and an alkoxy radical. That reaction is catalyzed by transition metals, such as iron or copper. Finally, during termination, alkyl, alkoxy, and/or peroxy radicals react or combine with each other, ending the oxidation process. This reaction results in the cross-linking of triacylglycerols. Cross-linking leads to the formation of large, insoluble, polymers. γ -Radiation can induce the formation of free radicals and thus promote the above reactions (20–22). Ionizing irradiation is used in industry to improve the properties of synthetic polymers by inducing cross-linking reactions (20, 23–25).

Drying reactions are complex (4, 26, 27) and can be difficult to monitor because many reaction steps occur at the

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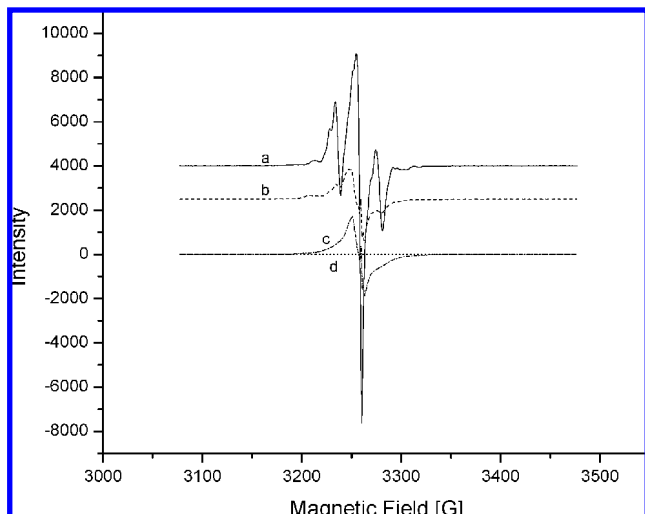


Figure 1. X-band EPR spectra of acetone and tung oil: a, irradiated acetone; b, irradiated tung oil and acetone mixture; c, irradiated tung oil; d, tung oil.

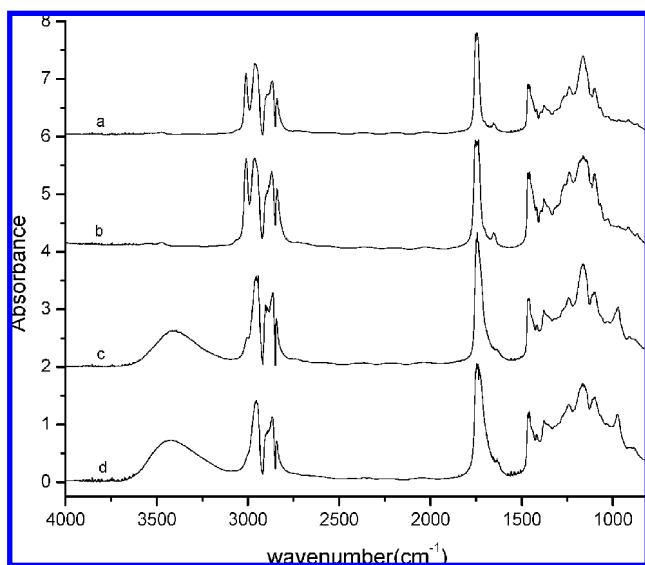


Figure 2. FTIR spectra for linseed oil containing 25% acetone and treated at 50 kGy: a, initial spectrum; b, after 4 h of exposure to air; c at 12 h of exposure; d at 24 h.

same time (17). Fourier transform infrared analysis (FTIR) has been applied to monitor the chemical changes that occur in thin films of linseed oil during drying (16, 25, 28). FTIR is a rapid and sensitive technique that can be applied to liquid or solid samples (29). It has been used to detect changes in the structure and properties of proteins, carbohydrates, and lipids (10, 25, 28, 30, 31). The objectives of this work were to investigate the effect of ionizing radiation on the rate of oxidation processes in drying oils. Linseed oil and tung oil were selected for the experiments. Linseed oil contains 10% saturated fatty acids, 22% oleic acid (18:1), 16% linoleic acid (18:2), and 48% linolenic acid (18:3). Tung oil contains 5% saturated fatty acids, 8% oleic acid (18:1), 4% linoleic acid (18:2), 3% linolenic acid (18:3), and 80% 9,11,13-octadecatrienoic acid with conjugated double bonds (8, 32–34). Acetone was used as a solvent for both linseed and tung oils. The incorporation of solvents was reported to increase the film through-drying rate (2).

