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Near-infrared transmittance spectroscopy for radiochemical ageing of EPDM†

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The feasibility of using near-infrared spectroscopy as a sensitive technique to follow the influence of γ-irradiation upon ageing of different EPDM (ethylene propylene diene monomer) elastomers has been evaluated. Although identification is difficult, differences can be observed between the non-irradiated and irradiated materials for total integrated doses from 50 to 450 kGy using a dose rate of 1 kGy h^{-1} under an oxygen flow. The decrease in intensity of bands at 7040, 4610 and 4910 cm^{-1} are linked to the disappearance of additives present in the elastomer such as excess of vulcanising or antioxidant agents and occur for the lowest irradiation dose. This disappearance is confirmed by TGA (thermogravimetric analysis). The increase in band intensities assigned to the formation of hydroxyl and carbonyl groups (5100, 4860 and 4670 cm^{-1}) irradiation indicates an increase in oxidation with irradiation in the presence of oxygen. No bands linked to the presence of C=C from the diene have been detected, probably owing to the low concentration in the material and the weak intensity in near-infrared region. For strong irradiation doses (450 kGy), the three formulations studied show no difference in their NIR spectra, which is confirmed by the TGA of these irradiated materials. PCA performed at 5000–4600 cm^{-1} or 7090–6980 cm^{-1} shows efficient discrimination.

1. Introduction

The mechanisms, property changes and kinetics of the photo-oxidation and photodegradation of polymer materials are subjects of active interest in academia, industry and government research. All unstabilized organic polymers undergo degradation or oxidation reactions when exposed to natural or artificial radiation. This behaviour severely limits the useful practical lifetime of many polymer materials. Oxidation of polymers under the action of radiation occurs as a result of free radicals combining with diffused oxygen.[1] The evaluation of radiochemical effects in ethylene–propylene elastomers has already been studied.[2,3] It has been shown that exposure of cross-linking type polymers to γ-irradiation or to accelerated electrons provides increased stability and improved mechanical properties.[4] The viscoelastic response and dynamic mechanical analysis have been used to follow the radiochemical ageing of EPDM.[5] Ethylene–propylene elastomers are able to form intermolecular links when irradiated.[6] Mid-infrared spectroscopy is widely used to monitor such reactions, but if spectra are obtained by transmission then samples are restricted to thin films, which can change the morphology of the sample. Alternatively, attenuated total reflectance (ATR) can be used if only thick films are available, but in this case only the sample surface (a few tenths of a micrometre) is probed and problems of bad contact between sample and prism can occur after ageing. Moreover, sometimes the degradation due to irradiation is different between the surface and the bulk of the polymer. Microspectroscopy can also be used to follow the ageing of polymers,[7] but sample preparation requires a microtome and the thin slices obtained may also have undergone changes in surface morphology. Near-infrared spectroscopy does not require any sample preparation and can be applied to thick samples (1–10 mm). Conventional dispersive Raman or Fourier transform (FT) Raman spectroscopy could also be used to study changes in the C=C vibrations.[8] Near-infrared (NIR) spectroscopy is useful for quantitative and qualitative quality control[9] and has wide applications such as in the pharmaceutical field using the transmission mode to analyse solid drugs.[10] NIR spectroscopy is also very useful for textile materials, *e.g.*, to analyse *in situ* the surface of reinforcements after sizing treatments.[11] The analysis of packaging films in multilayer polymers has been done by NIR spectroscopy. The weak absorption of bands in the NIR range allows one to work in the transmission mode through all the layers and to control the finished product.[12] The main research work on polymers at present concerns the use of chemometrics[13] to follow *in situ* reaction kinetics associated with NIR spectroscopy. It has been used to monitor the melt extrusion transesterification of ethylene–vinyl acetate copolymer.[14] The percentage of ethylene and propylene in EPDM has been previously determined by NIR spectroscopy[15] and analysis of EPDM terpolymer by NIR and PLS[13] (partial least squares) for the diene corresponding to hexadiene or norbornene has already been made in terms of changes in crystallinity and intrachain interactions,[16] but no ageing studies on EPDM using NIR spectroscopy have yet been published. One of the reasons for this is that C=O stretching vibrations, which are very intense in the mid-IR region, are very weak in the NIR region (the first overtone for C=O appears in the mid-IR at ~3400 cm^{-1}). Also, the C=C stretching vibrations, which are already weak in the mid-IR, will be even weaker in the NIR region. Chemometrics may be useful to detect this type of very weak spectral difference due to chemical modifications. Small effects due to the conformational changes observed during crystallinity studies using NIR spectroscopy in polymers have already given good results.[17,18] It was therefore decided to investigate the radiochemical ageing of polymers using NIR spectroscopy. Interpretative NIR spectroscopic studies have been used to help assignments in this work,[13,19,20] but band assignments can be ambiguous mainly for combination bands. This paper deals with the feasibility of using NIR spectroscopy to follow the effects of

