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Effect of gamma radiation on polyNIMMO

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Abstract

PolyNIMMO is regarded as an energetic polymer. It consists of a nitrate ester group and an ether linkage, which are known to degrade naturally with time, a process which is increased drastically with heat and/or light. The general mechanism for heat ageing of polyesters is the homolytic scission of the CH_2O-NO_2 bond to produce $CH_2O\cdot$ and $\cdot NO_2$ radicals. Often at low temperatures the $\cdot NO_2$ radicals can initiate autoxidation, reacting with oxygen resulting in chain scission of the polyether backbone. In this investigation polyNIMMO was subjected to gamma radiation which is a more aggressive form of radiation. Gamma irradiation of a polymer generally produces radicals, which in turn may produce more radicals through chain scission, chain transfer or quench radicals through recombination or crosslinking. Gamma radiation may also lead to internal plasticisation of the polymer. This is achieved by breaking the polymer backbone into smaller chain lengths, providing compatible, small molecules to plasticise the polymer. Thermal ageing of polyNIMMO tends to induce degradation, however, and surprisingly this was not observed in the bulk irradiation of polyNIMMO. Gamma radiation did not break down the polymeric chains into smaller lengths and therefore internal plasticisation did not occur.

Keywords: Energetic polymers; Gamma radiation; Polymer bonded explosives

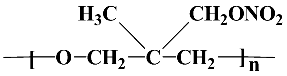
1. Introduction

Polymer bonded explosives (PBXs) were developed to reduce the sensitivity of the newly synthesized explosive crystals by embedding the explosive crystals in a rubber-like polymeric matrix. Work is being conducted on replacing inert prepolymers by energetic prepolymers in explosive compositions, in order to increase the explosive performance, without compromising its vulnerability to accidental initiation.

PolyNIMMO [poly (3-nitratomethyl-3-methyloxetane)] is an energetic prepolymer consisting of a nitrated ester group and an ether linkage [1] as shown in Fig. 1.

PolyNIMMO can be used as an energetic binder in low vulnerability gun propellants, high impulse rocket propellants, elastomer modified double-base propellants and high energy PBXs [2]. PolyNIMMO has been found to decompose to form gases when aged, leading to voids in the explosive composition [3]. If this composition is then violently stimulated the voids may collapse adiabatically forming hot spots which could lead to ignition. Degradation of polyNIMMO can lead to an increase in its cross-linking density resulting in a binder which is hard and brittle. This brittle binder would be vulnerable to shock waves which could result in an unwanted detonation [4]. Degradation of polyNIMMO can also lead to a decrease in its cross-linking density. Here plastic flow may arise resulting in changes to the surface area and burning characteristics.

The results from thermal studies show that the prepolymer polyNIMMO ages naturally with time, even at ambient temperature, and that decomposition is accelerated by an increase in temperature [5,6]. If the products of decomposition are not effectively removed they can further react with polyNIMMO, accelerating decomposition to autocatalysis [7]. When polyNIMMO is pyrolysed to temperatures >90 °C it darkens in colour and becomes more viscous with increasing heating time [8]. The results



$$\left[O-CH_2-\overset{H_3C\quad CH_2ONO_2}{C}-CH_2 \right]_n$$

Fig. 1. Molecular structure of PolyNIMMO.

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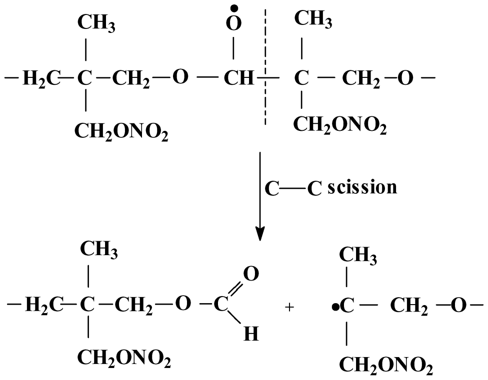


Fig. 2. Mechanism for the chain scission of polyether backbone for thermally aged polyNIMMO.

from gel permeation chromatography (GPC) show that thermally aged polyNIMMO undergoes chain scission and crosslinking. The results from infrared (IR) and nuclear magnetic resonance spectroscopy (NMR) show the presence of a carbonyl group in a formate ester. The formate ester is produced when a proton is abstracted from a methylene carbon in the polymer backbone resulting in a carbon radical which in turn is oxidised giving an unstable oxy radical. The adjacent C–C atoms then undergo bond scission resulting in a formate ester as well as an alkoxy radical, as shown in Fig. 2 [6].

IR spectroscopy also shows the presence of an N–O peak at 1550 cm^{-1} in thermally aged polyNIMMO. The loss of a nitroxide radical is said to be responsible for the peak [6]. This radical then reattaches itself to a newly created radical site on the polymer backbone as shown in Fig. 3.

