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Effect of UV and thermal radiation on polyNIMMO

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Abstract

To reduce the sensitivity of explosive compositions, inert polymers and plasticisers have been incorporated. The polymers bind the explosive crystals together whilst the plasticisers reduce the rigidity of the compositions. In order to improve the performance of these compositions without compromising on safety, energetic polymers and energetic plasticisers are now being investigated. While energetic plasticisers have been successfully developed energetic polymers are still very much in the research and development phase. The UK have for the past decade been concentrating on polyNIMMO and to a lesser extent, polyGLYNN. In order to understand the stability of these polymers to ageing, a study was conducted to investigate the effect of ultra-violet (UV) and thermal radiation on polyNIMMO. PolyNIMMO was found to thermally degrade in the presence and absence of oxygen at temperatures of 70, 100 and 130°C. DSC and FTIR results indicate that polyNIMMO undergoes degradation by three different mechanisms, namely homolytic scission of the O–NO_2 bond, scission of the polyether backbone and crosslinking of the polymer chains. PolyNIMMO was also found to degrade when subjected to UV radiation at ambient temperature. Evidence from analyses indicates that only two of the degradation mechanisms are taking place namely homolytic scission of the O–NO_2 bond, and scission of the polyether backbone. PolyNIMMO will only undergo crosslinking when subjected to UV at higher temperatures (i.e. 100°C).

Keywords: Energetic polymers; UV radiation; Thermal ageing

1. Introduction

Polymers are widely used in explosive compositions and are known as polymer bonded explosives (PBXs). In PBXs the polymer, very often mixed with a suitable plasticiser, binds the explosive crystals together to form a compact explosive composition. More importantly, the polymer and plasticiser reduces the sensitivity of the explosive composition. Many different polymers have been employed as polymeric binders in PBXs. These include polyamides, polytetrafluoroethylene, polyurethanes, polyesters and polystyrene [1]. Nowadays, besides the basic need to be chemically and physically stable, polymeric binders need to possess good mechanical properties over a wider temperature range (−55 to +70°C). The polymers must also possess high elasticity and a low glass transition temperature (T_g). Recent PBX formulations have tended to use elastomeric or rubbery binders such as hydroxy-terminated polybutadiene (HTPB) which fulfil these requirements.

In order to improve the performance of PBXs without compromising on safety, energetic polymers and energetic plasticisers are now being investigated for use in PBXs. While energetic plasticisers have been successfully developed, energetic polymers are still very much in the research and development phase. The UK have for the past decade been concentrating on polyNIMMO and to a lesser extent, polyGLYNN.

PolyNIMMO is prepared by the cationic polymerisation of the monomer, 3-nitratomethyl-3-methyloxetane (NIMMO) with boron trifluoride etherate/1,4-butanediol as the initiator. It exists as a pale yellow viscous liquid prepolymer with a T_g between −35 and −25°C depending on its functionality (either difunctional or trifunctional) and its molecular weight distribution. The chemical structures of NIMMO and polyNIMMO are shown in Fig. 1. In reality, polyNIMMO has been shown [2] to be a complex mixture of oligomers, both linear and cyclic, as shown in Fig. 1 (where X and Y are various end groups and n reaches a value of 20). As can be seen from Fig. 1, polyNIMMO consists of an ether backbone (–C–O–C–) with a pendant nitrated ester group (–ONO_2). The hydroxyl (OH) endgroup can be crosslinked or cured to a rubbery solid with a curing agent, such as a polyisocyanate. In order to understand the stability of these polymers to ageing, a study was conducted to investigate the effect of ultra-violet (UV) and thermal radiation on polyNIMMO.

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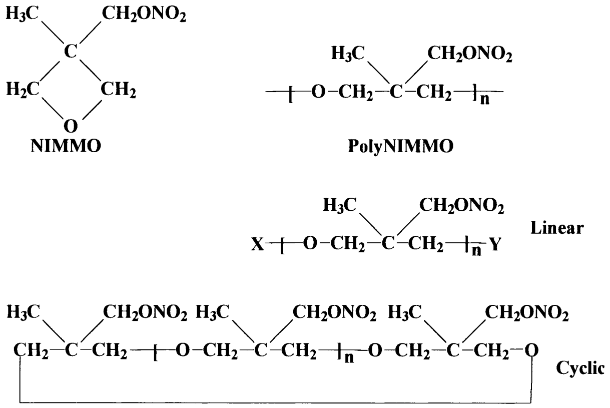