† Electronic Supplementary Information available. See http://www.rsc.org/suppdata/an/b1/b106822a/

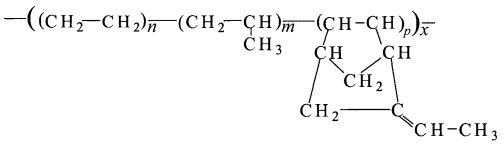
γ-irradiation on three different terpolymers (ethylene propylene diene monomers), so-called EPDM, where the diene is a 5-ethylidene 2-norbornene group. An attempt was made to assign some of the main bands which appear or disappear with the irradiation ageing. The aim of the work was not a fundamental study of the above-mentioned system but to consider NIR spectroscopy as a method for *in situ* and non-destructive monitoring of polymer degradations in nuclear power plants or, more generally, in other cases.

2. Experimental

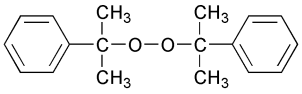
2.1 Materials

The EPDMs used were composed of 70% ethylene (*n*), 28% propylene (*m*) and 2% norbornene (the diene, *x*). Three formulations were studied and prepared by the CEA (Le Ripault-Tours, France): pure elastomer [A] = (EPDM 9), cross-

[A] = EPDM 9

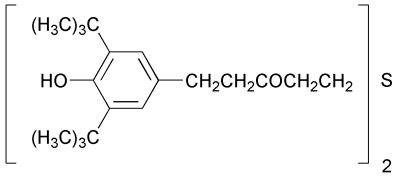


linked elastomer with 2.6% by weight of dicumyl peroxide [B] assigned EPDM 10 = (A + B) and protected with 0.1% in weight of a phenolic-type antioxidant agent [C] assigned EPDM 11 = (A + B + C), as can be seen in the formulae shown below:



[B]

EPDM 10 = [A] + [B]



[C]

EPDM 11 = [A] + [B] + [C]

The materials were exposed to γ-irradiation under oxygen at a fixed dose rate of 1 kGy h^{-1} for total integrated doses ranging from 50 to 450 kGy (CEA, Grenoble, France). Samples were stored under vacuum in a silica gel desiccator prior to and after irradiation, so that no water content (bands at 5250–5150 cm^{-1}) could be detected in the spectra. The thicknesses of the prepared samples were 100 μm and 1 mm and were obtained by melting the polymer under a hot press (180 °C). The 100 μm samples gave better results (no saturation) in the range 4000–4500 cm^{-1} but poor thickness reproducibility owing to the method of fabrication of the samples. These samples also gave rise to a low level of chemical modification detectable by NIR spectroscopy (since the pathlength is smaller than the 1 mm sample). In contrast, the 1 mm sample had better thickness uniformity and produces a better signal-to-noise ratio; ideally several layers of this 1 mm sample should have been studied or a sample of thickness >1 mm should have been used in order to observe ageing bands with weak absorption intensities. These two thicknesses were chosen in order to ensure homogeneous irradiation through the whole sample thickness taking into account the total integrated doses and the chosen dose rate.

