

ORIGINAL ARTICLE

Thermal luminescence spectroscopy of γ -irradiated elastomers using a multichannel Fourier-transform chemiluminescence spectrometer

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Chemiluminescence spectra of natural rubber, chloroprene rubber and ethylene propylene diene rubber were measured in N_2 and in air with a multichannel Fourier-transform chemiluminescence spectrometer. Samples were measured after γ -ray irradiation in air and in the absence of O_2 . No strong emission was observed for natural rubber heated in N_2 after the sample was γ -irradiated in the absence of O_2 , but a strong emission from the sample was observed at 631 nm in air. An emission from chloroprene rubber was observed around 659 nm even when the sample was not γ -irradiated. A similar band was observed after the sample was γ -irradiated in air and in the absence of O_2 . A strong emission from ethylene propylene diene rubber was observed in air only when the sample was γ -irradiated in air. The observed spectrum was separated into two bands at 678 and 523 nm, where the former and the latter were tentatively assigned to peroxidic compounds and excited carbonyl groups, respectively. The relative intensity of the two bands changed during the measurement. It is concluded that luminescence spectroscopy using a multichannel spectrometer is a powerful technique to examine the oxidative degradation of elastomers. *Polymer Journal* (2012) 44, 1015–1021; doi:10.1038/pj.2012.56; published online 18 April 2012

Keywords: chemiluminescence; elastomers; Fourier-transform (FT) spectrometer; γ -ray irradiation; Russell mechanism

INTRODUCTION

Ionizing radiation techniques have frequently been used for modification of polymers; for example, graft polymerization, crosslinking and chain scission.¹ There are two principal ionizing radiation techniques used by industry; one is γ -ray irradiation using a ⁶⁰Co radioisotope source and the other is high-energy electron-beam irradiation. The energy of the ionizing radiation is so high that electrons or atoms are ejected from polymers to generate excited molecules and/or activated free radicals at the initial stage of the complex reactions. Once the activated free radicals are generated, peroxy radicals can be formed by reaction with atmospheric O_2 that is adsorbed by the polymers, or introduced during a manufacturing process such as kneading. It is important to know how much oxidative degradation of polymers occurs at a particular penetration depth and dose rate of ionizing radiation. Therefore, several analytical techniques such as infrared (IR) spectroscopy, X-ray photoelectron spectroscopy (XPS) and nuclear magnetic resonance have been applied to irradiated polymers.^{2–9}

Chemiluminescence (CL) emission from polymers was first measured by Ashby,¹⁰ who emphasized that CL measurement is one of the most useful techniques to examine their oxidative degradation and

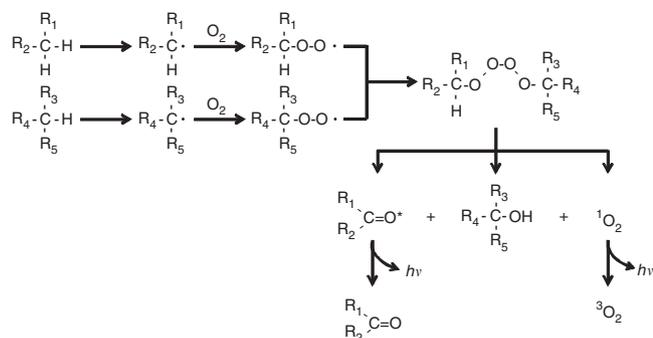
stability. This is because CL is more suitable for the detection of peroxy radicals in materials than is infrared spectroscopy or XPS.¹¹ Variation of CL emission intensity from commodity plastics such as polyethylene^{12,13} and polypropylene^{14,15} was measured to examine the effect of antioxidants.^{16,17} A review of CL studies on the oxidative degradation of polymers was reported by Jacobson *et al.*¹⁸

Shard and Russell¹⁹ proposed a mechanism for thermal oxidative degradation of polymers. Fundamental ideas of the so-called Russell mechanism, which is widely accepted in this field, are a production of peroxy radicals by combination of carbon radicals with O_2 . This is followed by a bimolecular combination of two peroxy radicals to form excited carbonyl compounds, alcohols and singlet oxygen molecules by a tetroxide intermediate,^{18,20} as shown in Scheme 1. The excited carbonyl compounds and singlet oxygen molecules formed in this reaction produce CL emission.

