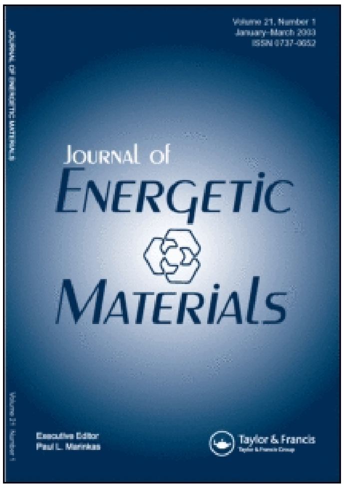

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S. Désilets[a]; F. Perreault[a]
[a] Defence Research Establishment Valcartier, Québec, Canada

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COMPARATIVE STUDY OF TWO METHODS USED FOR THE CHARACTERIZATION OF THE DEGRADATION OF THE POLYMER BINDER IN GAP-BASED PROPELLANTS

S. Désilets* and F. Perreault
Defence Research Establishment Valcartier
2459 Pie XI Blvd North
Val-Bélair, Québec, G3J 1X5
Canada

ABSTRACT

Reliability assessment for composite propellants calls for effective shelf-life predicting tools, implying the existence of appropriate accelerated-aging procedures and of quantitative methods for the characterization of the degradation process. Ideally, one would like to investigate stabilizer depletion as well as the mechanical integrity of the polymer network used as the binder. There are many available methods that can be combined to achieve this goal. In the present work, a comparative study of two of these methods has been performed. The first procedure makes use of FTIR spectroscopy to characterize the binder's degradation and of HPLC to follow stabilizer depletion. The other method, based on ^{1}H NMR spectroscopy allows the measurement of the polymer network degradation, the depletion of the stabilizer and the loss of

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plasticizer in a single step. Finally, the pros and cons of both procedures have been evaluated from the analysis of experimental data related to accelerated aging at 40, 60 and 80°C of GAP-based composite propellant formulations.

INTRODUCTION

Various methods have been proposed for the determination of propellant shelf-life. The most popular one is based on a stabilizer depletion technique[1,2], but other possible methods make use of heat generation and decrease of the mean molecular weight of the polymer[2], of gas evolution[3,4], or of the deterioration of the mechanical properties[5,6,7]. For composite propellants using a cross-linked polymer network as the binder, reliability is very dependent on mechanical integrity. In such a case, determining the extent of degradation of the polymeric binder appears to be a particularly good choice for aging studies.

Polyurethane networks are commonly used as the binder in propellant formulations. These insoluble, very high molecular weight cross-linked structures can not be easily characterized and indirect means of investigation are generally required. One possible way to monitor the binder's degradation is by measuring its soluble fraction. As a matter of fact, apart from the soluble fraction observed before aging which is a result of incomplete cross-linking, any extra soluble polymer appearing upon aging can only be the result of chain scission in the network. Precise determination of the increase in soluble fraction can therefore be related to binder degradation. As presented in recent work[8], the evolution of degradation as a function of aging time and temperature can be used for accelerated aging studies to predict the shelf-life of propellants.

Soluble fraction of the polymer binder can be quantified by different means. One popular method uses Fourier Transform Infrared Spectroscopy (FTIR) to measure the change in the transmittance of a characteristic band related to a functional group exclusive to the polymer binder[9]. In fact, any analytical method allowing the identification and quantification of the polymer chains present in the sol fraction could be used. For example, it should be possible to proceed through proton Nuclear Magnetic Resonance (^{1}H NMR) if the peaks associated with the polymer are well isolated in the spectra obtained for the extracted solutions.

This work presents the development of such a NMR method applied to the characterization of a propellant binder based on Glycidyl Azide Polymer (GAP). Accelerated aging behavior results obtained at three different temperatures for a typical propellant formulation are also used for a comparative evaluation of this new method against the more classical FTIR procedure, allowing the presentation of the pros and cons of the two methods investigated.

EXPERIMENTAL

Materials

The binder was based on a mixture of di and trifunctional GAP polymers purchased from Rocketdyne, California. A hydroxyl equivalent weight of 1210 g/eq. OH was determined for both these polymers by FTIR spectroscopy. A nominal 50/50 mixture of bis-(2,2-dinitropropyl) acetal/formal (BDNPA/F), obtained from Aerojet Ltd, was used as a plasticizer. Isophorone diisocyanate (IPDI) from Huels Corp. and N-100 from Bayer Canada were used as the isocyanates, while di-butyltin dilaureate (DBTDL) from Aldrich Chemicals was added as a cure catalyst. The oxidizer was ammonium nitrate (AN), phase stabilized with 3% wt of ZnO, purchased from Wickman. The stabilizer diphenylamine (DPA) was obtained from BDH Inc. Additives like Carbon Black from Cancarb Ltd, magnesium oxide (MgO) from Anachemia, Tepanol surface agent from 3M and boron carbide from Aldrich were also used. Dichloromethane (CH_2Cl_2) from Anachemia was the solvent used for the extractions.