2.2 Instrumentation

The FTIR NIR spectrometer used was a Spectrum One NTS (Near Infrared Testing System) lent by Perkin-Elmer. The NIR source was an air-cooled, pre-aligned tungsten–halogen source. The beamsplitter was made of calcium fluoride multilayers. The NIR detector was a temperature-stabilized fast recovery deuterated triglycine sulfate (FR-DTGS) system. The resolution used was 4 cm^{-1} and the number of scans recorded for each spectrum was 16. The range over which the spectra were recorded was 10000–4000 cm^{-1}. The TGA instrument was a TGA 2950 from TA instruments. Sample amounts of 10 mg placed between plates of 1 mm were heated to 800 °C at 10 °C min^{-1} under an inert atmosphere.

Multivariate analysis of NIR transmittance spectra was used for studying the level of EPDM ageing under γ-irradiation. The Quant+ software for PCA (principal component analysis) from Perkin-Elmer was used.

3. Results and discussion

Fig. 1 compares the FTNIR spectrum of an irradiated sample (EPDM 9) with that of a non-irradiated sample over the whole range and shows that no obvious differences can be detected, which means that the degradation due to irradiation is weak compared with the total spectrum of EPDM. It has been shown[5] that irradiation can induce a change in morphology, which can be followed by dynamic mechanical analysis. This can explain the slight offset of the observed baseline. Three main spectral ranges can be chosen without strong masking bands (7125–6940, 5000–4800, 4700–4600 cm^{-1}) which can be enhanced in order to show slight differences between irradiated and non-irradiated samples. Other regions of the spectrum cannot be exploited owing to the masking effect of high-intensity bands. No bands can be seen in the 5250–5150 cm^{-1} range owing to the presence of water,[21] which proves that the drying and storage procedure was correct.

3.1. Comparison of the three non-irradiated EPDM, (9, 10, 11)

Figs. 2, 3 and Fig. S1 (ESI)† show the three non-irradiated samples in the spectral ranges 7125–6935, 5000–4800 and

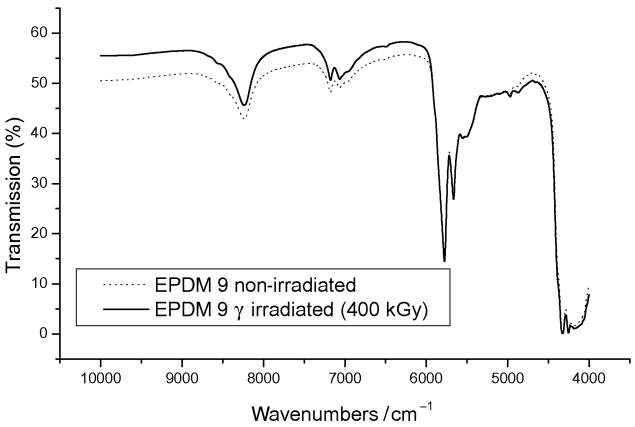


Fig. 1 10000–4000 cm^{-1} NIR spectra of EPDM 9 non-irradiated and γ-irradiated at 400 kGy.