These studies have shown that polyNIMMO decomposes readily under thermal conditions. PolyNIMMO has also been found to easily decompose when subjected to UV radiation [7–9]. However, there are no results reported in the literature on the behaviour of polyNIMMO when subjected to gamma radiation. Therefore this study was to investigate the decomposition products, radical formation and mechanism for the degradation of polyNIMMO when subjected to gamma radiation up to 750 kGy.

Gamma rays are electromagnetic waves, which are shorter in length than UV waves and higher in energy. Gamma rays do not have any mass or charge but interact with the material by colliding with the electrons in the shells of the atoms. The rays slowly lose energy in the material while generally travelling significant distances before being stopped. The amount of energy absorbed in the material in known as a ‘rad’. A rad is described as the quantity of radiation leading to the absorption of 100 ergs of energy per gram. Nowadays, the rad has been replaced by the ‘gray’, where 1 Mrad equals 10 kGy.

Gamma radiation has been used for many years to alter the molecular structure and microscopic properties of polymers as well as initiating polymerisation. Irradiation by gamma radiation produces radical sites on the polymer backbone. This is usually achieved by the abstraction of hydrogen atoms [10]. Irradiating polymers with gamma radiation can lead to a decrease in the molecular weight of the polymer caused by the breaking of the C–C bond. The molecular weight has also been found to increase where two radical species on the polymer backbone recombine to form a new bond. Gamma radiation can also lead to the decomposition of polymers resulting in gas evolution or the creation of double bonds.

This study was to investigate the effect of gamma radiation on the prepolymer polyNIMMO.

2. Experimental

PolyNIMMO was obtained from the MOD. Five gram samples of the prepolymer polyNIMMO were dried then degassed for several hours by applying a high vacuum of approximately 200 Pa, in order to remove any residual dissolved gases which may have been present due to natural ageing, as well as any reactants from the synthesis process.

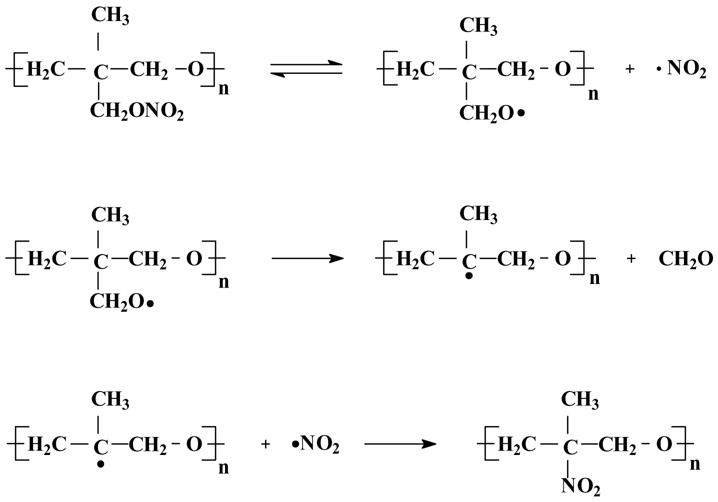


Fig. 3. Mechanism for the homolytic scission of the O–NO_2 bond for thermally aged polyNIMMO.