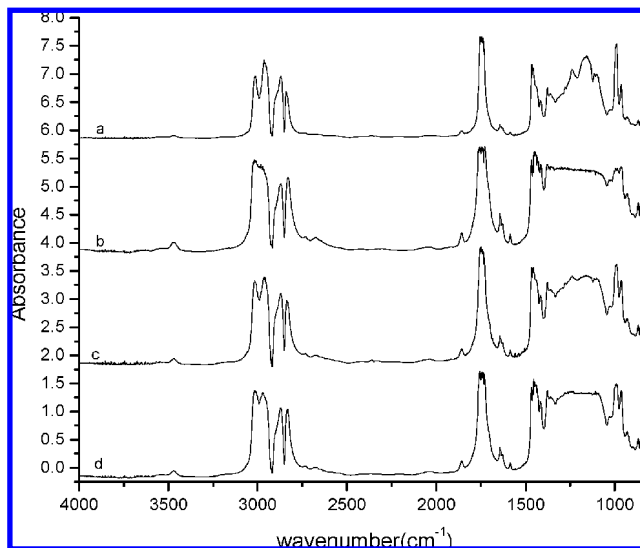


Figure 3. FTIR spectra for tung oil containing 25% acetone and treated at 50 kGy: a, initial spectrum; b, after 4 h of exposure to air; c, at 12 h of exposure; d, at 24 h.

Table 1. Characteristic Infrared Absorption Frequencies (8, 19)

bond	compound type	frequency range, cm^{-1} , and intensity
O—H	monomeric – alcohols, phenols	3640–3160 (s, br) ^a stretch
	hydrogen bonds – alcohols, phenols	3600–3200 (br) stretch
=C—H	alkenes	3000–2500 (br) stretch
	(C—H)CH ₃	3080–3000 (m) stretch
(C—H)CH ₂	methylenes	~2960 (sh) asymmetric stretch
	methylenes	2926 (s) asymmetric stretch
C=O	aldehydes, ketones, carboxylic acids, esters	1747 (s) stretch
	C=C	trans–trans conjugated double bonds
C=C	trans–cis conjugated double bonds	950

^a s, strong; m, medium; w, weak; br, broad; sh, shoulder.

MATERIALS AND METHODS

Materials. Linseed oil and tung oil were obtained from Sigma-Aldrich, St. Louis, MO. Acetone was of ACS spectroscopic grade, $\geq 99.5\%$ (Sigma-Aldrich).

Irradiation Treatment. Linseed and tung oils were mixed with acetone at ratios of 0, 25, and 50% acetone (v/v) and placed in glass bottles. Oil and acetone mixtures were irradiated in a laboratory size irradiator (Gamma Cell 2000, MDS Nordion, Canada) loaded with a cobalt-60 source. The irradiation dose applied was 0, 50, or 100 kGy. After irradiation, samples were kept under refrigeration until FTIR measurements.

Detection of Free Radicals by Electron Paramagnetic Resonance (EPR). EPR or electron spin resonance (ESR) is a spectroscopic technique that can be used for the identification and quantification of free radicals (35). Tung oil mixed with acetone (1:1 v/v) was placed in EPR tubes and kept in liquid nitrogen for the irradiation treatment. X-band EPR spectra were collected on a Varian E-122 spectrometer equipped with a rectangular microwave cavity.

FTIR Measurements. Sample drops of irradiated oils were placed on polyethylene infrared sample cards (International Crystal Laboratories, Garfield, NJ). Sample oil droplets were exposed to the open air while infrared spectra were collected (Thermo Nicolet FTIR spectrometer, Nexus 670 Madison, WI). Spectra were collected (resolution = 2 cm^{-1} , 64 scan summation) for 24 h at specific time intervals. Sample