4700–4600 cm^{-1}, respectively. The four bands of interest are at 7040, 4910, 4670 and 4610 cm^{-1}, respectively. The bands at 7040, 4910 and 4610 cm^{-1} are present in the spectra of EPDM 10 and 11 but not in that of EPDM 9. Although they could not be assigned with certainty, it is probable that they are linked to the presence of the additives in the material as shown in the Experimental section (such as antioxidant [C] and left over vulcanising agents [B] even if in small quantities). The NIR spectra of norbornene and dicumyl peroxide have been recorded. Dicumyl peroxide, as can be seen in Fig. S2 (ESI)† (A, B, C) shows weak bands at 4910, 4670 and 4620 cm^{-1}. Norbornene also exhibits weak bands at 4960, 4920, 4635 and 4605 cm^{-1} but these bands should be even weaker since the proportion of norbornene (2%) is small compared with the total composition of EPDM 10 and 11. The band at 4670 cm^{-1} which is present in EPDM 9 increases in intensity and shows a slight wavenumber shift for EPDM 10 and 11. This band could be due to an aromatic combination band[22] and/or to a combination band of carbonyl[14,23] and could be present in EPDM 9 owing to normal degradation with time due to ageing in air. The band at 4610 cm^{-1} could be due to a combination band involving the C=C (combination band of =C–H stretching at 3040 cm^{-1} and C=C stretching at 1688 cm^{-1}) characteristic of the norbornene group in the mid-infrared region.[24] However, no combination bands (starting at ~4700 cm^{-1}) linked to the C=C double bond of EPDM 9 can be found in its total spectrum, as reported previously.[25] This is probably due to the fact that in the mid-IR region these bands are already weak or not observable[24] and that the percentage of norbornene in the terpolymer is very low. Hence the disappearance of these bands upon vulcanizing the elastomer cannot be followed in the NIR spectra of EPDM 10 or 11. The band at 7040 cm^{-1} could be assigned to the second overtone of hydroxyl stretching formed by the degradation of a residue of dicumyl peroxide after vulcanisation.[26,27] The band at 4910 cm^{-1} (ref. 24) could be due to norbornene or a residue of dicumyl peroxide disappearing but more probably to combination of hydroxyl stretch and hydroxyl deformation.

3.2. Comparison between γ-irradiated and non-irradiated samples for each type of EPDM

Fig. 4 (EPDM 10, 11), Fig. 5 (EPDM 9, 10, 11) and Fig. S3 (ESI)†show the same spectral windows discussed above for non-irradiated and irradiated samples at different total integrated doses. The influence of irradiation can be followed on seven bands: 7040, 4970, 5100, 4910, 4860, 4670 and 4610 cm^{-1}. Fig. 5 shows that the band at 4910 cm^{-1} decreases as the band at 4860 cm^{-1} increases with γ-irradiation for EPDM 9, 10 and 11. Therefore, the band at 4910 cm^{-1} seems to be linked to groups which are disappearing with γ-irradiation coming probably from residues of dicumyl peroxide not used for the cross-linking process in the case of EPDM 10 and 11 and coming from the disappearance of oxidized species at the surface of EPDM 9. Fig. S2 (ESI)†, already discussed in the previous section, showed the NIR spectrum of dicumyl peroxide where combination bands such as those at 4910 and 4610 cm^{-1} are clearly present. The band at 4860 cm^{-1} could be assigned to a combination band of OH stretching and OH deformation[19,20] or a combination of C=O with CH_3.[22] The band at 4670 cm^{-1} decreases then increases with irradiation for EPDM 9, 10 and 11 [see Fig. S4 (ESI)† for EPDM 10]. It could be assigned to an aromatic combination band[22] and/or to a combination band of carbonyl.[23] The formation of hydroxyl and carbonyl groups with irradiation is expected since the samples were γ-irradiated in the presence of a flow of oxygen. The same work in the mid-IR region has already been done by another research group with which we collaborate and has already been reported.[28,29] The group which did this study had to re-prepare

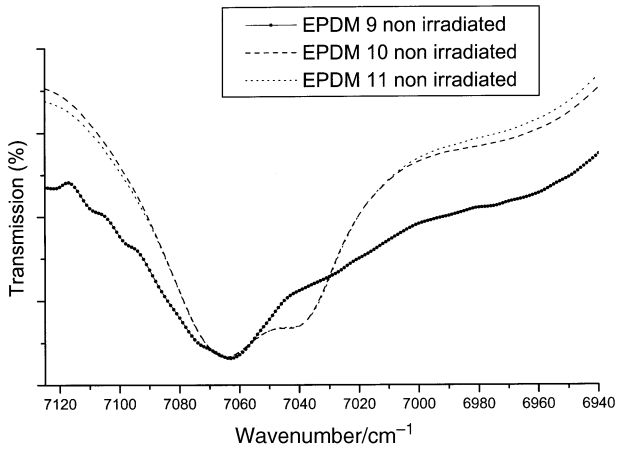


Fig. 2 7125–6935 cm^{-1} NIR spectra of EPDM 9, 10 and 11 non-irradiated.