Formulations

The binder was based on a mixture of di and trifunctional GAP cured by a mixture of IPDI and N-100. The system was plasticized at a plasticizer/polymer ratio of 2/1. The oxidizer consisted of 73% wt of phase-stabilized AN, and all formulations included 1% of DPA. Formulation 2969 contained no other additives, while 2970 included MgO and 2971 MgO and Tepanol, both of them accounting for less than 0.5% wt of the total formulation.

Sample preparation and aging

The ingredients were blended at 60°C, under dynamic vacuum in a 8CV Helicone Mixer from Atlantic Research. Moulded blocks were cured at 50°C until their hardness remained constant. The propellant blocks were cut into 6-mm thick slices before they were placed in sealed antistatic plastic bag at 40, 60 and 80°C for various periods of time for aging. An unaged sample of the propellant was also kept at room temperature for comparison. A detailed presentation of the aging schedules can be found in Table I.

TABLE I. - Aging Schedule at 40, 60 and 80°C.

Temperature(°C)	Aging periods (days)
40	14,28,56,84,112
60	14,28,56,84,112
80	7,14,28,56

Extraction procedure

Soxhlet extractions were performed with dichloromethane for 18 hours on finely cut pieces (of approximately 5 g) of the propellant mixtures. The extracted solutions were diluted to 100 ml for FTIR and HPLC analysis. Non-extracted material was dried and weighed to determine, by difference, the total amount of extracted material, as required for calculation of the extraction percentages of the components of interest. For NMR analysis, part of these solutions were evaporated under vacuum and the remaining material was dissolved in $CDCl_3$ and placed in 5 mm NMR tubes. Only DPA, BDNPA/F and free polymer chains (not attached to the binder network) were extractable from the propellants. The network itself can be swollen but not dissolved, and the solubility of the solid ingredients is very low in organic solvents. This particularity provides us with a convenient method to quantify the degradation of the binder. As a matter of fact, an increase in the extractable part of a propellant as compared to what is observed for non-aged samples indicates more labile polymer chains, most probably explained by the degradation of the polymer network.

FTIR-HPLC analytical method

Characterization of the propellant's aging behaviour by FTIR spectroscopy alone was not possible. A combination of two analytical methods was therefore required. While Fourier Transform Infrared Spectroscopy is used to quantify the cross-linked binder's degradation, a chromatographic procedure was necessary for the characterization of stabilizer depletion.

FTIR spectroscopy

The extracted solutions were analyzed using a Bomem spectrometer (Model M-110). A typical example of the spectra obtained for extracted solutions shows two major asymetric stretching bands observed at 2110 cm^{-1} and 1580 cm^{-1}, which can be assigned to the azide group of the GAP chains and to the nitro group of the BDNPA/F respectively. From such transmittance spectra, the GAP concentration in the solutions was determined using the intensity of the azide band at 2110 cm^{-1}. The samples analyzed in dichloromethane solution were compared to a calibration curve obtained from GAP solutions of known concentrations. The percentage of GAP extracted from the propellant mixture as a function of aging has been calculated from these measurements.

High Performance Liquid Chromatography (HPLC)

The concentration of stabilizer as a function of aging time was determined using High Performance Liquid Chromatography (HPLC). The experimental set-up used is composed of a model 590 Waters pump system, a CSC-spherisorb column (ODS 2, 5 μm) and a Hewlett Packard multiple wavelength detector (series 1050) at λ = 254 nm. Integration of the peak corresponding to diphenylamine (DPA) was performed on spectra of extracted solutions from aged propellant blocks. A 70/30 methanol-water mixture was used as the mobile phase with a 1.0 ml/min flow rate.

NMR analytical method

^{1}H NMR spectra of the extracted material (DPA, BDNPA/F, GAP) were acquired with a Bruker WP-200 spectrometer. For each sample, 400-1000 scans were made with a relaxation delay of 20 s between each acquisition. A typical ^{1}H NMR spectra for the extracted solutions is presented in Figure 1. Peaks of interest can be found between 3.2-3.8 ppm for the GAP, 1.3, 2.2, 4.3, 4.8 and 4.9 ppm for BDNPA/F and between 6.8-7.4 ppm for DPA stabilizer. Calculation of the percentage of GAP in mixtures were made by the integration of the representative peaks according to equation 1. For this calculation, the peak at 2.2 ppm was chosen for BDNPA/F, while peaks at 3.2-3.8 ppm and at 6.8-7.4 ppm were used for GAP and DPA respectively. The % of GAP extracted from the formulations was then deduced using equation 2 given that the total weight of the extractable material (see Extraction procedure) and the initial weight of GAP in the sample used for the extraction are known.