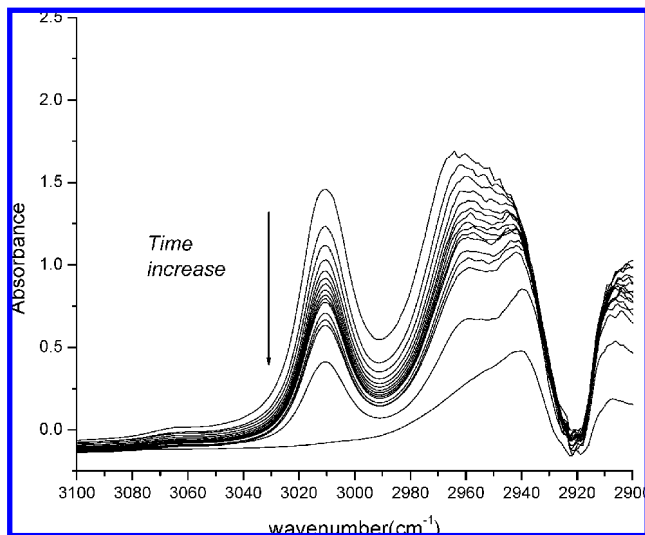


Figure 4. FTIR spectra from 3100 to 2900 cm^{-1} of linseed oil containing 25% acetone and treated at 50 kGy. Spectra were collected at 1 min intervals from 0 to 10 min, every 5 min from 10 to 30 min, at 1 h, and at 24 h.

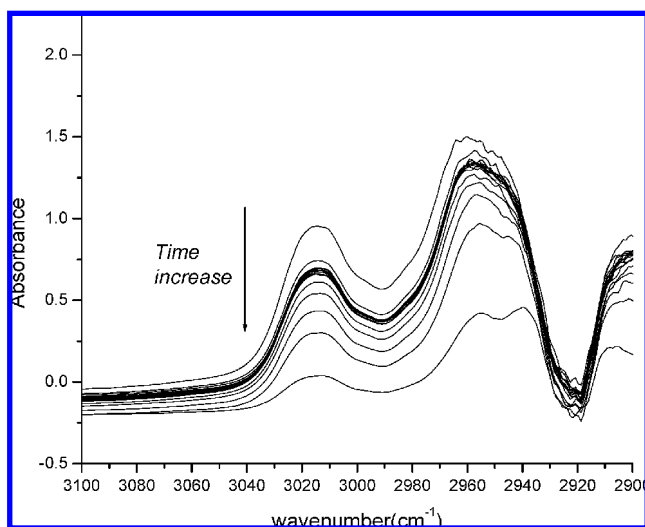


Figure 5. FTIR spectra from 3100 to 2900 cm^{-1} of tung oil containing 25% acetone and treated at 50 kGy. Spectra were collected at 1 min intervals from 0 to 10 min, every 5 min from 10 to 30 min, at 1 h, and at 24 h.

cards were placed in a dark room between measurements. Collected spectra were standardized to the same baseline for comparisons.

RESULTS AND DISCUSSION

EPR. Acetone can be dissociated into acetyl and methyl radicals under ionizing radiation (36). EPR spectra of samples of tung oil, irradiated tung oil, irradiated mixtures of tung oil with acetone (1:1 v/v), and irradiated acetone are shown in **Figure 1**. Sharp peaks in the 3200–3350 G region are observed in all four spectra. Tung oil that was not treated by irradiation was used as a control. No free radicals were detected in non-irradiated tung oil. For irradiated acetone, the triplet peaks at 3233, 3254, and 3274 G indicated alkyl free radicals (e.g., $\text{CH}_3\text{COCH}_2^{\cdot}$). The spectrum of irradiated tung oil had a larger peak at 3250 G than the spectrum from the irradiated tung oil/acetone mixture, but lacked the triplet peaks that indicate the alkyl radicals. The spectrum of irradiated tung oil with acetone was similar to that of irradiated acetone, but with much smaller

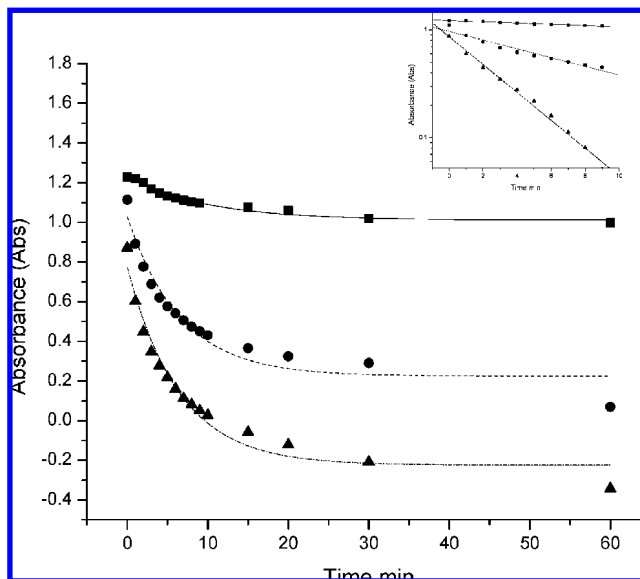


Figure 6. Effect of radiation dose on 3010 cm^{-1} absorbance for linseed oil containing 25% acetone: (■) 0 kGy; (●) 50 kGy; (▲) 100 kGy. Lines represent fitted exponential functions for each radiation level. (Inset) Semilog plot of the initial part of each curve.