In the present study, we have measured CL spectra of γ -irradiated elastomers with a multichannel Fourier-transform CL spectrometer. The elastomers used here are natural rubber (NR), chloroprene rubber (CR) and ethylene propylene diene rubber (EPDM), the structures of which are shown in Figure 1. EPDM is frequently used as an insulating material or fender in nuclear atomic equipment, and its

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Scheme 1 A typical scheme of the Russell mechanism: peroxy radicals are produced by combination of carbon radicals with O_2 . Excited carbonyl compounds, alcohols and singlet oxygen molecules are formed by a bimolecular combination of two peroxy radicals via a tetroxide intermediate.

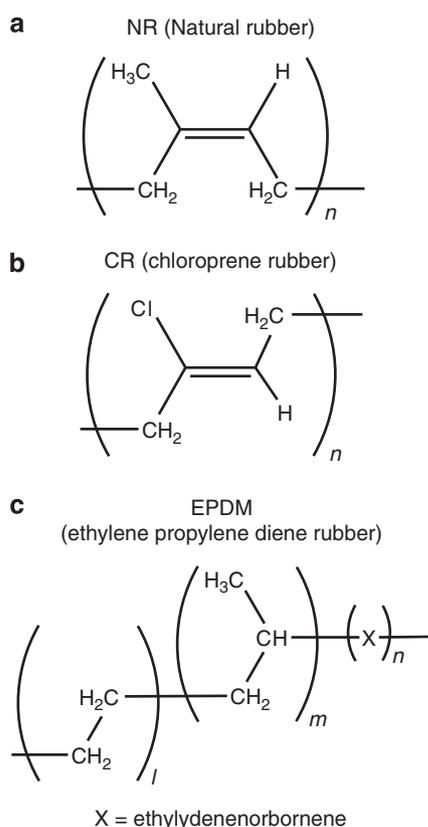


Figure 1 Structures of the elastomers: (a) NR, (b) CR and (c) EPDM.

degradation by γ -ray irradiation is one of the most important problems to be solved. To elucidate the processes of oxidative degradation due to the γ -ray irradiation, we exposed these three elastomers to γ -ray radiation from ^{60}Co and monitored both the intensity and the wavelength of CL emission bands. We focused our interest on the effect of O_2 during the γ -ray irradiation and compared the CL spectra measured in N_2 with that measured in air. The complex CL spectra obtained from EPDM after γ -ray irradiation in air were modeled by least-squares fitting using Gaussian-type curves. These experimental CL spectra could be reproduced using a model with two characteristic CL bands. This is the first report of the formation of more than one luminescent species in γ -irradiated polymers, observed using a multichannel Fourier-transform-CL spectrometer.

EXPERIMENTAL PROCEDURE

Commercial samples of the three elastomers, NR (SMR, Kuala Lumpur, Malaysia, CV-60), CR (DENKA, Tokyo, Japan, DC35) and EPDM (JSR, Tokyo, Japan, EP107F), were used without further chemical treatment. They were irradiated in air and in the absence of O_2 by a γ -ray irradiator (Nordion, Ottawa, Canada), where the activity of the ^{60}Co source was 5.3×10^{15} Becquerel. For O_2 -free irradiation, the samples were sealed in a laminated aluminum package with an oxygen absorber (RP20A, Mitsubishi Gas Chemicals Inc., Tokyo, Japan) and left to stand overnight before irradiation. Samples for air irradiation were put in a similar laminated aluminum package without sealing. The administered irradiation dose was about 100 kGy, which was estimated by using an alanine dosimeter (Harwell Dosimeters Ltd., Oxford, UK), and the irradiation time was about 5 h. CL measurement for the O_2 -free irradiated samples was carried out immediately after opening the package.

Each sample sheet of 25×25 mm with a thickness of 5 mm was placed in an aluminum sample dish heated at 413 K for NR and CR or 453 K for EPDM so as to avoid thermal denaturation. The sample dish was placed on the sample stage (52 mm diameter with a thickness of 8.9 mm), which was heated by a tungsten heater. A hot stream of N_2 or air heated by the sample stage was directed onto the sample surface. The gas flow rate was of the order of 0.1 l min^{-1} and maintained by a ball valve. The temperature was monitored by a thermocouple (Pt100) and controlled by a conventional electronic temperature controller. CL emission from the whole sample through a quartz window of 30-mm diameter, located at the top of the sample chamber 17.5 mm from the sample stage, was measured with a multichannel Fourier-transform-CL spectrometer (Japan Applied Technology Inc., Tokyo, Japan; MS-8310). The instrument comprises a Savart plate, polarizers and a quartz lens as previously described.^{21,22} The sensor was a charge-coupled device with 512×512 pixels, the total effective size of which was 12.288 (horizontal) \times 12.288 (vertical) mm. The interferogram was accumulated for 10 min and converted to the corresponding spectrum by Fourier transform. This procedure was carried out six times continuously and repeatedly at the same temperature.