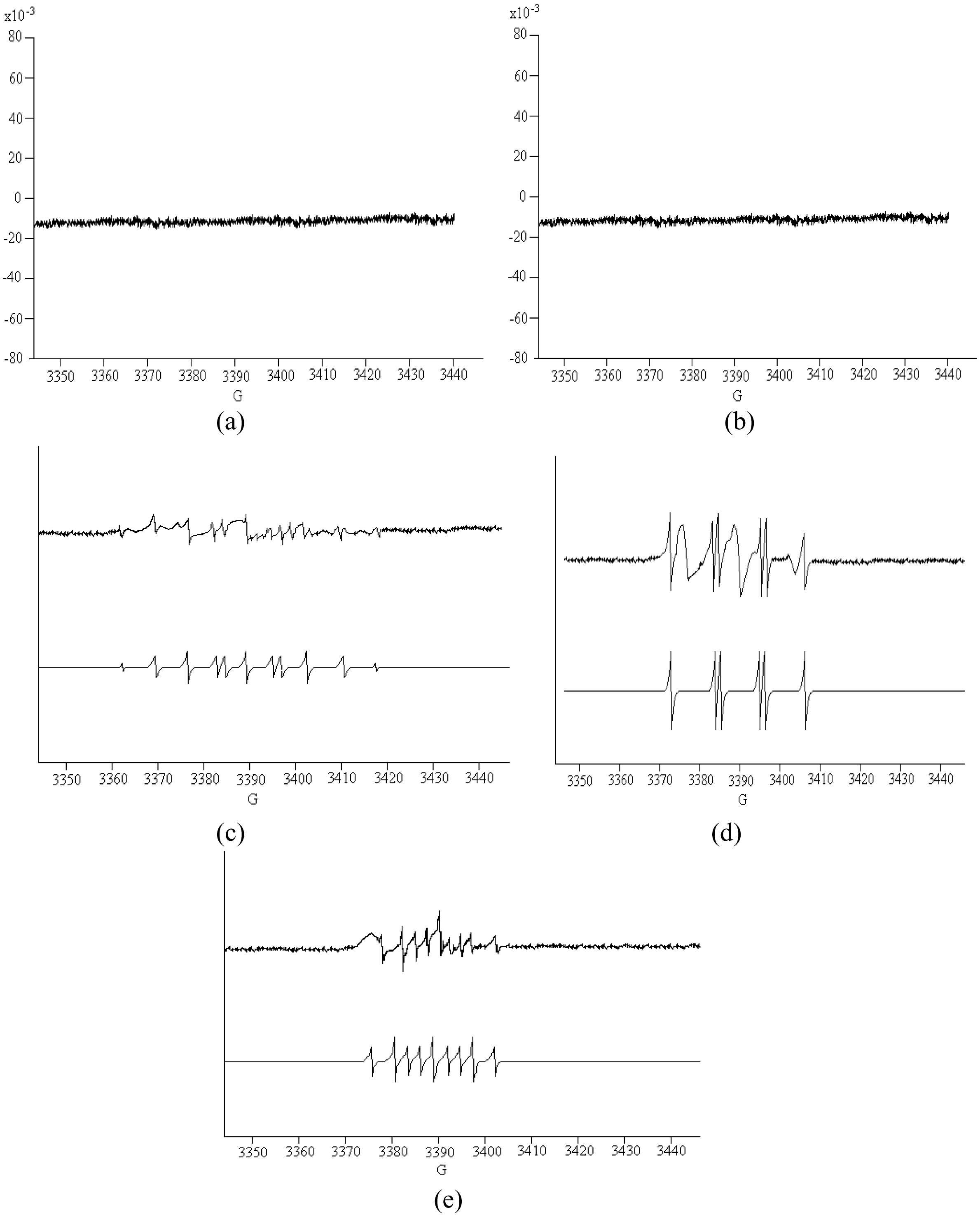
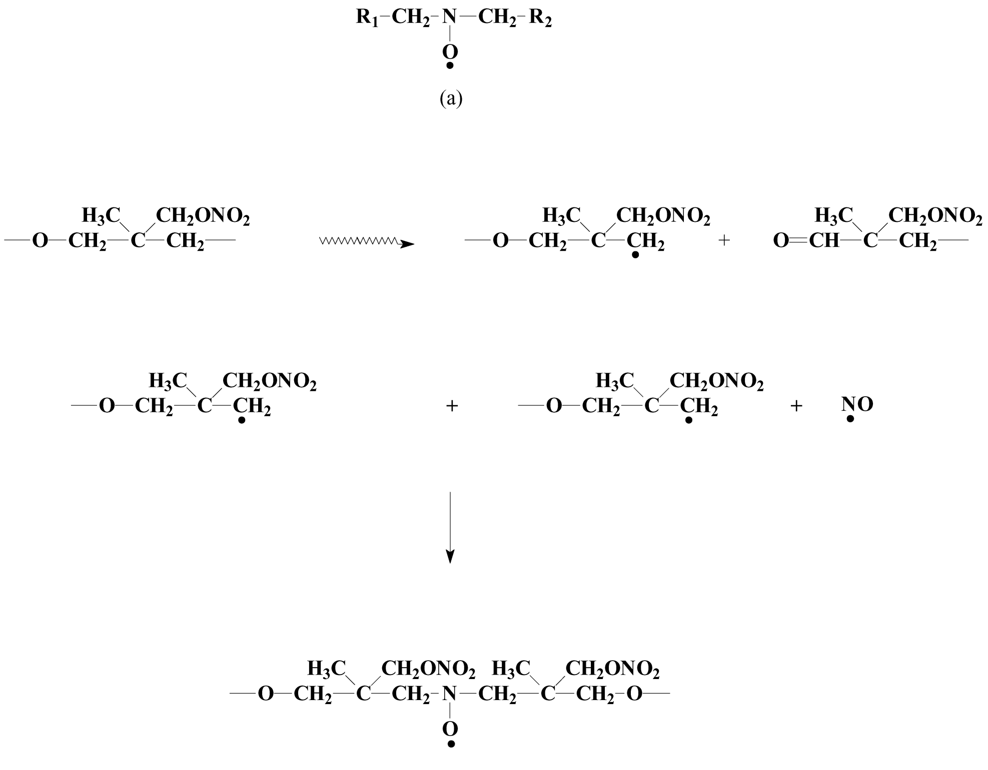