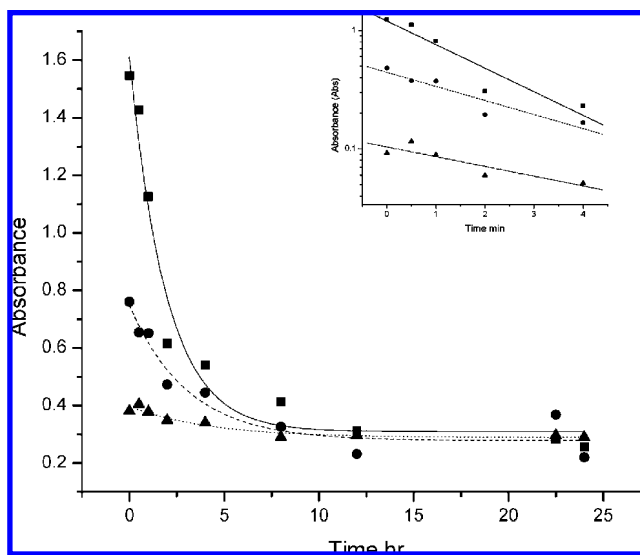


Figure 7. Effect of acetone level on 3015 cm^{-1} absorbance for tung oil treated at 100 kGy: (■) 0% acetone; (●) 25% acetone; (▲) 50% acetone. Lines represent fitted exponential functions for each acetone content level. (Inset) Semilog plot of the initial part of each curve.

peaks. The spectra suggest that the free radicals generated by the irradiated acetone reacted with the free radicals produced by irradiated tung oil, thus reducing the concentration of tung oil free radicals. By analogy, the formation of free radicals was presumed for linseed oil, but no spectra were collected.

FTIR. Chemical changes in linseed and tung oils upon exposure to air after irradiation treatments were monitored by FTIR spectroscopy. Typical spectra are shown in **Figures 2** and **3**. They show, respectively, spectral changes with time for linseed and tung oils containing 25% acetone and irradiated at 50 kGy. **Table 1** shows a list of relevant peaks based on literature reports (8, 19). It is generally accepted that the peak at 3010 cm^{-1} corresponds to $=\text{C}-\text{H}$ stretching vibration of the cis double bond (8, 19, 31, 37). Peaks at 2960 and 2926 cm^{-1} represent the methylene stretching vibration of $(\text{C}-\text{H})\text{CH}_3$ and $(\text{C}-\text{H})\text{CH}_2$ (8), whereas peaks at 987 and 950 cm^{-1} correspond

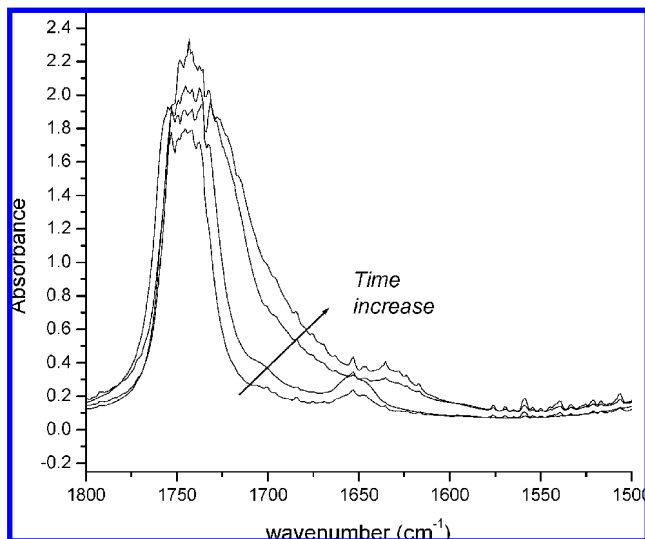


Figure 8. FTIR spectra from 1800 to 1100 cm^{-1} of linseed oil containing 25% acetone and treated at 50 kGy. Spectra were collected at 0, 2, 12, and 24 h.