RESULTS AND DISCUSSION

CL spectra of NR

The main-chain structure of NR is *cis*-2-butene as shown in Figure 1a, with pendant methyl groups bonded to it. To find the effect of γ -ray irradiation on elastomers, we first measured CL emission from the sample before γ -ray irradiation. As shown in Figure 2a, no strong emission was observed in N_2 or in air, implying that the sample of NR was thermally stable at 413 K; no carbon radicals or peroxy radicals were produced even when the sample was heated in air. The sample γ -irradiated in the absence of O_2 also showed no CL emission when it was heated in N_2 , as shown in the left of Figure 2b. However, the same material showed a strong CL emission over a wide range between 450 and 850 nm with a maximum peak of 631 nm when it was heated in air, as shown in the right of Figure 2b. It is possible that hydrogen atoms from the main chain or methyl group are detached to yield carbon radicals by γ -ray irradiation in the absence of O_2 . As no emission from the same sample was observed when it was heated in N_2 , as shown in the left of Figure 2b, O_2 molecules are required for the carbon radicals to give CL emission. Therefore, we assume that the carbon radicals produced by γ -ray irradiation in the absence of O_2 are non-luminescent and react with O_2 in air during CL measurement to yield peroxy radicals, and then strong CL emission around 631 nm arises from peroxidic compounds produced by, for example, cross-termination of the peroxy radicals. This assumption is supported by the fact that the intensity of this band increased gradually as the reaction with O_2 in air proceeded during the CL measurement, as shown in the right of Figure 2b, where the spectra denoted by the open symbols are stronger than those by the closed symbols.