Fig. 4. ESR spectra of polyNIMMMO, (a) unirradiated, (b) irradiated to 1 kGy at room temperature, (c) irradiated to 50 kGy and warmed from − 196 to 7 °C, (d) Sample (c) warmed from 7 to 33 °C, and (e) irradiated to 50 kGy and warmed from − 196 to 7 °C (run ESR spectrum after 23 h).

The samples were placed into 10 ml Chromacol glass vials. The vials were then capped and sealed in air and argon atmospheres. All the vials containing polyNIMMO were irradiated using a ^{60}Co as a source of high-energy gamma radiation.

A radical trap diphenyl picrylhydrazyl (DDPH), supplied by Aldrich, was used to determine the formation of radicals. The DDPH changes colour from purple to yellow indicating the presence of radicals. After irradiation the samples were dissolved in 5 ml of 10^{-4} M DPPH in acetonitrile.

A Bruker EMX 10/12 spectrometer operating at 9.5 GHz with 100 kHz modulation was used to obtain electron spin



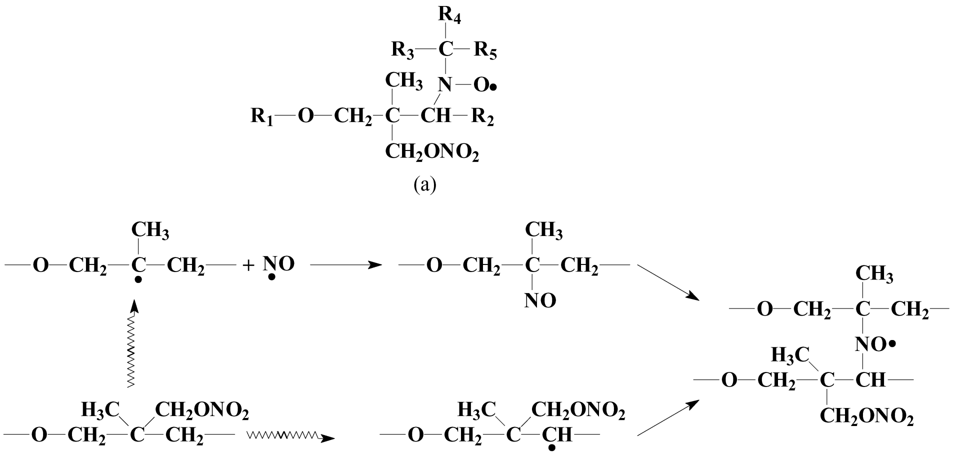
(a)

(b)

Fig. 5. (a) Proposed structure and (b) mechanism for a radical species containing one nitrogen and four hydrogen atoms.

resonance (ESR) spectra on unirradiated and irradiated polyNIMMO in order to detect the presence of radicals. A Bruker Simfonai computer simulation package was used to identify the radical species. ESR spectra were initially recorded on samples at room temperature to determine the radical species. ESR spectra of the radiated samples were also recorded at various temperatures, here the samples were subjected to gamma radiation at a temperature of − 196 °C and then gradually warmed up to 33 °C. All ESR spectra were run on samples which were in the liquid state.

A Fisons MD800 GC/MS mass spectrometer with electron impact in conjunction with a Dani 3950 Automatic Headspace Unit with split injection system was used to analyse the sample headspace for permanent gases. A Chrompack PoraPLOT Q fused silica column and a Chrompack Molsieve 5A fused silica porous-layer open tubular (PLOT) column were installed in series. Switching between the columns was achieved using a Valco 10 port valve. The oven temperature was kept at 50 °C whereas the water bath for the Headspace was maintained at 40 °C. The carrier gas was helium. The columns were used to detect CO_2, O_2, N_2, Ar, N_2O, CO and NO [11].



(a)

(b)

Fig. 6. (a) Proposed structure and (b) mechanism for a radical species containing one nitrogen and one hydrogen atom.