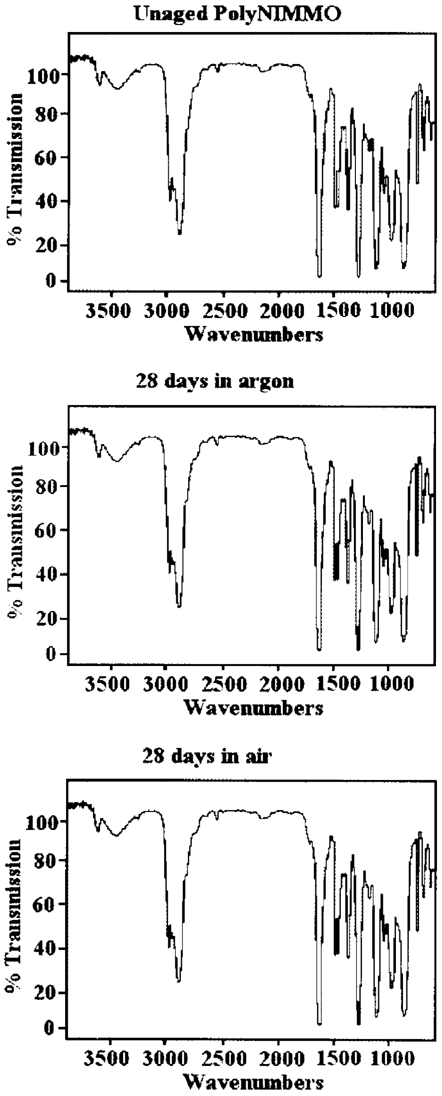
Fig. 1. Structural formulae of NIMMO and polyNIMMO.

2. Experimental—thermal degradation

PolyNIMMO was manufactured by ICI Explosives. All experiments were carried out on the polyNIMMO prepolymer which contained no stabilisers. Thermal radiation was achieved by ageing three different temperatures over five different times. The temperatures were 70, 100 and 130°C and the times were 2, 4, 7, 14 and 28 days [3,4].

Five g of polymer was placed into 20-ml glass vials. The glass vials were fitted with a rubber septum and aluminium cap which was crimped closed to provide an air tight seal. Half of the glass vials were sealed in air, and the remaining glass vials evacuated for 2 h to remove any air or absorbed gas and then sealed under an argon atmosphere.

After the required time the samples were removed from the oven, cooled to ambient temperature before being visually examined for any obvious signs of degradation. These signs include bulging of the rubber septum, bulging and loosened aluminium cap, gas bubbles, colour change, viscosity change and curing. The samples were weighed and then stored in a refrigerator in darkness.


Unaged PolyNIMMO

28 days in argon

28 days in air

Fig. 2. FTIR spectra of unaged polyNIMMO and polyNIMMO held at 70°C for 28 days.

Table 1
% weight loss and T_g of polyNIMMO held ambient, 70, 100 and 130°C

70°C			100°C			130°C			Ambient		
Time	% Weight loss	T_g °C	Time	% Weight loss	T_g °C	Time	% Weight loss	T_g °C	Time	% Weight loss	T_g °C
In air											
2 days	0.06	−33.0	2 days	0.18%	−34.1	2 days	7.29	−28.7	28 days	0.00	−32.5
4 days	0.04	−33.0	4 days	0.21%	−34.2	4 days	13.61	−25.0			
7 days	0.00	−32.8	7 days	0.51%	−34.1	7 days	20.01	−17.5			
14 days	0.04	−32.8	14 days	1.17%	−33.9	14 days	26.99	[a]			
28 days	0.02	−33.4	28 days	2.69	−32.4	28 days	34.72	[a]			
In argon											
2 days	0.08	−32.9	2 days	0.22	−34.1	2 days	7.01	−30.8	28 days	0.00%	−32.5
4 days	0.14	−32.9	4 days	0.26	−34.1	4 days	13.06	−26.2			
7 days	0.22	−32.9	7 days	0.63	−33.4	7 days	19.78	−19.8			
14 days	0.14	−32.9	14 days	1.40	−32.7	14 days	26.72	[a]			
28 days	0.10	−32.6	28 days	3.08	−31.5	28 days	32.37	[a]			

[a] These samples were too solid to be extracted for analysis by DSC.

In order to determine any change in mobility of the polymeric chains, T_g was measured using Mettler 4000 Differential Scanning Calorimetry (DSC). FTIR spectra were recorded using a BioRad SPC 3200 analyser operating an FTS-7 FTIR spectrometer to determine if there was a change in structure of the polymer.

3. Results

The results of the % weight loss and T_g of the thermally aged polymer at ambient temperature, 70, 100, and 130°C are presented in Table 1. It can be seen from Table 1 that there is no change in the % weight loss for samples held at ambient temperature. The T_g for these samples was found to be −32.5°C. At 70°C the samples did not show any significant change in % weight loss, T_g, and appearance. Fig. 2 shows FTIR spectra of unaged polyNIMMO and polyNIMMO held at 70°C for 28 days in air and in argon. Again there seems to be no significant difference between these spectra.

