EFFECTS OF GAMMA AND THERMAL NEUTRON RADIATION ON NITROCELLULOSE

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ABSTRACT

The effects of gamma and thermal neutron radiation on the nitrogen content of wet nitrocellulose using the SLOWPOKE-2 nuclear reactor were investigated. By irradiating the nitrocellulose, it was expected that its nitrogen content would be decreased following breakage of the chemical bonds between the NO_2 groups and the main cellulose structure since these bonds possess a relatively low bond energy. If the technique of irradiation appears to be effective for the above purpose, it may be possible to neutralize and convert the stocks of aged and unstable nitrocellulose explosives into commercially useful products.

Three stock solutions of commercial grade nitrocellulose were used: 12.11%N, 12.60%N and 13.11%N. These samples of about 1 g each contained in sealed polyethylene vials were irradiated for various times ranging from 2 to 24 hrs. In order to assess the extent of change in the nitrogen content, solutions of nitrocellulose samples in tetrahydrofuran were analysed using Gel Permeation Chromatography (GPC) and Fourier Transform Infrared Spectroscopy (FTIR). A decrease in molecular mass was observed from GPC results which indicated the possibility that breaking of nitro groups may have occurred together with some chain scission inside the cellulose backbone. New solutions of irradiated samples were scanned using FTIR. Two specific absorption bands of the nitro groups: one at 1660 cm^{-1} (primary group) and the second at 1270 cm^{-1} (secondary) were focussed for determining their respective fluctuations resulting from radiation doses. The results revealed a decrease in both absorption bands with the second band having larger decrease in concentration than the primary peak of nitro groups with radiation dose. The samples that originally had the highest percentage of nitrogen (13.11% N) decreased the most, and the samples that originally had the lowest nitrogen content (12.11% N) decreased the least. The longer the samples were irradiated, the more the nitrogen content decreased. This relatively large effect on the nitrogen content of nitrocellulose may be attributed to the very low chemical bond energy of the $-O-NO_2$ groups attached to the main structure of cellulose.

BACKGROUND ON NITROCELLULOSE IN MILITARY APPLICATIONS

Nitrocellulose or Cellulose Nitrate [1] is the oldest cellulose derivative obtained from cellulose, a natural polymer which is the main constituent of wood, through a chemical process called nitration using a mixture of strong acids such as nitric acid, sulfuric acid and phosphoric acid. Depending upon the extent of nitration, the total nitrogen content of the resulting nitrocellulose may theoretically vary up to 14.11%; however, this maximum value is practically very difficult to be reached because of the severe experimental synthesis conditions. Figure 1 illustrates the chemical structure of nitrocellulose resulting from the nitration of cellulose.

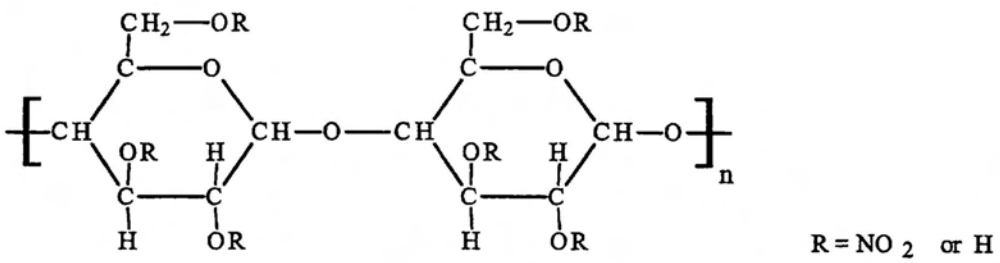

Figure 1. Nitrocellulose

Nitrocellulose of nitrogen content [2] between 12.6 and 13.2% is the base explosive compound used in the preparation of propellant systems currently in use in the Canadian Forces: for example, 105 mm tank rounds, naval rounds, mortar and small arms ammunition. The prime requirements of a propellant for service in the military show ballistic regularity and should be non-erosive, flashless, smokeless and stable. Propellants must be stable in storage and must not deteriorate so that they can be transported easily and stored without danger. Unfortunately, because of the polymeric nature of cellulose as well as the low energy of the chemical bond of the nitro groups, nitrocellulose of high nitrogen content becomes unstable with respect to high temperature, solar radiation, and long period of storage. This instability causes an important problem of sensitivity and security for the storage of nitrocellulose explosives. The rate of deterioration of nitrocellulose depends on its nature (mainly its nitrogen content), the temperature of storage and the ambient humidity. Chemical changes due to exothermic breakdown of the nitro groups could cause an autocatalytic reaction leading to spontaneous ignition. This dangerous situation fosters the need for periodic testing and eventual disposal. The present practice for disposal is to burn the deteriorated or obsolete propellants in a barren field. This presents a twofold problem: the first is the unsafe transportation of a potentially unstable explosive and the second is the release of noxious and toxic gases due to the nitrogen content.