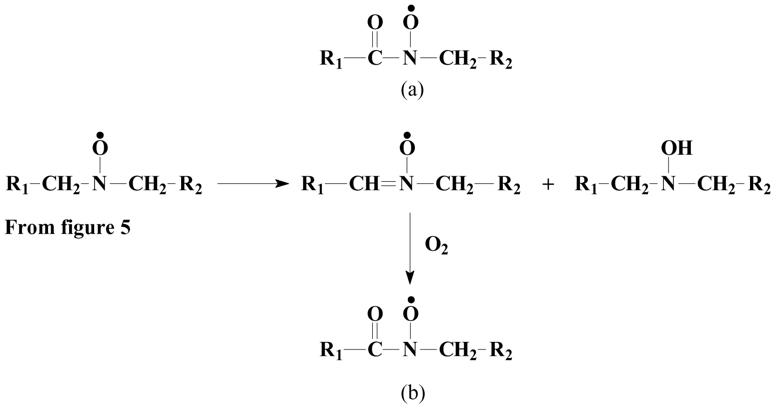


Fig. 7. (a) Proposed structure and (b) mechanism for a radical species containing one nitrogen and two hydrogen atoms.

IR analyses of the samples using an attenuated internal reflection (ATR) apparatus were carried out using a Perkin–Elmer 983 Infrared Spectrophotometer.

GPC was carried out to determine the molecule weight of the samples using a Viscotek Size Exclusion Chromatography (SEC) unit. The viscotek pump was coupled to a Waters auto sampler and refractive index detector using Millennium software for data collection and processing. The GPC was calibrated using polystryene samples supplied by Polymer Laboratories. The calibration standards had a range of molecular weights from 580 to 283.300 Mp with an average M_w/M_n of 1.02.

7 mg/ml of PolyNIMMO dissolved in tetrahydrofuran was injected into the columns.

A Bruker DPX250 (250 MHz) NMR spectrometer was used to produced ^1H and ^{13}C NMR spectra of polyNIMMO. 0.2 mg/ml of PolyNIMMO was dissolved in 1 ml of TMS.

3. Results and discussion

The radical trap (DPPH) was employed to determine the presence of radicals, with its colour changing from purple to yellow as it combines with radicals. On addition of 5 ml of DPPH to the irradiated polyNIMMO, colour changes were observed. For unirradiated samples, the colour was a deep purple. As the radiation dose increased to 11 kGy the colour changed from dark orange (0.1 kGy) to yellow (11 kGy). These results suggest that at low doses of gamma radiation, radicals are present.

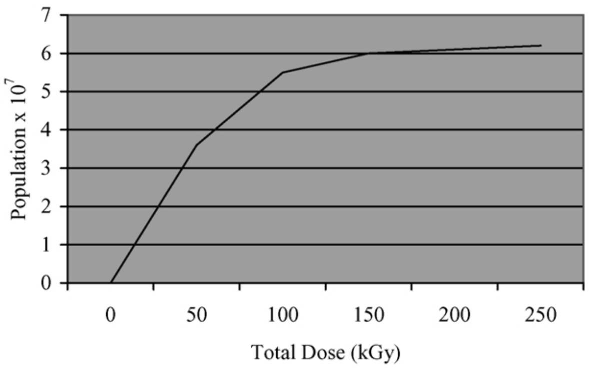


Fig. 8. Population of radicals formed on irradiated polyNIMMO irradiated to 250 kGy.

ESR spectra were recorded on irradiated polyNIMMO at room temperature to determine the radical species. Examples of ESR spectra of polyNIMMO and irradiated polyNIMMO are shown in Fig. 4a and b. No peaks were observed in the ESR spectrum of untreated polyNIMMO and polyNIMMO irradiated at very low levels of radiation (i.e. 1 kGy) thus suggesting that ESR could not detect any radicals. ESR spectra were then carried out on polyNIMMO which was subjected to gamma radiation up to 50 kGy. In order to slow down the radical decay the samples were initially held at − 196 °C and then gradually warmed up to 33 °C. The ESR spectra were recorded at various temperatures. At very low levels of radiation (up to 1 kGy) no peaks in the ESR spectrum were observed. However, the ESR spectrum of samples irradiated to 50 kGy showed broad peaks suggesting the presence of radicals. On raising the temperature of this sample to 7 °C the ESR spectrum showed a presence of a radical species as shown in Fig. 4c. Using computer simulated ESR spectra the radical species was identified as containing one nitrogen and four hydrogen atoms.