Samples held at 100°C had become more transparent, less viscous and contained tiny gas bubbles. A progressive darkening of the samples were observed, ranging from no noticeable colour change for the 2 and 4 day samples, to dark yellow for the 7 day samples, to orange for the 14 day samples and finally to reddish brown for the 28 day samples. Bulging of the rubber septum could be seen for samples aged for 28 days in air and argon. At 100°C the % weight loss was observed to increase with increasing time of thermal radiation for samples held in air and argon up to a maximum of about 3%. The results from DSC show only a small change in the T_g. The FTIR spectra (Fig. 3) show the appearance of two new peaks at 1550 and 1729 cm^{-1}. The peak at 3455 cm^{-1} was also observed to slightly increase in intensity with time after 28 days.

All samples held at 130°C had bulging rubber septums and bulging aluminium caps which had loosened. This

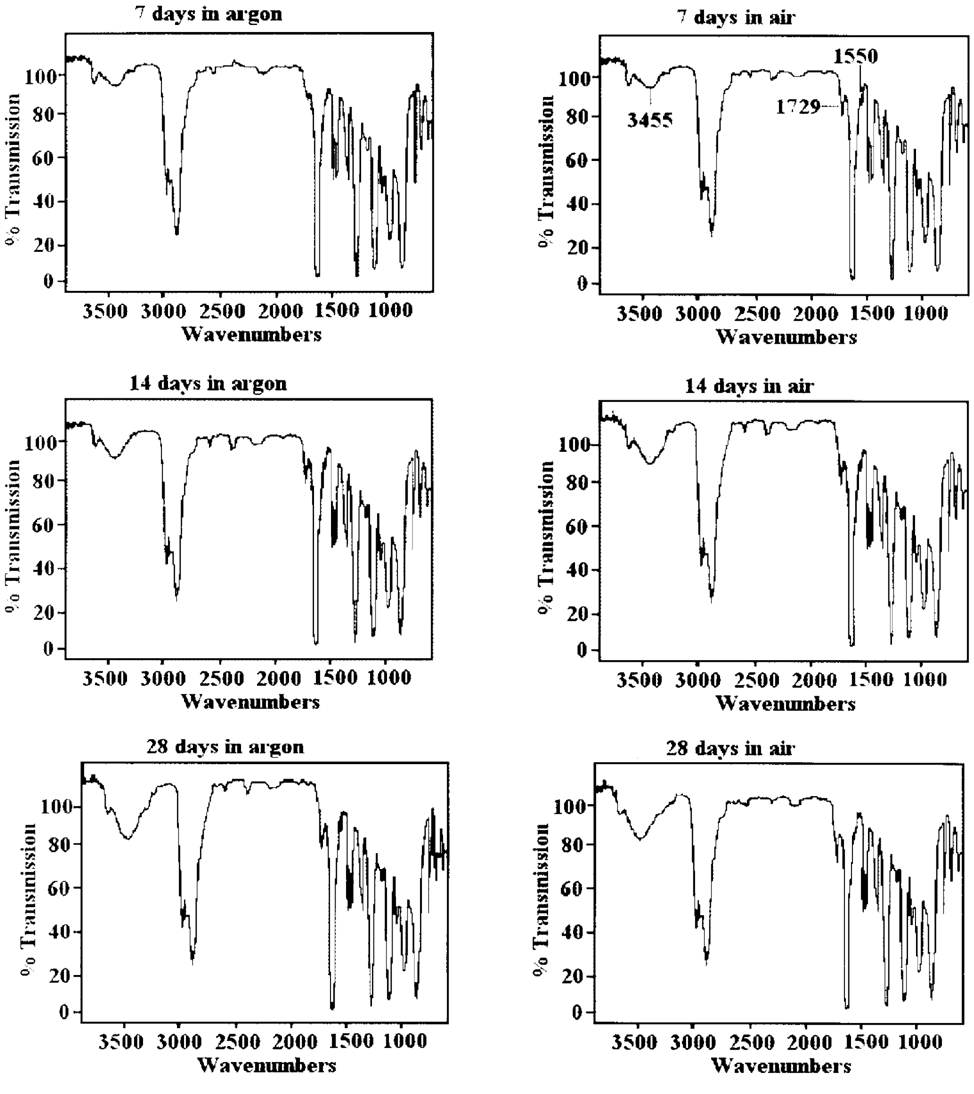


Fig. 3. FTIR spectra of polyNIMMO held at 100°C for 7, 14 and 28 days in air and in argon.