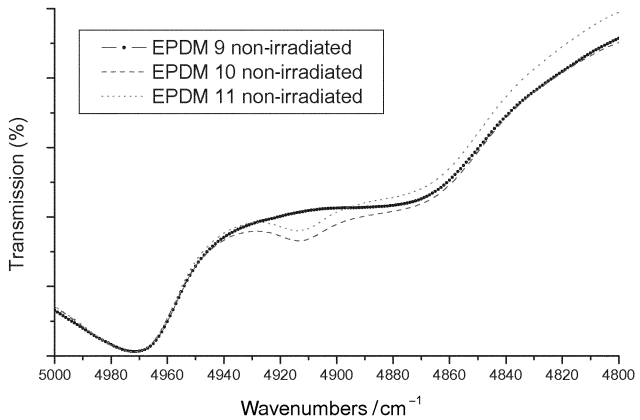


Fig. 3 5000–4800 cm^{-1} NIR spectra of EPDM 9, 10 and 11 non-irradiated.

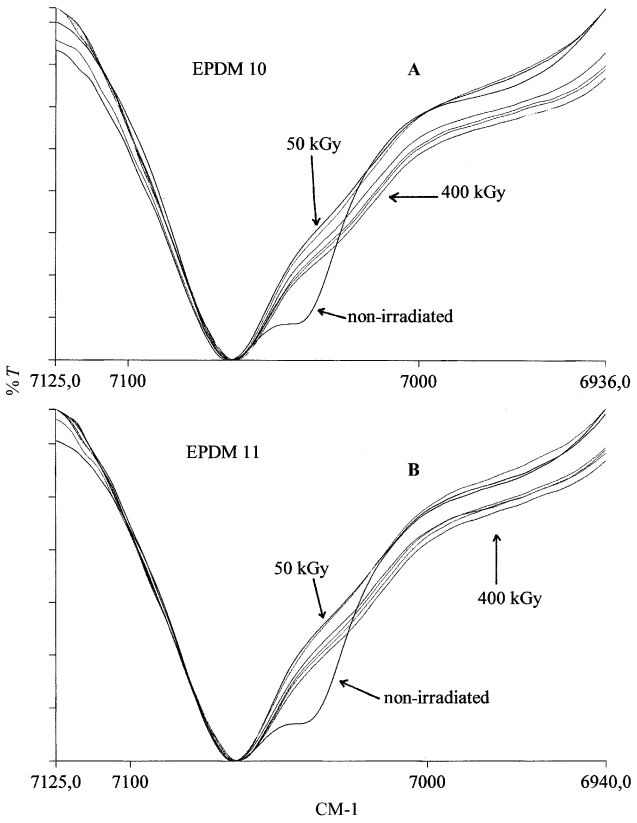


Fig. 4 7125–6935 cm^{-1} NIR spectra of (A) EPDM 10 and (B) EPDM 11 non-irradiated and γ-irradiated at different doses.

the EPDM samples (we used them as received from the CEA) to obtain thin films giving a suitable absorbance level and no excess of dicumyl peroxide. The conclusion of this work was to reveal an increase in carbonyl and hydroxyl functionalities and a decrease of the norbornene (C=C) content with increasing irradiation dose (not seen by us because NIR spectroscopy is not sensitive enough to C=C groups). Hence irradiation leads to the creation of oxidised species and also increases the cross-linking content in the material (owing to decrease in C=C from the norbornene groups) then leading to chain scissions. The main disadvantage of the mid-IR method is that the samples studied are not the real ones. In contrast, NIR spectroscopy can be used on real industrial samples as received.