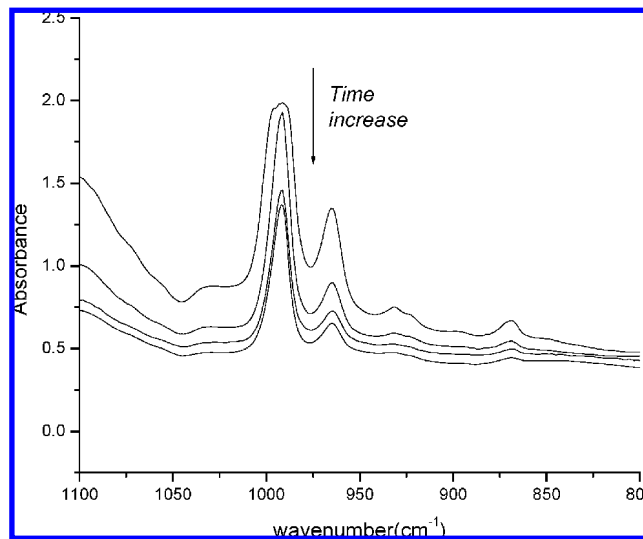


Figure 10. FTIR spectra from 1100 to 800 cm^{-1} of tung oil containing 25% acetone and treated at 50 kGy. Spectra were collected at 0, 2, 12, and 24 h.

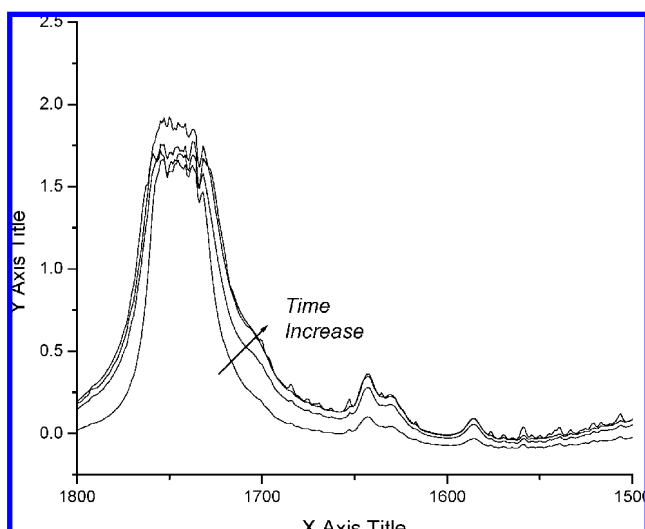


Figure 9. FTIR spectra from 1800 to 1100 cm^{-1} of tung oil containing 25% acetone and treated at 50 kGy. Spectra were collected at 0, 2, 12, and 24 h.

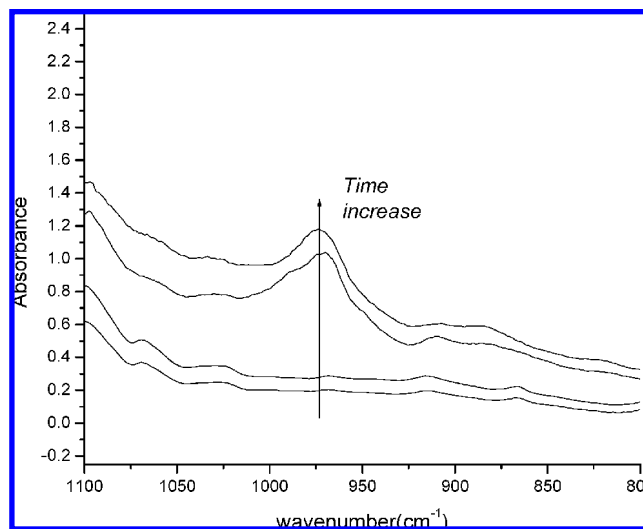


Figure 11. FTIR spectra from 1100 to 800 cm^{-1} of linseed oil containing 25% acetone and treated at 50 kGy. Spectra were collected at 0, 2, 12, and 24 h.

to the vibrations of trans–trans conjugated double bonds and trans–cis conjugated double bonds (19), respectively. The broad peak at 3600–3200 cm^{-1} corresponds to the hydroxyl group (8, 19) and the peak at 1750 cm^{-1} represents the contribution of C=O (7).