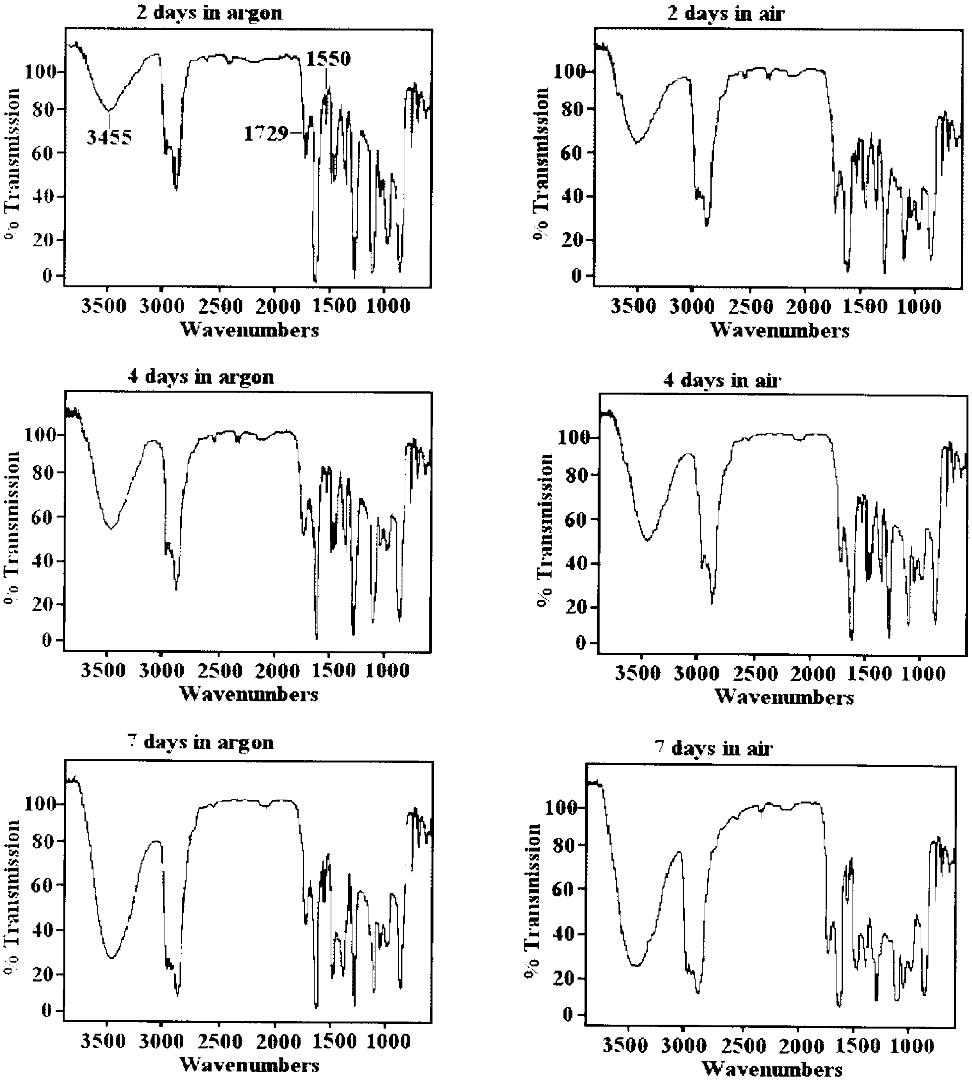


Fig. 4. FTIR spectra of polyNIMMO held at 130°C for 2, 4 and 7 days in air and in argon.

indicates that an excessive amount of gas had been produced. The colour of the samples had changed from pale yellow to a very dark brown for the 2 day samples towards almost black for the longer times. There was also presence of tiny gas bubbles and transparent liquid droplets on the inside of the glass vials. The viscosity of the polymer was found to increase with time, and samples held for 14 days or longer had completely cured to become solid. These solid samples were placed into a suitable solvent (dichloromethane) to see if they would dissolve but only swelling occurred which indicates that the samples had crosslinked, with the 28 day sample doubling its size. The samples showed significant weight loss at 130°C, from about 7% to about 33%. Samples sealed in air showed marginally a greater weight loss than those sealed under argon. The T_g had increased significantly over the period of time, which supports the observation of a progressive decrease in the chains mobility possibly due to crosslinking. FTIR spectra showed the appearance of two new peaks at 1550 and 1729 cm^{-1} as shown in Fig. 4. The peaks at 1550 and 1729 cm^{-1} were seen to increase in intensity with time. The peak at 3455 cm^{-1} was also observed to increase in intensity with time. The peaks seem to be more intense

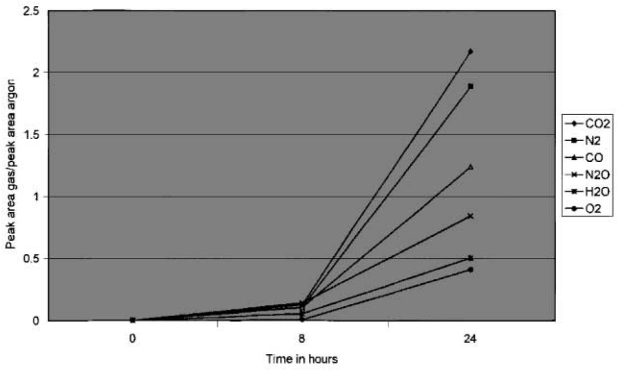


Fig. 5. Gases evolved by thermally degraded polyNIMMO.