The proposed structure and mechanism for this radical species is given in Fig. 5. When this sample was then warmed to 33 °C the ESR spectrum changed considerably as shown in Fig. 4d suggesting that another radical species was now present. Using computer simulated ESR spectra the radical species was identified as containing one nitrogen and one hydrogen atom. The proposed structure and mechanism for this radical species is given in Fig. 6. The two radicals species discussed above were short-lived radicals and decayed after ∼3 h at room temperature. However, a long-lived radical was detected in samples which had been irradiated to 50 kGy and held at 7 °C for 23 h. The ESR spectrum is presented in Fig. 4e together with the computer generated spectrum. The long lived radical species was

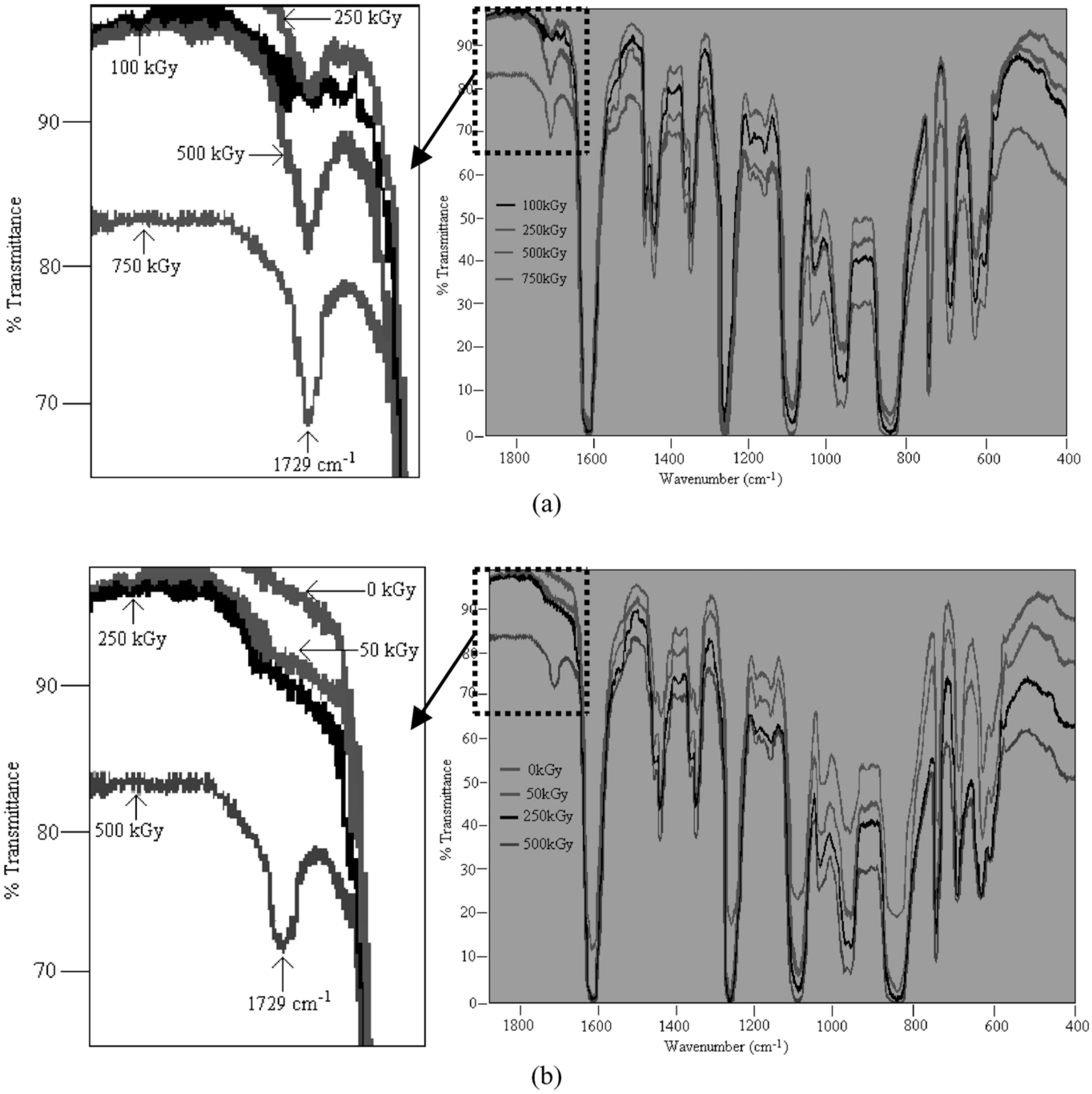


Fig. 9. IR spectrum of polyNIMMO irradiated (a) in air and (b) in a vacuum irradiated to 500 kGy.

identified as containing one nitrogen and two hydrogen atoms as shown in Fig. 7.

Fig. 8 shows the relationship between radiation dose and the population of radicals formed on the irradiated polyNIMMO. It can be seen that the population of radicals increases with increasing radiation dose up to 100 kGy. Above 100 kGy it can be seen that radical formation is slightly higher than the radical decay.

In order to determine the degradation products of polyNIMMO subjected to gamma radiation, gas chromatography linked to mass spectrometer (GS/MS) was carried out. Five grams samples of polyNIMMO sealed in gas tight vials were irradiated up to 100 kGy. The decomposition gases were then analysed by GC/MS. There was no change observed in the levels of CO, CO_2 and N_2O gases for all the samples analysed. The levels of O_2 and N_2 gases were found to increase when radiated to 70–100 kGy which may be due to the polyNIMMO degrading.