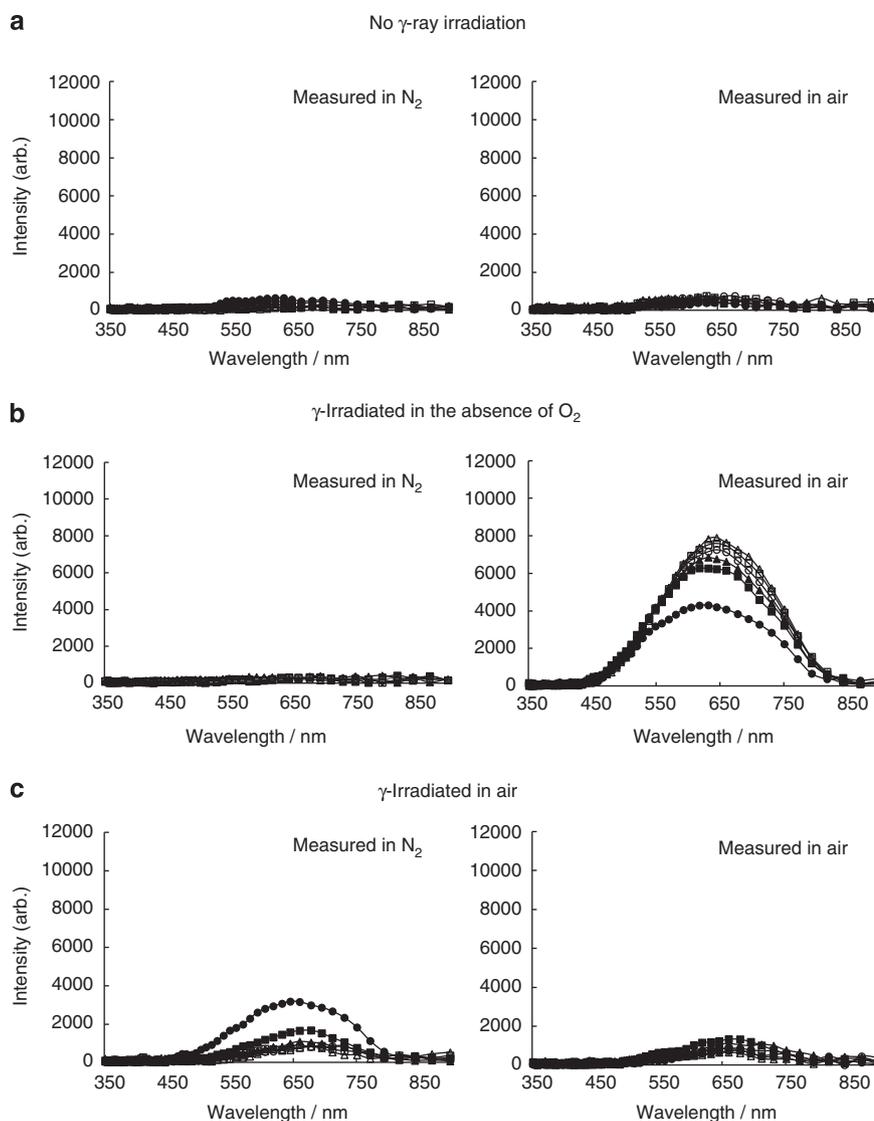


Figure 2 Thermal chemiluminescence spectra of NR at 413 K: (a) measured in N_2 and in air before γ -ray irradiation; (b) measured in N_2 and in air after γ -ray irradiation (100 kGy) in the absence of O_2 ; (c) measured in N_2 and in air after γ -ray irradiation in air. Curves with symbols of \bullet , \blacksquare , \blacktriangle , \circ , \square and \triangle represent spectra measured at the periods between 0–10, 11–20, 21–30, 31–40, 41–50 and 51–60 min, respectively.

A similar CL spectrum with a maximum peak of 631 nm was observed in N_2 or in air after γ -ray irradiation in air, as shown in Figure 2c. The intensity of the band decreased with the CL measurement time, where the spectra denoted by the open symbols are weaker than those by the closed symbols, contrary to the behavior shown in the right of Figure 2b. These findings suggest that the peroxidic compounds are produced by the reaction between the carbon radicals and O_2 in air during γ -ray irradiation, and decomposed gradually in heating during CL measurement in N_2 or in air at 413 K. As the peroxidic compounds had already been produced during the γ -ray irradiation in air before heating the sample, they start to show CL emission immediately and then the intensity decreases, as shown in Figure 2c, because the peroxidic compounds are consumed with increasing CL measurement time. It was also found that the intensity of the CL emission band measured in air was weaker than that measured in N_2 , implying that the peroxidic compounds were consumed by other reactions with O_2 in air to produce non-luminescent species during heating.

CL spectra of CR

As shown in Figure 1b, the main-chain structure of CR is *trans*-2-butene, with pendant chlorine atoms bonded to it. When a sample of CR was heated in N_2 at 413 K before γ -ray irradiation, no CL emission was observed, as shown in the left of Figure 3a. However, a weak CL emission was observed around 650–750 nm with a maximum peak of 659 nm when the sample was heated in air, as shown in the right of Figure 3a. The intensity of this CL band increased with the CL measurement time, where the spectra denoted by the open symbols are stronger than those by the closed symbols, implying a thermal reaction occurred to show a stronger CL emission after heating in air. It is reasonable to assume the following CL emission processes: (1) a small number of carbon radicals are yielded thermally by detachment of Cl atoms in CR, even when γ -ray irradiation was not carried out; (2) peroxy radicals are thermally produced during the CL measurement by a reaction of the carbon radicals with O_2 in air; (3) peroxidic compounds produced from the peroxy radicals give CL emission. This assumption may be supported by the report that