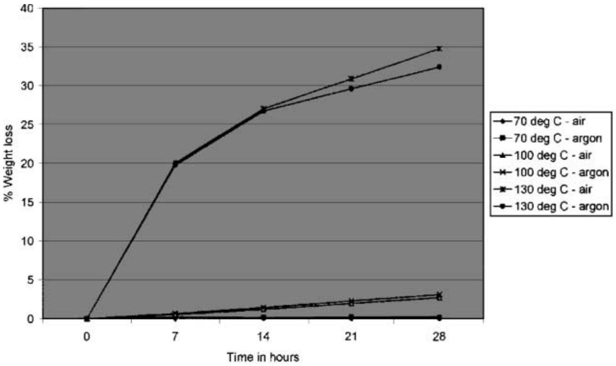


Fig. 6. % weight loss of polyNIMMO with respect to time at various temperatures.

for those samples sealed in air compared to those samples sealed under argon.

In order to determine the degradation products (i.e. gases), gas chromatography (GC) was carried out on samples held at 130°C for 8 and 24 h. The GC used in this investigation was Carlo Erba Strumetazione HRGC 3300 Gas Chromatograph. The results from the GC showed that N_2, O_2, CO, CO_2, N_2O and H_2O gases were present in the headspace of the glass vials and the concentration of the gases increased with time as shown in Fig. 5.

4. Discussion

From these results it is clear that some form of change or degradation has taken place in polyNIMMO when subjected to thermal radiation in air and argon. The discolouring, % weight loss, T_g, and GC results all confirm this. Fig. 6 shows the % weight loss with respect to time at the various temperatures. It can be clearly seen from Fig. 6 that the most significant weight loss was for samples held at 130°.

Thermal degradation of polyNIMMO may proceed by several subsequent reactions involving the highly reactive alkoxyl radical and the nitro group following the homolytic scission of the O–NO_2 bond as shown in Fig. 7 [3,4]. The elimination of formaldehyde (CH_2O) from the side chain of the highly reactively alkoxyl radical is likely to occur to produce the more stable tertiary carbon-centre radical to which some of the evolved NO_2 may subsequently reattach itself. The nitro group attached to a tertiary carbon results in the production of a peak at 1550 cm^{-1} in the FTIR spectrum due to the asymmetric stretch of this nitro group. The nitro group may decompose or combine with formaldehyde to form other gaseous products as shown in Fig. 8. Evolution of various gases have also been observed [3,4] such as N_2O, NO, CO_2 and CO from polyNIMMO when thermally aged. The GC analysis detected these gases in our samples. The weight loss and FTIR results for this study can to a certain extent verify this degradation mechanism involving the homolytic scission of the O–NO_2 bond resulting in the loss of the nitro group (NO_2) and the subsequent loss of formaldehyde (CH_2O) from the polymer side chain. It can also be seen that the peak at 1550 cm^{-1} increases in intensity with an increase in weight loss for samples held at 100 and 130°C in air and argon. The little change in weight loss and the lack of the peak at 1550 cm^{-1} for samples held at 70°C suggests that these samples did not undergo degradation.

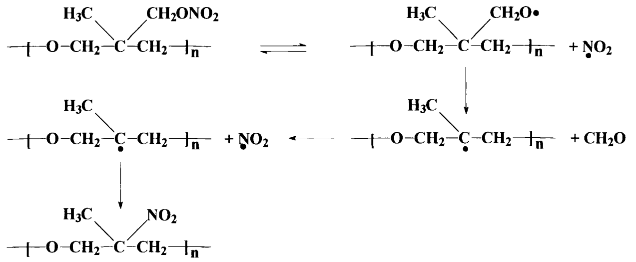


Fig. 7. Mechanism for the homolytic scission of the O–NO_2 bond for polyNIMMO.

$$4NO_2 \rightleftharpoons 2N_2O_4 \longrightarrow 2N_2O + 3O_2$$

$$2NO_2 \rightleftharpoons 2NO + O_2$$

$$7NO_2 + 5CH_2O \longrightarrow 7NO + 2CO_2 + 3CO + 5H_2O$$

Fig. 8. Decomposition and reaction of nitro groups evolved from degraded polyNIMMO.