Other methods of disposal include chemical and biological treatment. In chemical treatment: the explosive is mixed with a 10% solution of sodium hydroxide in a ratio of one to five. The resulting alkaline solution can be treated in a wastewater plant; however, the reaction may be inherently dangerous. In the Biological treatment, the nitrocellulose is mixed with a bulking agent (eg. straw and sawdust) at temperature between 45 and 60 °C where some enzymatic reactions occur to neutralize the nitro groups. This method is not recommended for materials of almost pure nitrocellulose, therefore, it is not viable for the disposal of nitrocellulose explosives.

In this work, it is proposed to irradiate nitrocellulose of relatively high nitrogen content wetted by water or isopropanol for different times in order to lower the nitrogen content by dissociating the chemical bonds involved in the nitro groups. The nitrogen content variation could then be monitored by infrared spectroscopy.

BACKGROUND ON THE POLYMER - RADIATION INTERACTION

The effects of radiation on polymers [3] depend strongly on the molecular structure, for instance the presence of tertiary or quaternary carbon as well as the presence of oxygen in the structure, the presence of additives and the radiation environment itself. When the radiation consists of electromagnetic photons (X-rays or gamma rays), the predominant mechanisms of interaction of the photons with the matter are the Compton, the photoelectric effects and the pair production. The consequences of these effects are essentially the ejection of free electrons from the atoms (primary ionization) and the secondary ionization of the surrounding molecules and atoms. The positive ions and the ejected electrons can then recombine to produce highly excited molecules which undergo decay to their respective ground states, usually with the emission of radiation. They may also release part of their energy through chemical reactions by heterolytic bond cleavage producing ions or by homolytic bond cleavage leading to the formation of free radicals. As a whole, the effects of radiation depend essentially on the type and cumulative dose of the incident radiation. The presence of hetero elements such as oxygen and nitrogen complicates these reactions further. After the formation of free radicals, polymerization is terminated by way of recombination to form a cross-link or chain scission. Both may occur simultaneously, but one is usually predominant, depending on the structure of the polymer.

In the case of nitrocellulose, according to its chemical structure (Figure 1), there is one chemical bond which is susceptible to be rapidly dissociated by electromagnetic radiation or ionizing radiation because of its relatively low bonding energy. That is the O-N bond which links a nitro group NO_2 with the main backbone of the cellulose structure. The energy of that bond [4] is 175 kJ mol^{-1} while those of other bonds such as C-C, C-O and C-H are 344, 350 and 415 kJ mol^{-1}, respectively. Therefore, by irradiating the nitrocellulose, it was proposed that the nitrogen content would be decreased by breaking the N-O bond, leading to a safer nitrocellulose grade which could be commercially useful.

METHODOLOGY

Materials. Three commercial grade nitrocellulose samples of nitrogen contents 12.11, 12.60 and 13.11%, respectively, were used in this work. They are powder form and wetted with about 25% in weight of water in order to prevent autoignition during the transportation, handling or storage.

Irradiation. About 1. g of a selected nitrocellulose sample (in the wetted state) was weighed into a cylindrical vial made in polyethylene and the vial was then sealed. Set of many vials was then introduced into the SLOWPOKE-2 reactor pool at RMC-CMR for a determined irradiation time. The irradiation periods ranged from 2 to 24 hours. The vials were thereafter removed from the reactor pool and permitted the determination of cool for many days.

Gel Permeation Chromatography (GPC). In order to determine the change in molecular weight of irradiated nitrocellulose, solutions of nitrocellulose (non-irradiated or irradiated) of 0.1% in weight in tetrahydrofuran were injected in a stainless steel column packed with styragel where the solvent flowrate was kept constant at 1 mL min^{-1}. The eluted solution was detected using a Refractive Index detector. The GPC system was previously calibrated using five different polystyrene standards whose molecular weights ranged from 17700 and 600 000. The GPC chromatogram of nitrocellulose together with the calibration curve allowed us to determine the number- average-molecular weight, M_n and the weight-average-molecular weight, M_w, of the nitrocellulose sample.

Nitrogen Content by Fourier Transform Infrared Spectroscopy (FTIR).

The nitrogen content of nitrocellulose is commonly[5] determined by a chemical method in which the nitrate ester is converted into an inorganic nitrate in an alkaline medium. Then, the ammonia formed is determined by titration with a strong acid standard. Alternatively, nitrocellulose is decomposed with concentrated sulfuric acid in the presence of mercury and an inert gas. Then, the nitric oxide formed is measured volumetrically. In 1973, a physical method[6] was proposed using an Infrared (IR) spectrometer for the determination of nitrogen content of raw nitrocellulose and of nitrocellulose in propellants. With this method, a calibration curve is drawn using the absorbance of the IR band at 1653 cm^{-1} as a function of nitrogen content. This calibration curve is then used to determine the nitrogen content of the unknown samples. This method requires between 30 and 300 mg of sample and it shows an accuracy of about 0.05% N.