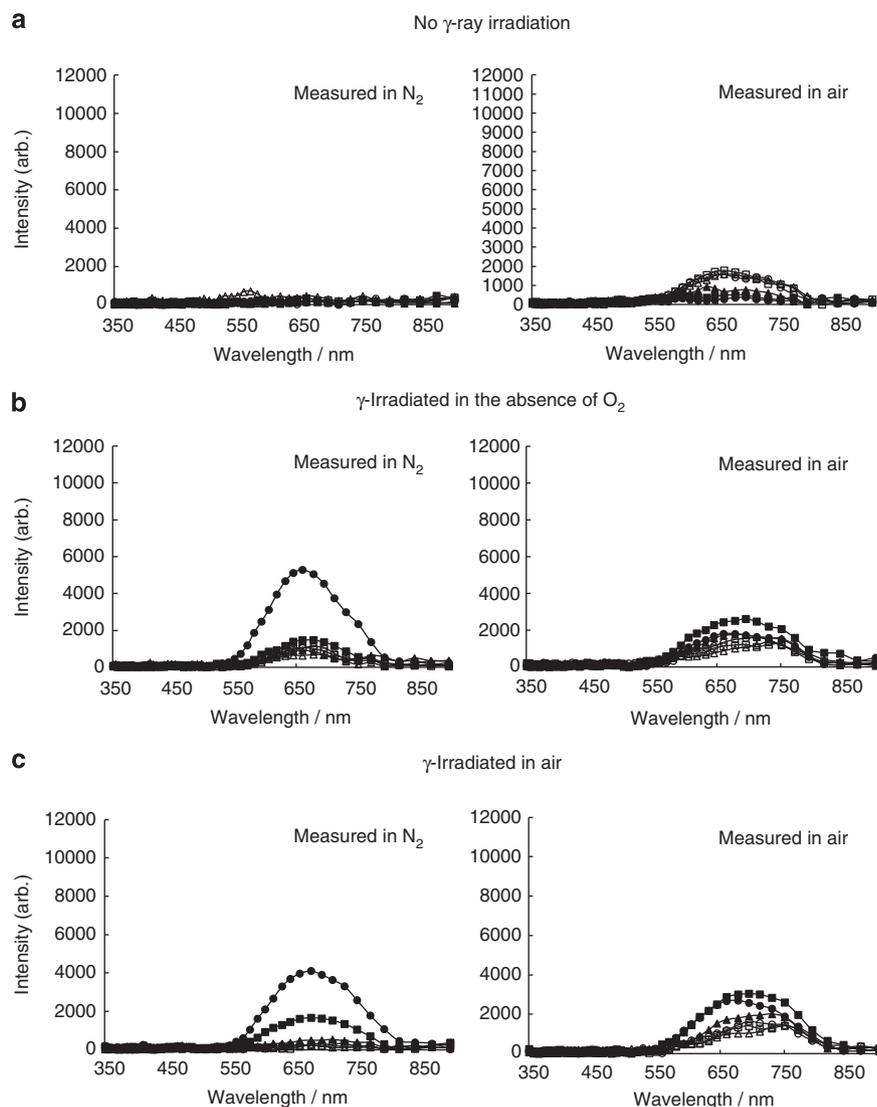


Figure 3 Thermal chemiluminescence spectra of CR at 413 K: see the caption of Figure 2.

conjugated diene compounds are thermally produced from CR by peroxy radicals by detachment of Cl and H atoms.²³ One may claim that the double bonds in the main-chain structure of CR were thermally oxidized to yield the carbon radicals.²⁴ If this is true, NR, which has double bonds in the main-chain structure like CR, should show CL emission when it is heated in air before γ -ray irradiation. However, we observed no CL emission from NR when it was heated in air before γ -ray irradiation, as shown in the right of Figure 2a.

When the sample of CR was γ -irradiated in the absence of O_2 and heated in N_2 , we observed a strong emission as shown in the left of Figure 3b, where the wavelength of the maximum peak, 659 nm, is similar to that of the CL emission measured before γ -ray irradiation, as shown in the right of Figure 3a. The intensity of this CL band was strongest in the first 10 min of measurement and decreased afterwards. Therefore, we assume that the carbon radicals produced by detachment of Cl atoms in CR had accumulated during the γ -ray irradiation in the absence of O_2 . We also assume that these radicals thermally reacted with O_2 adsorbed and/or introduced during a manufacturing process such as kneading to produce peroxy radicals, even when the sample was heated in N_2 . As NR gives no CL emission in N_2 when the

sample was γ -irradiated in the absence of O_2 , as shown in the left of Figure 2b, the amount of O_2 adsorbed in NR seems to be negligible unlike CR, probably because of naturally contained antioxidants or impurities such as minerals that work effectively as an antioxidant. It is noted that the wavelength of the maximum for CL emission from CR, 659 nm, is apparently longer than that for NR, 631 nm. This wavelength difference may reflect that CL emission is influenced by the structure of the original peroxy radicals; for example, oxidized on main-chain or side-chain carbon atoms.