Thermal degradation of polyNIMMO may also proceed by scission of the polyether backbone involving the oxidation and subsequent cleavage of the C–C bond resulting in the formation of a formate ester, as shown in Fig. 9 [3,4]. Degradation via oxidation is a common phenomenon in polymers and this degradation is again exacerbated by heat, the process being referred to as thermal-oxidation [5]. The formate ester would produce a peak at 1729 cm^{-1} in the FTIR spectrum. This peak was observed in the FTIR spectra of polyNIMMO which was thermally aged at 100 and 130°C. The intensity of this peak was found to be the highest for samples held at 130°C, and increased in intensity with time and % weight loss. For this degradation mechanism to occur O_2 would need to be present. However some of the samples used in this investigation were sealed under argon. Traces of O_2 may well have been present in the samples from the beginning, or O_2 may have entered through the glass vials. The seal of the glass vials may have become damaged due to the excessive pressure

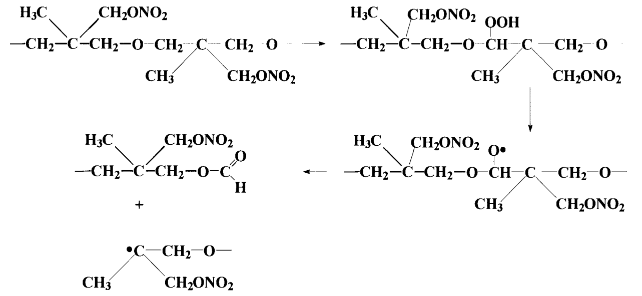


Fig. 9. Mechanism for the chain scission of polyether backbone for polyNIMMO.

build-up inside the glass vials. The caps on the glass vials were all observed to be loose for samples held at 130°C. Lastly O_2 could have be generated internally by the decomposition of the evolved NO_2 following the homolytic scission of the O–NO_2 bond as shown in Fig. 8. The peak at 1729 cm^{-1} was seen to be slightly higher in intensity for the samples, which were thermally aged in oxygen.

Under the influence of heat, the polymer chains could also undergo crosslinking (or chain lengthening), even in the absence of a curing agent. It is likely that water could be formed as a by-product from this process as shown in

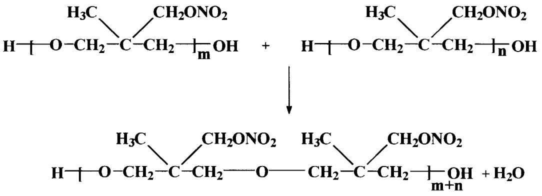


Fig. 10. Mechanism for crosslinking reaction of polyNIMMO.

Table 2
% weight loss and T_g of polyNIMMO subjected to UV radiation at ambient temperature and at 100°C

At ambient temperature									At 100°C		
30W Deuterium lamp			2 kW Mercury lamp			Control			400 W Mercury lamp		
Time	% Weight loss	T_g °C	Time	% Weight loss	T_g °C	Time	% Weight loss	T_g °C	Time	% Weight loss	T_g °C
Distance of 90 mm			Distance of 100 mm			4 h	0.00	− 32.5	Distance of 90 mm		
20 min	0.01	− 32.6	30 min	0.03	− 32.9	8 h	0.00	− 32.5	1 h	1.61	− 31.3
40 min	0.02	− 32.3	Distance of 190 mm						2 h	3.64%	− 27.3
1 h	0.02	− 32.4	30 min	0.03	− 33.2				4 h	6.45	− 25.8
2 h	0.02	− 32.6							8 h	13.35	− 21.5
4 h	0.05	− 32.4							Distance of 180 mm		
									1 h	0.63	− 31.4
									2 h	1.23	− 29.9
									4 h	2.10	− 28.5
									8 h	3.28	− 28.5