The bands at 7040 (see Fig. 2) and 4610 cm^{-1} [see Fig. S1 (ESI)†] which were already present in the spectra of the non-irradiated EPDM 10 and 11 samples decrease in intensity and could be due to the residue of dicumyl peroxide disappearing with increasing irradiation dose. These two bands disappear for the lowest available dose of irradiation used in this study, *i.e.*, 50 kGy, which implies that the residue is easily and quickly eliminated. TGA experiments were performed in order to confirm this hypothesis and it can be observed in Fig. S5 (ESI)† that 0.45–0.7% weight loss occurs between 100 and 400 °C for EPDM 10 and 11, respectively (in contrast to only a 0.05% weight loss for EPDM 9). The same evolution can be observed for the band at 4910 cm^{-1} (disappearance with irradiation), which means that this band is also linked to a residue of dicumyl peroxide decreasing with irradiation (see Fig. 5). The band at 4860 cm^{-1} increases with irradiation for EPDM 10 and 11 (see Fig. 5), which leads to the same conclusion as for EPDM 9, *i.e.*, that this band could be assigned to a combination band of OH stretching and OH deformation.[19,20] The band at 5100 cm^{-1} present in EPDM 9, 10 and 11 which increases with irradiation [see Fig. S3 (ESI)†] could be assigned to the third overtone of the carbonyl stretching, the degradation due to oxidation explaining the increase in intensity of these two last peaks with irradiation. For strong total integrated doses (450 kGy), the three samples have an almost identical behaviour, which is confirmed according to their NIR spectra and in agreement with results given by TGA [see Fig. S5 (ESI)†]. Two-dimensional NIR correlation spectroscopy studies of polymer blends by Ren and Ozaki[31] has shed some light on the assignments of bands linked to aromatic groups and some of these bands are similar to those observed in our spectra, such as the bands at 4967, 4647 and 4836 cm^{-1}. NIR spectroscopy coupled with the polarisation modulation technique has been used to investigate molecular orientation in uniaxially stretched polymers by Buffeteau *et al.*[31]

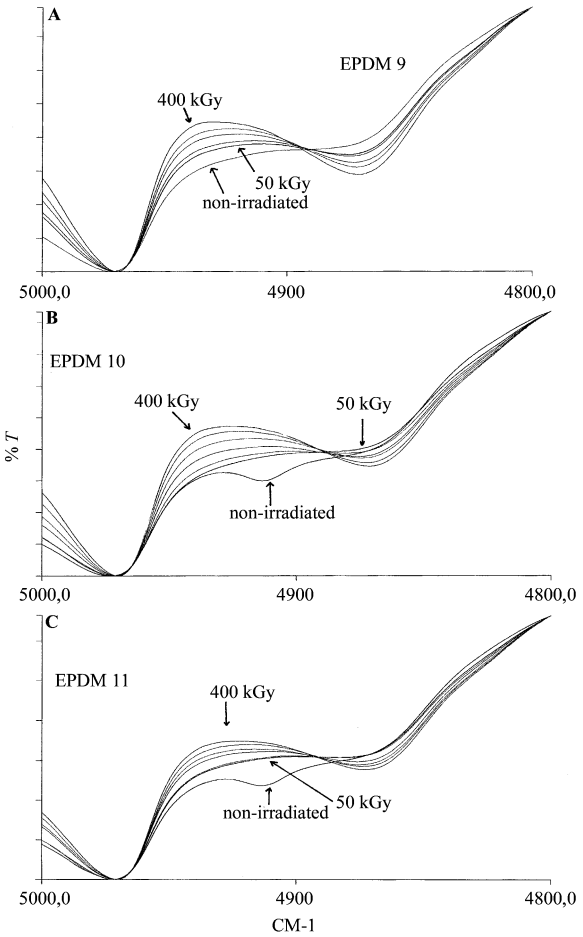


Fig. 5 5000–4800 cm^{-1} NIR spectra of (A) EPDM 9, (B) EPDM 10 and (C) EPDM 11 non-irradiated and γ-irradiated at different doses.