Based on the above IR method, in this work, a FTIR spectrometer equipped with an automatic integrator was used to determine the N content of non-irradiated and irradiated nitrocellulose. The accuracy of this method can be of about 0.01% N. The calibration curve was established using solutions of the 12.60% N sample in tetrahydrofuran, with concentrations varying from 0 to 0.8% weight/volume. Two specific nitrate absorbance bands, eg. at 1660 and 1270 cm^{-1}, were investigated. Attention was put on preventing the loss of tetrahydrofuran through evaporation during measurements due to very high volatility.

RESULTS AND DISCUSSION

Molecular Weight from GPC. Using the calibration curve established from different polystyrene standards, the M_n and M_w values for non-irradiated and irradiated nitrocellulose samples were determined and presented in Table 1 as a function of the radiation exposure time. Between 2 and 4 h of irradiation, a slight increase in molecular weight is observed for all three nitrocellulose samples. This increase may be explained by the contribution of two opposed effects. First, the dissociation of the N-O bond in the nitrate groups had released different nitrogen oxide gases (NO_x) or pure N_2 and O_2 gases which reduced a little the total weight of nitrocellulose molecule. However, this bond breaking left a free electron at the O atom which might then recombine with an other radical to form a cross-link with a neighbouring molecule, resulting in an increase in molecular weight of the irradiated nitrocellulose. However, since the irradiated samples were still well dissolved in solvent, this suggested that the cross-linking extent, if it exists, is very limited. For longer periods of radiation exposure, it is believed that the nitro groups dissociation continued to increase, and at the same time, the chain scission of the backbone of the nitrocellulose molecule might have occurred through the breaking of the etheric bonds leaving shorter nitrocellulose molecules in the irradiated samples. This is supported by the continuing decrease in the molecular

weights with radiation times up to 24 h.

Table 1. Molecular Weight of Nitrocellulose (NC) from GPC

Exposure [hr]	NC (12.11% Nitrogen) M_n x 10^5	NC (12.11% Nitrogen) M_w x 10^5	NC (12.60% Nitrogen) M_n x 10^6	NC (12.60% Nitrogen) M_w x 10^6	NC (13.11% Nitrogen) M_n x 10^6	NC (13.11% Nitrogen) M_w x 10^6
0	2.64	3.78	1.84	2.74	1.84	2.34
2	2.75	4.11	1.52	2.32	1.73	2.69
4	2.61	3.80	2.08	3.12	2.01	2.95
8	2.41	3.61	1.84	2.72	1.70	2.50
16	2.48	3.85	1.70	2.73	1.51	2.47
24	2.05	3.33	1.32	2.16	1.34	2.35

Nitrogen Content of Irradiated Nitrocellulose from FTIR

As already mentioned in the Methodology Section, due to the high precision of the FTIR system combined with the careful preparation of the nitrocellulose solutions, the uncertainty in the N content determination is ± 0.01%, which is much better than that of previous methods. The determined N contents of irradiated samples are reported in Table 2 as a function of the radiation exposure time. It is found that after a short period of 2 h, all samples had a large extent of decrease in N content, and the change is proportional with the original N content of the sample. This is attributed to the fact that the greater the nitration extent the more unstable the nitro group is, this makes it easier to be removed from the cellulose molecule.

Table 2. Nitrogen content from FTIR (± 0.01%)

	Exposure time (hours)				
	2	4	8	16	24
NC (12.11% N)	11.79%	N/A	11.26%	11.30%	11.77%
NC (12.60% N)	9.15%	9.32%	8.74%	8.67%	7.33%
NC (13.11% N)	7.98%	8.02%	9.22%	11.31%	3.88%

In overall, the high efficiency of decreasing the N content by irradiation using the SLOWPOKE reactor with the estimated [7] dose rate of 2400 Gy h^{-1} (75% gamma and 25% thermal neutrons) is likely attributed to the low energy of the N-O bond constituting the nitrate groups of nitrocellulose molecule. Some secondary questions remain to be answered in this work, such as the relative importance of the neutrons versus that of the gammas in the nitrocellulose degradation process. Other refinements to the study would be in the analysis of the irradiated nitrocellulose samples using other techniques such as Nuclear Magnetic Resonance (NMR), permitting to confirm the change in chemical configuration of nitrocellulose resulting from irradiation.

CONCLUSION

This work has demonstrated that radiations are very efficient in degrading nitrocellulose molecules by reducing their N contents to values well below that of explosive grades. The work was carried, for obvious safety reasons,

with wetted samples, but the presence of oxygen in water or isopropanol molecule had a positive effect in accelerating the breaking of nitrate bonds [3]. The confidence in the results is high, as the error analysis indicates that the accuracy of detection of the N content by FTIR, using a modern instrument coupled to appropriate computer hardware and software, is better than ± 0.01% N.

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