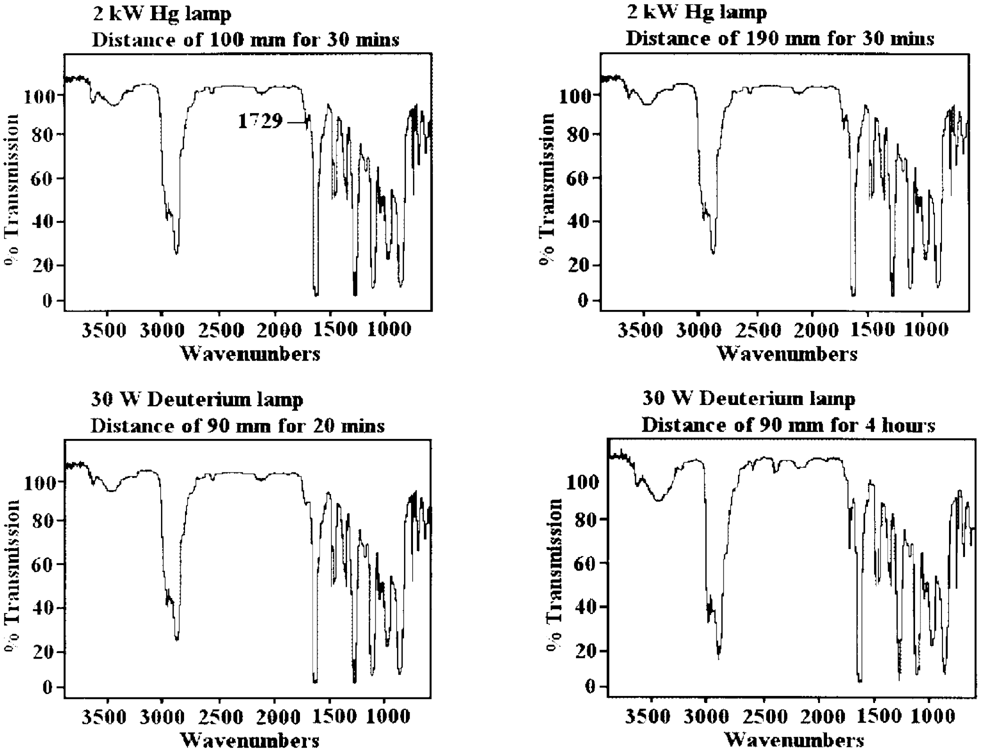


Fig. 11. FTIR spectra of polyNIMMO irradiated with a 2 kW Hg lamp and a 30 W deuterium lamp at ambient temperature.

Fig. 10. For thermal ageing at 130°C it was obvious that the samples in both air and argon had undergone crosslinking. The appearance and increase in T_g verified this. The 7 day samples had in fact shown a dramatic increase in T_g of about 14°C. Samples held at 100°C (after 28 days) and 130°C also had an IR peak at 3455 cm^{-1}, which is due to the H-bonded –OH [6] found in water. Transparent liquid droplets were seen on the inside of the glass vials which is most likely to be water and is probably the by-product from the crosslinking reaction.

5. Experimental—UV degradation

Five g of polyNIMMO was place into a 15 ml wide neck glass bottle which was transparent to UV radiation. Five samples were irradiated with a 30 W deuterium lamp at distance of 90 mm for 20 min, 40 min, 1, 2 and 4 h at ambient temperature. A thin film of polyNIMMO smeared over a NaCl disk, was also irradiated under the same conditions given above and then analysed by FTIR. Two samples were irradiated by a 2 kW Hg lamp at distance of 90 and 100 mm for 30 min at ambient temperature, and eight samples were irradiated with a 400 W lamp at distance of 90 and 180 mm for 1, 2, 4 and 8 h at 100°C [2].

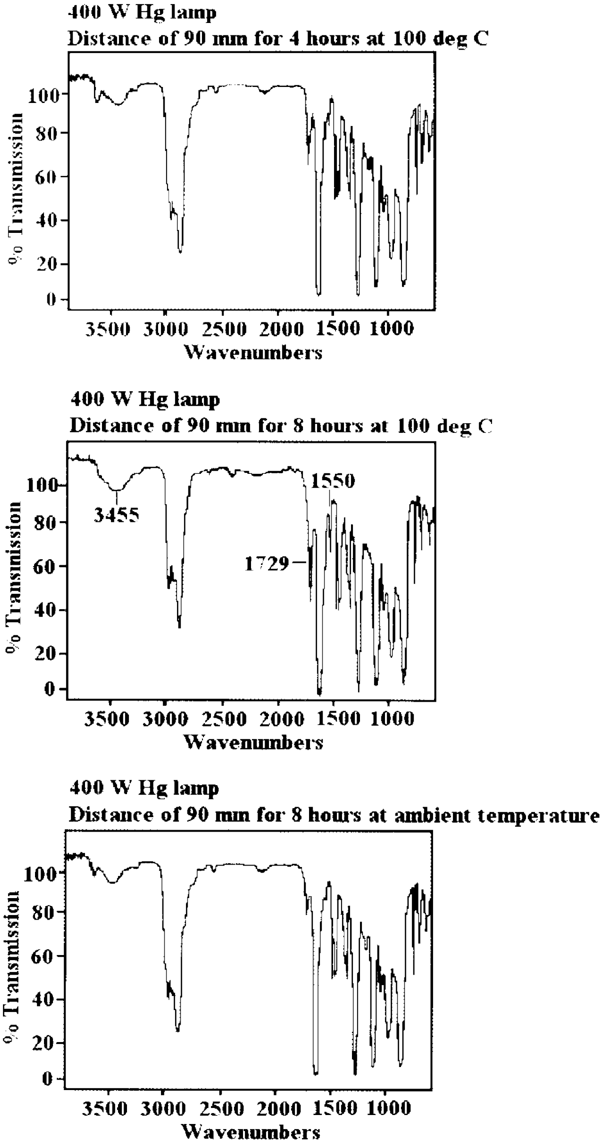
After irradiation the samples were visually examined for any obvious signs of degradation, then weighed and stored in a refrigerator in darkness. DSC and FTIR spectra were run on the samples. The % weight loss and T_g results are presented in Table 2.