3.3 Multivariate analysis

Multivariate techniques allow the exploitation of complex and large sets of spectra by improving at the same time selectivity and reliability.[11,13,14] The main goal is data reduction without loss of information. The multivariate strategy leads to data with a higher information content. PCA (principal component analysis) can be used to reveal small variations in spectra for samples with differences in the chemical (or physical) composition.[32] The advantage of identification using PCA is that only a limited number of the scores of a spectrum are used. An illustration of that is given in Fig. S5 (ESI)† for EPDM 9. Principal components one and two (PC1 and PC2) contained enough useful information and were used for score plots. After standard normal variate (SNV) pre-treatment of the spectra in the ranges 5000–4600 and 7090–6980 cm^{-1}, the classification of polymers irradiated at different levels can be quickly performed and a clear separation by irradiation level can be seen from Fig. 6(A) and (B). However, the results obtained depend on the spectral range selected for the set of vectors. It can be seen from these preliminary results that the PCA discrimination according to irradiation level is very efficient even if the samples available were limited in our case. Further experiments have to be done to correlate these first results with more samples since this multivariate method can be validated only for a large number of samples. It can be seen from Fig. 6(B) that non-irradiated EPDM 11 and 10 are close together but far from the cluster formed by the irradiated samples. Non-irradiated EPDM 9 are close to but still separated from irradiated EPDM 10 (weak doses). For high doses of irradiation, EPDM 9 (400 kGy) is close to EPDM 10 (400 kGy), which is in good agreement with what was found before using normal NIR spectroscopic

Table 1 Summary of the assignments proposed for the bands that have been detected as characteristic of our materials and their evolution with irradiation

Vibrational band/cm^{-1}	Evolution of band intensity with irradiation	Tentative assignment
7040	Decreases	Second overtone of hydroxyl stretching[26,27]
4970	Remains constant	CH stretch and first overtone of CH in-plane bending (aromatic)[30]
5100	Increases	Third overtone of carbonyl stretching
4910	Decreases	Combination of hydroxyl stretch and hydroxyl deformation
4860	Increases	Combination band of OH stretching + OH deformation[14,19,20]
		Combination of C=O with CH_3[14,22]
4670	Decreases then increases	Aromatic combination band[22]
		Combination band of carbonyl[14,23]
4610	Decreases	Aromatic combination band[22,23]