The intensity of CL emission from CR measured in air after γ -ray irradiation in the absence of O_2 is weaker than that of NR. This finding suggests that the detachment of Cl atoms from CR occurred by γ -ray irradiation in the absence of O_2 , and that peroxidic compounds produced by the reaction of the carbon radicals with O_2 adsorbed or contained in CR were present before CL measurement. Therefore, the CL band intensity decreased with CL measurement time, as shown in the right of Figure 3b, where the spectra denoted by the open symbols are weaker than those by the closed symbols. Similar behavior of the CL bands measured in N_2 or in air after γ -ray irradiation in air was observed as shown in Figure 3c. This

finding suggests that similar peroxidic compounds were produced during γ -ray irradiation in both N_2 and O_2 .

CL spectra of EPDM

The main-chain structure of EPDM is composed of single C–C bonds, where ethyldene norbornene is contained as a third monomer. It is expected that the CL spectrum is different from those of NR and CR. In fact, no strong CL emission was observed before or after γ -ray irradiation in the absence of O_2 , as shown in Figures 4a and b. A weak CL emission was observed at 453 K during the measurement in N_2 when the sample was γ -irradiated in air. It may be related to the reaction of the third component, ethyldene norbornene, with O_2 in air during γ -ray irradiation, but this is not clear from our experimental results at present. Neither luminescent species nor peroxy radicals were produced by γ -ray irradiation, even in air. This is in contrast to the post-irradiation oxidation reactions; that is, oxidation occurring during γ -ray irradiation that affected the CL emission after heating, which was proposed in CL studies on γ -irradiated polyethylene.¹⁷

However, the CL spectra of the same sample measured in air were surprisingly different from those measured in N_2 . The intensity of the CL emission gradually increased with the CL measurement time, implying that the oxidation reaction of non-luminescent species generated by γ -ray irradiation in air occurred to produce luminescent species during heating in air for CL measurement. Additionally, the band shape dramatically changed and the wavelength of the peak shifted to the shorter wavelength region, as shown in the right of Figure 4c. These findings suggest that the observed spectrum is composed of more than one CL bands. We therefore fitted each observed spectrum with Gaussian-type curves using a least-squares fitting procedure,²² with the result that all the observed CL spectra were reproducible by two CL bands at 678 and 523 nm, as shown in Figure 5. The 678-nm band may be because of peroxidic compounds produced from the peroxy radicals, as already explained for NR and CR. Another possibility for the assignment of the 678-nm band is dimol singlet oxygen, which is well known to give strong emission around 650 nm,²⁴ but we have no evidence.