6. Results

Samples which had been irradiated by the 2 kW Hg lamp and the 30 W deuterium lamp for all times and distances did not show any significant change in the % weight loss and T_g. However FTIR spectra did show the appearance of a new peak at 1729 cm^{-1} as shown in Fig. 11. This peak was seen to increase in intensity with an increase in time of irradiation.

Samples which had been irradiated by the 400 W Hg lamp at 100°C at 90 and 180 mm for 1 and 2 h, showed no visible signs of degradation, whereas the samples irradiated for 4 and 8 h had darkened in colour, with the 8 h sample being darker than the 4 h sample. The T_g of these samples was found to decrease as the % weight loss increased. FTIR spectra of samples held for 4 and 8 h are shown in Fig. 12. The appearance of two new peaks around 1550 and 1729 cm^{-1} were observed for samples irradiated for 8 h. Both peaks increased in intensity with increasing time of irradiation. No significant increase in the peak height at 3455 cm^{-1} was observed for all samples.

In order to determine that the degradation was due to thermal radiation rather than UV radiation, a sample was irradiated by the 400 W Hg lamp at ambient temperature for 8 h. After irradiation the sample was visually examined for any obvious signs of degradation, then weighed and stored in a refrigerator in darkness. The FTIR spectrum is presented in Fig. 12. There was no noticeable sign of degradation and the % weight loss was found to be 4.84%. From Fig. 12 it can be seen that the peaks at 1729 and 1550 cm^{-1} were considerably smaller than the FTIR spectrum of the sample which had been UV radiated at 100°C. Therefore suggesting that the major factor in degrading polyNIMMO is thermal rather than UV.


400 W Hg lamp
Distance of 90 mm for 4 hours at 100 deg C

400 W Hg lamp
Distance of 90 mm for 8 hours at 100 deg C

400 W Hg lamp
Distance of 90 mm for 8 hours at ambient temperature

Fig. 12. FTIR spectra of polyNIMMO irradiated with a 400 kW Hg lamp at 100°C and at ambient temperature at a distance of 90 mm.

7. Discussion

Samples irradiated by the 400 W Hg lamp at 100°C showed the highest degree of degradation. Samples which had been irradiated for 8 h appeared brown in colour and had a % weight loss of around 13%. Although, the changes seen in these samples would be in part due to thermal radiation, evidence from the other experiments showed that UV radiation does have an effect on polyNIMMO.

The appearance of the peak in the FTIR spectra at 1550 cm^{-1} suggests the presence of a nitro group attached to a tertiary carbon, as shown in Fig. 7. This in turn suggests that polyNIMMO when subjected to UV degradation may have undergone homolytic scissions of the $O–NO_2$ bond.The appearance of a peak in the FTIR spectra at 1729 cm^{-1} suggests that the backbone chain of polyNIMMO is also undergoing chain scission to form the formate ester via oxidation as shown in Fig. 9.

In thermal ageing the peak at 3455 cm^{-1} was observed to increase in intensity due to the presence of water resulting from the crosslinking of the polymer (see Fig. 10). However this peak did not change in intensity for the samples subjected to UV ageing at ambient temperature. The T_g of these samples also remained constant (see Table 2) which suggests that samples subjected to UV at ambient temperature do not undergo crosslinking. Samples which were subjected to UV radiation at 100°C did behave differently. The viscosity of the polymer was seen to increase, the samples were observed to turn a brown colour, and the T_g values increased significantly which suggests a reduction in the polymeric chain mobility possibly due to crosslinking. However if crosslinking did take place, water would have been produced as a by-product (see Fig. 10) leading to an increase in the peak height at 3455 cm^{-1}. This was not observed in these samples (see Fig. 12). One possible explanation is that the samples were subjected to UV degradation in open glass bottles, and if water was produced at 100°C it probably would have evaporated.

8. Conclusions

From this investigation polyNIMMO prepolymer was degraded by thermal radiation in the presence and absence of oxygen. At moderate ageing temperatures of 70°C polyNIMMO was found to be quite stable. At higher temperatures up to 130°C polyNIMMO was found to degrade. This could be observed from the appearance of polyNIMMO, its T_g and % weight loss, and the appearance of new peaks in the FTIR spectrum.

The thermal degradation is likely to follow three different mechanisms, namely homolytic scission of the $O–NO_2$ bond, scission of the polyether backbone and crosslinking of the polymer chains. While loss of the nitro group is a phenomenon which occurs in nitrate esters all the time, evidence from this investigation indicate that chain scission and crosslinking reactions could also be taking place at the same time, resulting in an increase and decrease in molecular weight.

PolyNIMMO was also found to degrade via UV radiation. The mechanisms for UV degradation proceeds via homolytic scission of the $O–NO_2$ bond, and scission of the polyether backbone. Surprisingly crosslinking only took place when the polyNIMMO was subjected to UV radiation at higher temperatures (i.e. 100°C).

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