PolyNIMMO samples, which had been irradiated up to 750 kGy in air, were then analysed by IR to determine if any structural changes had occurred. No noticeable changes were observed in the IR spectrum for samples irradiated up to 250 kGy. However, samples irradiated between 250 and 750 kGy did show changes in the IR spectrum as shown in

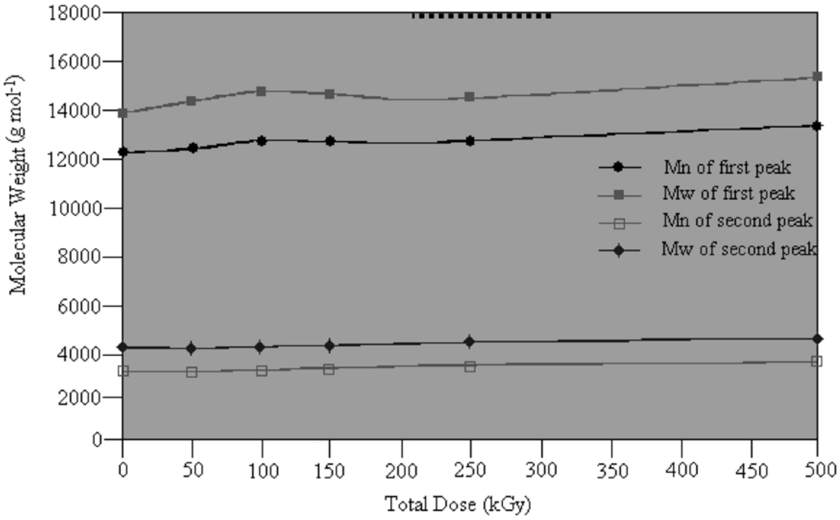


Fig. 10. Molecular weight values from GPC of polyNIMMO irradiated to 500 kGy.

Fig. 9a. Here it can be seen that the carbonyl peak at 1729 cm^{-1} is increasing in height with increasing radiation dose. A peak at 3455 cm^{-1} was also observed which is due to the H-bonded –OH [8] found in water. The appearance of a carbonyl group is probably due to the peroxidation of the methylene carbon as shown in Fig. 2 resulting in chain scission of the polyNIMMO backbone. In order to determine if oxygen in the air was assisting the formation of the radicals by peroxidation, irradiation of dried polyNIMMO was carried out in vials which were capped and sealed under a vacuum. The resultant IR spectrum is presented in Fig. 9b. It can be seen from Fig. 9b that the carbonyl peak at 1729 cm^{-1} does not start to grow until the radiation dose reaches 500 kGy. This results suggests that the presence of oxygen does encourage the peroxidation of the methylene carbon resulting in chain scission of the polyNIMMO backbone.