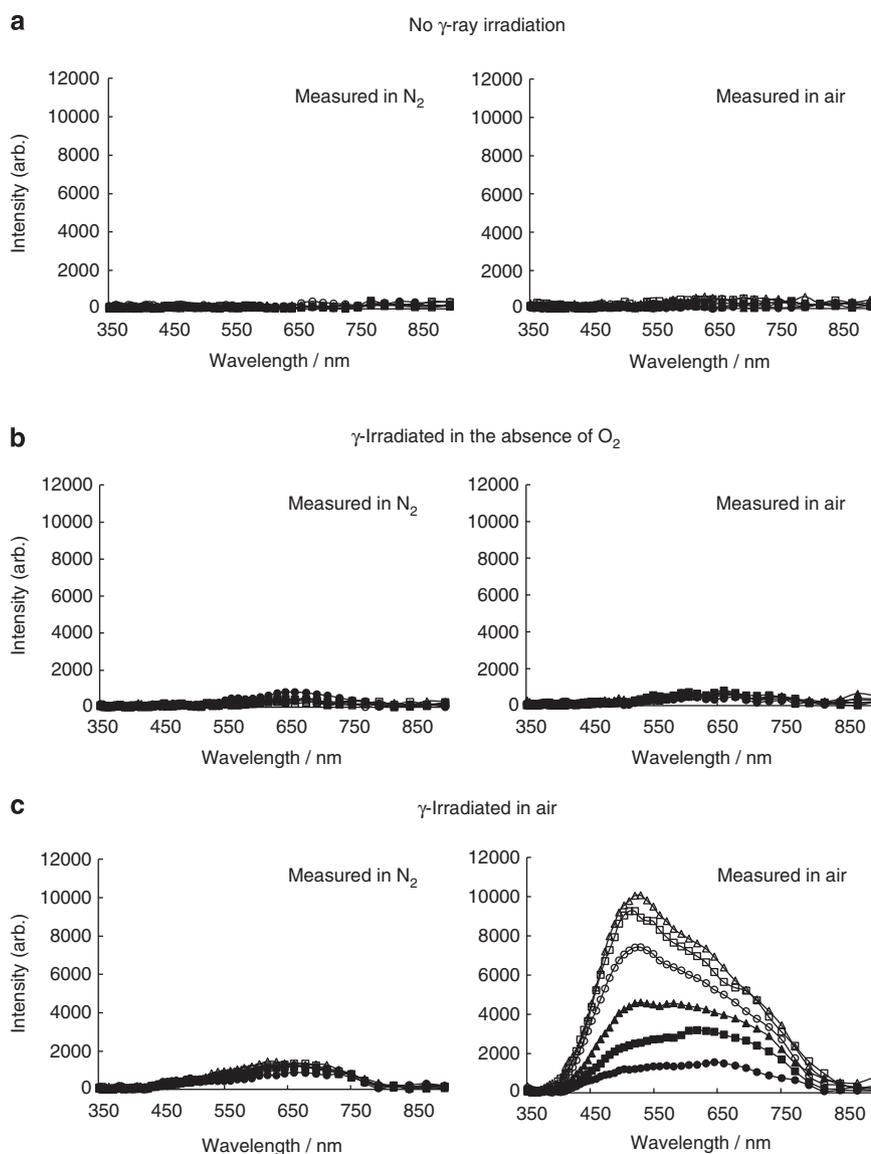


Figure 4 Thermal chemiluminescence spectra of EPDM at 453 K: see the caption of Figure 2.

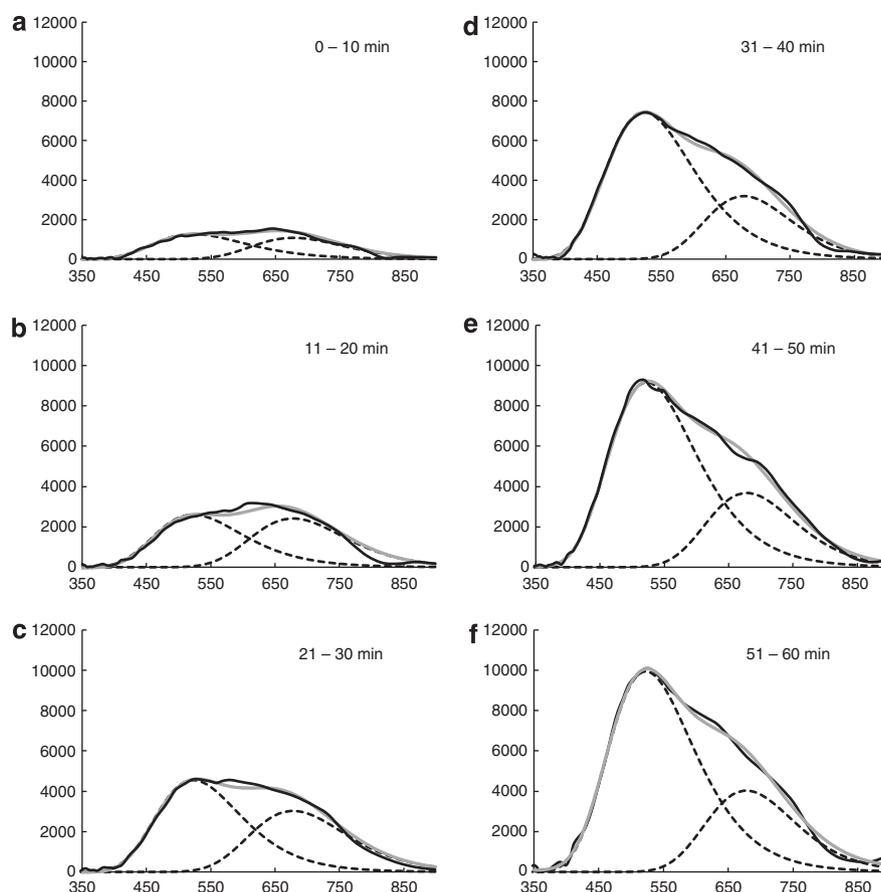


Figure 5 Fitting curves for CL spectra of EPDM and intensity changes of CL bands measured in air after γ -ray irradiation (100 kGy) in air; (a) measured at the period between 0–10 min; (b) 11–20 min; (c) 21–30 min; (d) 31–40 min; (e) 41–50 min; (f) 51–60 min. The bands appearing at 678 and 523 nm (broken lines) are tentatively assigned to peroxidic compounds and excited carbonyl compounds, respectively.