Figures 4 and 5 show, respectively, the 3100–2900 cm^{-1} region of the FTIR spectra for linseed and tung oil samples containing 25% acetone and treated with 50 kGy. Linseed oil (Figure 4) shows initially a peak at 3010.5 cm^{-1} , which shifted gradually with time toward 3010.26 cm^{-1} . The peak continuously decreased in height until it disappeared after 24 h of oil exposure to air. FTIR absorption bands around 3010 cm^{-1} represent the =C–H stretching vibrations of cis alkenes in unsaturated fatty acids (8, 38, 39). Cis =C–H bond absorption was observed at 3010.57 cm^{-1} in linseed oil, at 3005.4 cm^{-1} in olive oil, and at 3007.5 cm^{-1} in rapeseed oil (40). Ioakimoglou and co-workers (41), studying linseed oil oxidation, attributed the decrease of the 3010 cm^{-1} peak to C=C migration and the reconfiguration from cis to trans (15, 37, 41) occurring in the early stages of oil oxidation. The 3010 cm^{-1} peak decrease was linked to the progress of oil oxidation (15). Similarly, tung

oil (Figure 5) shows initially a peak at 3015.3 cm^{-1} , which shifted gradually with time toward 3013.6 cm^{-1} . The peak continuously decreased in height; however, it did not disappear within 24 h of oil exposure to air.

Figure 6 shows the decrease with time of the 3010 cm^{-1} peak for linseed oil as affected by radiation dose. Curves were fitted with exponential functions of the form $\text{Abs} = \text{Abs}_0 \exp(-t/k)$, where Abs_0 is the initial absorbance and $1/k$ is the rate constant for the peak decay. Values for k were 9.91 ($R^2 = 0.98$), 6.59 ($R^2 = 0.95$), and 6.44 ($R^2 = 0.97$) for radiation levels of 0, 50, and 100 kGy, respectively. The R^2 values indicated a good fit of the exponential function and suggested that oil oxidation follows a first-order kinetics for the three radiation levels. The k values suggested that oil oxidation rate increased with radiation dose. The rate increase was faster from 0 to 50 kGy than from 50 to 100 kGy. Beyond 50 kGy, increases in radiation dose had less of an effect. Peak values at 60 min of air exposure for 50 and 100 kGy treatments appear to deviate from the model prediction, pointing out the possibility of secondary factors affecting the oxidation rate. The decrease in

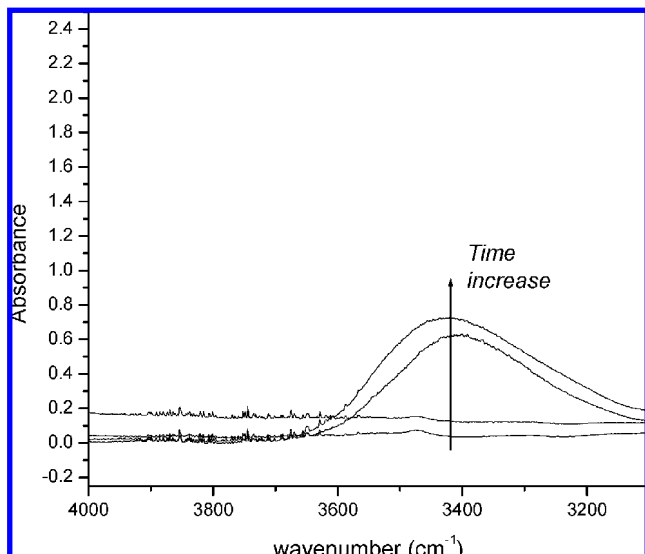


Figure 12. FTIR spectra from 4000 to 3100 cm^{-1} of linseed oil containing 25% acetone and treated at 50 kGy. Spectra were collected at 0, 2, 12, and 24 h.