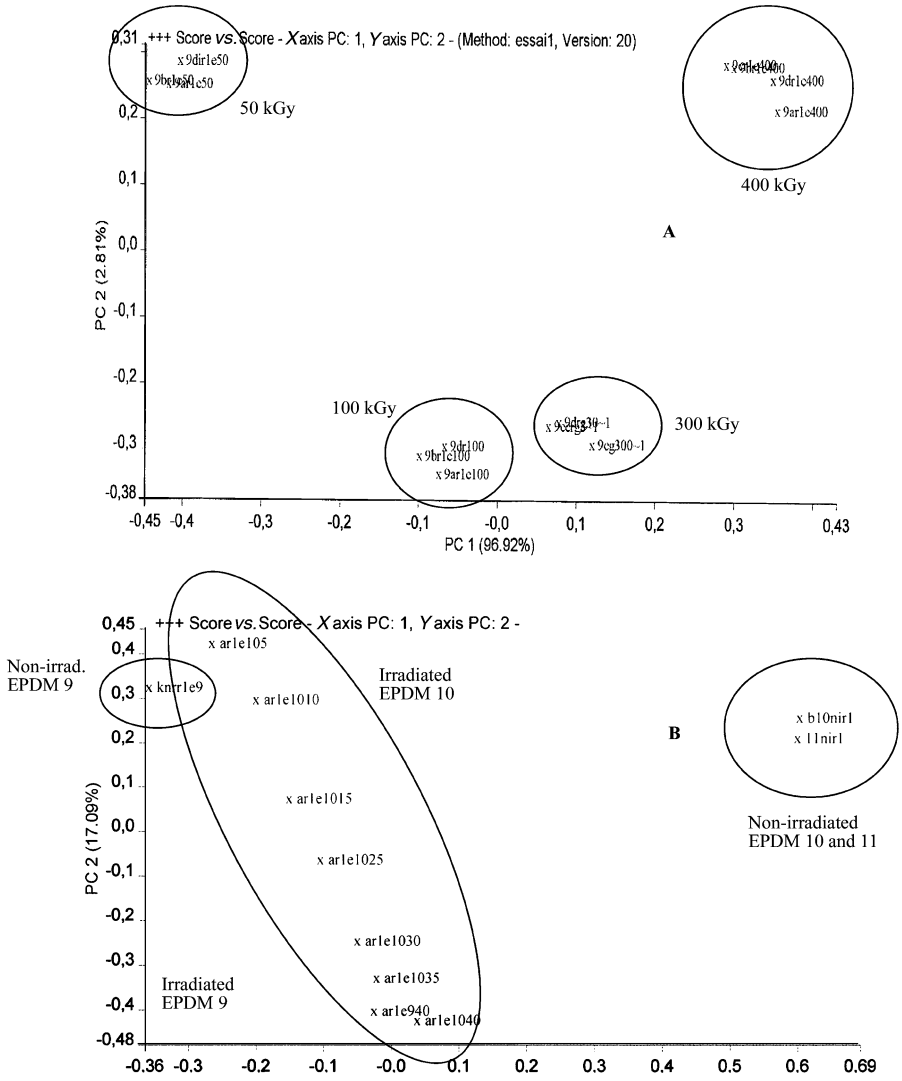


Fig. 6 PCA score plots on (A) EPDM 9 and (B) EPDM 9, 10 and 11 for different irradiation doses.

analysis. This preliminary multivariate study opens up a cost-effective opportunity for the *in situ* and non-destructive monitoring of polymer degradation in nuclear power plants.

4. Conclusions

The feasibility of using NIR spectroscopy to monitor radiochemical ageing of different EPDM elastomers at different levels of irradiation has been demonstrated. It provides information on the molecular modifications linked to the radiochemical ageing. In this case, the main practical aspects have been proved, which are that there is no or little sample preparation and the method is non-destructive and relatively cheap. The increase in the bands at 4670, 4860 and 5100 cm^{-1} with γ-irradiation assigned to combination bands of OH and C=O groups is in agreement with the creation of oxidised species (carbonyl, hydroxyl) already seen by mid-IR spectroscopy. The decrease in the band intensity at 7040, 4610 and 4910 cm^{-1} can be correlated with the disappearance of residues of vulcanising agent when comparing the NIR spectra of EPDM 9 with those of EPDM 10 and 11. The comparison of non-irradiated and γ-irradiated samples has shown that this residue of dicumyl peroxide is eliminated for the lowest total integrated dose available (50 kGy). For strong total integrated doses, the three samples behave almost identically. The improvements brought about by chemical modifications of the initial EPDM (antioxidant) seem to be inefficient as soon as first irradiation doses are applied. It will be interesting to study samples irradiated at weaker doses than 50 kGy to detect the beginning of the sensitivity of the NIR technique to the modifications due to irradiation. PCA has been used to reveal small variations of spectra for EPDM samples with small differences in the chemical (or physical) composition. Chemometrics (multivariate analysis on NIR transmittance data) on the EPDM samples has been used to study the level of EPDM ageing under γ-irradiation. The NIR spectroscopic method after careful calibration with chemometrics can provide a means to quantify, quickly and reliably, the dose received *in situ* by EPDM cables used in nuclear power stations after careful calibration with chemometrics.

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