On the other hand, the 523-nm band is consistent with the formation of excited carbonyl groups according to the Russell mechanism,¹⁹ as described in Introduction. The production of carbonyl compounds by γ -ray irradiation was confirmed by infrared spectroscopy,^{15,19} solid-phase nuclear magnetic resonance¹⁵ and X-ray photoelectron spectroscopy.¹⁸ We assume that carbon radicals are generated at the position of the tertiary carbon atom in the propylene unit of EPDM by γ -ray irradiation, and the excited carbonyl compound, alcohol and singlet oxygen molecules are thermally produced during heating in air for CL measurement by a tetroxide intermediate according to the Russell mechanism.^{18,20} If so, these carbonyl compounds will produce strong CL emission if the Russell mechanism is correct. Our assignment of the 523-nm band is also supported from the report that unsaturated carbonyls produced by thermal oxidation of polybutadiene showed 520-nm emission.²⁵

It was found that the relative intensity of the CL bands for the carbonyl compounds (523 nm) and peroxidic compounds (678 nm) changed with CL measurement time, as shown in Figure 5. All the observed CL spectra can be satisfactorily reproduced by a sum of the two bands, where peroxidic compounds give CL emission earlier in the oxidation process than carbonyl compounds. These insights are not derived solely from intensity analysis of CL emission measured with an earlier system using many optical band-path filters.²⁶ We emphasize that thermal CL spectroscopy using a multichannel Fourier-transform-CL spectrometer makes it possible to elucidate the progress and mechanism of oxidative degradation in polymers.

Table 1 Summary of thermal chemiluminescence bands of elastomers

γ -ray irradiation	CL measurement	Elastomers		
		NR	CR	EPDM
No irradiation	In N ₂	—	—	—
	In air	—	IN ^a	—
In the absence of O ₂	In N ₂	—	DE	—
	In air	IN ^b	DE	—
In air	In N ₂	DE	DE	—
	In air	DE	DE	IN ^c

Abbreviations: DE, intensity of luminescence decreases after starting CL measurement; IN, intensity of luminescence increases after starting CL measurement.

^aCarbon radicals are thermally produced by detachment of Cl atoms, and peroxidic compounds (659 nm) are produced via peroxy radicals by heating in air during CL measurement.

^bCarbon radicals are produced during γ -ray irradiation by detachment of hydrogen atoms, and peroxidic compounds (631 nm) are produced via peroxy radicals by heating in air during CL measurement.

^cCarbon radicals are produced during γ -ray irradiation in air, and peroxidic compounds (678 nm) and excited carbonyl compounds (523 nm) are produced via peroxy radicals by heating in air during CL measurement, according to the Russell mechanism.

CONCLUSION

CL spectra of NR, CR and EPDM that had been γ -irradiated in air or in the absence of O₂ were measured in N₂ and in air. In the case of NR, no strong CL emission was observed by heating in N₂ after the sample was γ -irradiated in the absence of O₂ (see Table 1). A strong

CL emission was observed when the sample was heated in air during CL measurement. It was concluded that O₂ molecules from air are required for NR to produce the strong CL emission, whereas non-luminescent species were assumed to be produced by γ -ray irradiation in the absence of O₂ by thermal detachment of hydrogen atoms. In the case of CR, CL emission was observed during heating even when the sample was not γ -irradiated. A similar CL band was observed during heating in N₂ after γ -ray irradiation in the absence of O₂. It was assumed that carbon radicals were produced by detachment of Cl atoms by γ -ray irradiation; these reacted with O₂ adsorbed or contained in the polymer to produce peroxy radicals. Peroxy compounds are formed from the peroxy radicals, producing strong CL emission. In the case of EPDM, a strong CL emission was observed by heating in air, after the sample was γ -irradiated in air. It was found that the spectra were composed of two bands appearing at 678 and 523 nm. The relative intensities of these two CL bands changed with the heating time. The 678-nm band is tentatively assigned to peroxidic compounds and the 523-nm band to excited carbonyl compounds, which are generated according to the Russell oxidation mechanism.

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