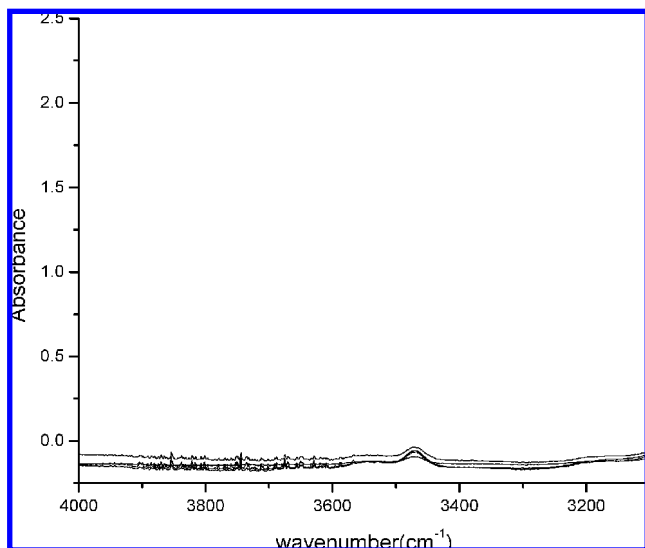


Figure 13. FTIR spectra from 4000 to 3100 cm^{-1} of tung oil containing 25% acetone and treated at 50 kGy. Spectra were collected at 0, 2, 12, and 24 h.

time of the 3015 cm^{-1} peak for tung oil also followed an exponential decay.

Figure 7 shows the decrease with time of the 3015 cm^{-1} peak for tung oil as affected by the level of acetone in the sample. **Figure 7** shows the effect of sample dilution on initial absorbance. Initial absorbance values decreased from 1.55 to 0.76 and to 0.38 for samples with acetone concentrations of 0, 25, and 50%, respectively. Initial absorbance values reflected a lower concentration of chemical bonds as sample dilution increased. **Figure 7** also shows that the 3015 cm^{-1} peak followed an exponential decay. As above, $1/k$ is the rate constant for the peak decay. Values for k were 1.94 ($R^2 = 0.97$), 3.05 ($R^2 = 0.94$), and 4.16 ($R^2 = 0.94$) for acetone concentrations of 0, 25, and 50%, respectively. The k values suggested the rate of oxidation decreased as acetone content increased, possibly due to a larger number of free radicals generated under irradiation at higher acetone levels. Acetone free radicals may have reacted with those produced by tung oil, decreasing the oxidation rate.

Figures 8 and **9** show the broadening with time of the 1745 cm^{-1} peak for linseed and tung oils, respectively. The 1745 cm^{-1} peak is related to C=O-containing species (36). Peak broadening indicates the formation of new carbonyl compounds, that is, aldehydes and ketones (31). The concentration of carbonyl species is related to the extent of free radical production and oxidation (32). Linseed oil (**Figure 8**) showed a wider peak shoulder than tung oil (**Figure 9**), indicating a greater number and variety of carboxyl compounds were formed in linseed oil. Oyman and co-workers (36) observed that linseed oil absorbed larger amounts of oxygen during oxidation than in tung oils.

Peaks at 990 cm^{-1} and 960 cm^{-1} correspond to trans–trans and trans–cis conjugated double bonds, respectively (19). **Figure 10** shows the concentration of conjugated double bonds in tung oil decreasing continuously during drying. After 24 h, only a small peak is visible. In contrast, the spectra of linseed oil (**Figure 11**) initially showed no peaks at 990 cm^{-1} or 960 cm^{-1} since linseed oil contains no conjugated double bonds. However, a peak appeared at ca. 960 cm^{-1} after 12 h of drying, indicating that conjugated double bonds were formed during drying. This was expected since conversion of nonconjugated double bonds into conjugated double bonds takes place before hydroperoxide formation and decomposition in oils (32).

Figure 12 shows FTIR spectra from 4000 to 3100 cm^{-1} for linseed oil samples containing 25% acetone and treated at 50 kGy. A broad peak appeared at approximately 3450 cm^{-1} after 12 h. It was attributed to hydroxyl groups, for example, alcohols and carboxylic acids (19, 32). Initially, there were no peaks in the 3100–3600 cm^{-1} region because no oxidation had occurred yet. After samples were exposed to oxygen in air and began drying, a broad peak appeared between 3100 and 3600 cm^{-1} centered at 3450 cm^{-1} and increased with time from 0 to 24 h. No peaks were observed in tung oil samples (**Figure 13**). Oyman and co-workers (36) observed a higher amount of OH-containing species formed in linseed oil than in tung oil. They related their results to the higher amount of hydroperoxides formed in linseed oil than in tung oil as a result of more oxygen being absorbed by the former.

The effect of radiation dose on oxidation rate of linseed and tung oil was investigated by FTIR. The peak at ca. 3010 cm^{-1} corresponding to the =C–H stretching vibration of the cis double bond was useful to monitor oil oxidation rate. Absorbance at 3010 cm^{-1} followed an exponential decay with time, as oxidation progressed. Rate constants obtained from curve fitting showed that oxidation rate increased with radiation.

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