In order to determine the functional species which

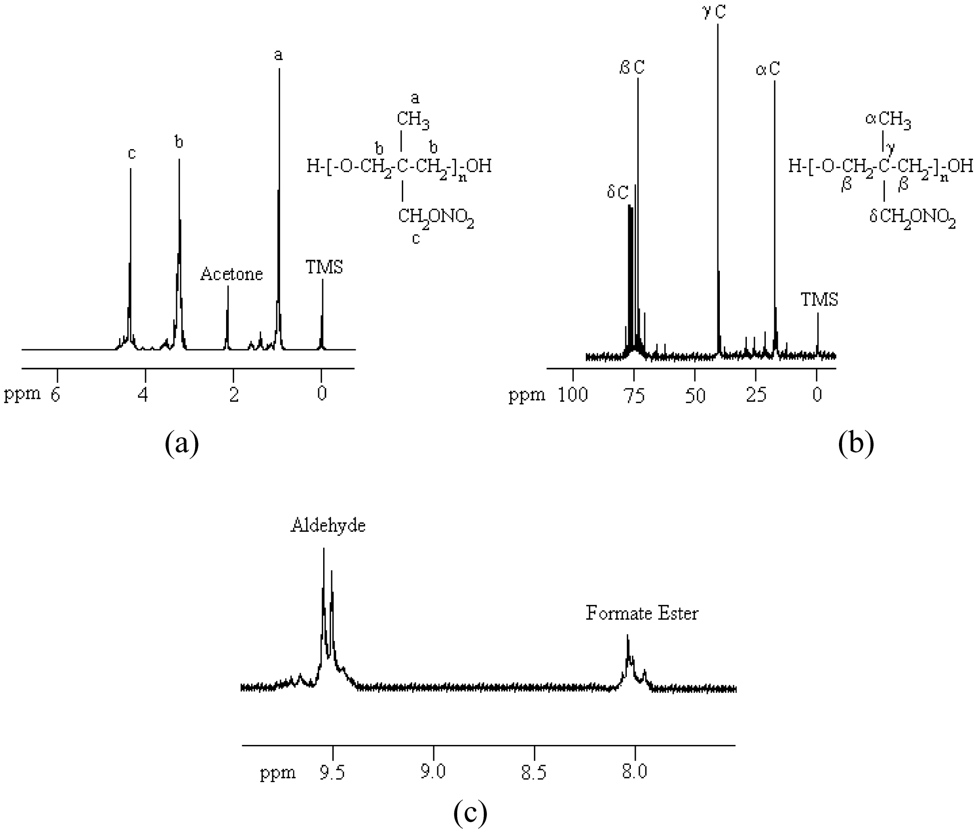


Fig. 11. (a) ^1H and (b) ^{13}C NMR spectrum of polyNIMMO irradiated to 250 kGy, and (c) ^1H NMR spectra of polyNIMMO irradiated to 750 kGy.

contains the carbonyl group (i.e. aldehyde, ketone etc.), the samples which were irradiated to 500 kGy were immersed in Tollens reagent. The results indicated the presence of aldehyde groups.

In order to see if there has been a change in the molecular weight of irradiated polyNIMMO (i.e. chain scission), GPC was carried out on evacuated samples which had been irradiated up to 500 kGy. Here two large peaks were observed with average molecular weights (M_w) of 14,000 and 4000. From Fig. 10 it can be seen that there is no significant change in the molecular weight, for irradiated samples.

Finally the irradiated samples were analysed using ^{1}H and ^{13}C NMR to determine if any structural changes had occurred. ^{1}H and ^{13}C NMR spectra of polyNIMMMO are presented in Fig. 11a and b, together with the assignment of the major peaks. From the NMR spectra no structural changes were observed for polyNIMMO which had been irradiated up to250 kGy. At higher doses (i.e. 750 kGy) a doublet was observed at 9.6 ppm, with a smaller peak appearing at 8.1 ppm as shown in Fig. 11c. These peaks were probably due to the presence of an aldehyde and format ester group.

4. Conclusions

Degradation of polyNIMMO by heat and light [4–7] has been reported and the mechanisms have been proposed. Gamma radiation is known to be a penetrating form of high energy radiation which is a more aggressive form of radiation compared to heat and light. Therefore before this study was undertaken it was thought that polyNIMMO would easily degrade when subjected to gamma radiation at low doses, following the mechanisms suggested by Barton [7,8]. However, the results reported here show that polyNIMMO is very stable to gamma radiation up to doses of 250 kGy. Although radicals are produced at this level and lower levels of radiation they are short-lived and do not cause structural changes in polyNIMMO. At higher levels of radiation up to 750 kGy structural changes were observed. Here the presence of an aldehyde group and format ester were observed in the NMR spectra. The formation of an aldehyde group was also seen in the IR spectra, together with a peak resulting from the presence of water. The results from the GPC analyse showed no change in the molecular weight.

The proposed mechanisms for thermal degradation of polyNIMMO are shown in Figs. 2 and 3. In Fig. 2, the degradation process results in chain scission and the formation of a format ester and an alkoxy radical. In Fig. 3, there has been major structural changes with the –CH_2ONO_2 being removed and replaced by a NO_2 group. The length of the polymeric chain has not altered.

The results from the experiments conducted in this study do not appear to agree with either mechanism. The suggested mechanism for degradation of polyNIMMO by gamma radiation is shown in Fig. 12. Here a hydrogen atom is abstracted at the methyl carbon site. Oxygen then attaches itself to the radical resulting in peroxidation. The peroxide rearranges itself to give an aldehyde and water as a by-product.

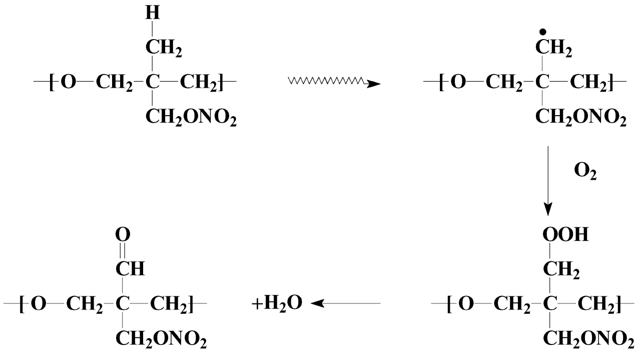


Fig. 12. Proposed mechanism for the formation of an aldehyde group by side chain peroxidation.

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