Equation 1

$$\%GAP = \frac{\left(\frac{I_{GAP}}{5} \times MW_{GAP}\right) \times 100}{\left(\frac{I_{GAP}}{5} \times MW_{GAP}\right) + \left(\frac{I_{BDNPAF}}{6} \times MW_{BDNPAF}\right) + \left(\frac{I_{DPA}}{10} \times MW_{DPA}\right)}$$

MW_{GAP} = Molecular weight of GAP (99.1)

MW_{BDNPAF} = Average molecular weight of BDNPA/F (319.2). From a mixture of 50% BDNPA (326.2) and 50% BDNPF (312.2)

MW_{DPA} = Molecular weight of DPA (169.2)

I_{Gap} = Area of the GAP peaks between 3.2-3.8 ppm

I_{BDNPAF} = Area of the BDNPA/F peak at 2.2 ppm

I_{DPA} = Area of DPA peaks between 6.8-7.4 ppm

Equation 2.

$$\%GAP_{extracted} = \frac{\%GAP(W_e)}{W_{Gap}}$$

%GAP = Percentage of GAP in the extracted mixture as determined by equation 1.

W_e = Weight of the extracted mixture (GAP + DPA + BDNPA/F)

W_{GAP} = Weight of GAP in the sample before the extraction (known from the formulation).

RESULTS AND DISCUSSION

The evolution of the extractable % of GAP polymer as a function of aging time at 80°C is presented in Figure 2 for various propellant formulations. As can be seen, both the NMR and FTIR methods show similar results and the discussion below applies to both cases.

This type of measurement can be readily used to characterize the degree of stability or the evolution of the degradation of the polymer network in composite propellants. Results obtained here demonstrate a small dependence of the degradation behavior over the composition of the propellant mixture at short aging times. Differences between formulations become evident at longer times only. After 56 days at 80°C, the stabilizing effect of MgO, and to a lesser extent that of Tepanol, can be readily observed. As a matter of fact, curve 2971, which is related to the formulation containing all three additives (DPA, MgO and Tepanol), shows the best resistance to degradation. Curve 2970, associated to the mixture containing DPA and MgO but no Tepanol, also shows acceptable stability while curve 2969 demonstrates that, after 56 days at 80°C, the polymer network is almost completely destroyed for the formulation containing only DPA.

FTIR and NMR techniques were also compared using results obtained at various aging temperatures, from 40°C to 80°C, for the most stable formulation containing DPA, MgO and Tepanol additives. As seen in Figure 3, the degradation behaviour shows a strong dependence upon aging temperature. Note here the different time scales used for results at 60 and 80°C. While a significant degradation can be seen after 56 days at 80°C, it takes more than 100 days to reach an extracted GAP percentage of 30% at 60°C and no significant degradation is observed after 112 days at 40°C. Slight differences observed in the FTIR and NMR results, especially at 60°C, could not be satisfactorily explained and were attributed to the experimental limits of both methods.

The depletion of DPA stabilizer was also measured by NMR and compared with the more classical HPLC technique. As shown in Figure 4, curves obtained from both methods are similar. It is interesting to note here that for the formulations investigated, no trace of any major nitro derivatives of DPA has been detected on the NMR spectra or HPLC chromatograms of the degraded propellants. Also, no signal of DPA or its derivatives linked to the polymer chain was observed by NMR spectroscopy. This suggests that the DPA depletion is a result of evaporation from the sample during aging and not of stabilizer consumption or reaction with the polymer. An alternative explanation might be that DPA is reacting with a propellant ingredient to give a charged compound and thus insoluble derivative. Even if both methods allow such an observation, characterization of the nitro derivatives can be more readily done using the HPLC technique for which even small quantities of a given chemical species can be isolated and analyzed qualitatively or quantitatively. As a matter of fact, stabilizer concentration is rather low in propellant formulations, around 1%, and as degradation proceeds, peaks corresponding to the various stabilizer in ^{1}H NMR spectra become difficult to distinguish from the noise. Also, peaks attributed to DPA derivatives will often overlap, rendering identification and analysis difficult.

The major advantage of the NMR technique is that it allows the characterization of all components of the extractable part of the propellants in a single operation. Given this, the BDNPA/F content upon degradation could be checked with this method, while extra measurements would have been necessary using the FTIR technique. In all cases investigated in this study, no significant change in the BDNPA/F content has been observed during the aging process.

CONCLUSIONS

In a single step, the NMR technique has allowed the measurement of the polymer network degradation, the depletion of the stabiliser, and the loss of plasticizer. The degradation curves were in agreement with combined results from FTIR and HPLC. Contrary to FTIR and HPLC, the NMR technique does not need calibration curves, and gives an evaluation of all the ingredients at the same time. Its only drawback is the impossibility to characterize small amounts of DPA and their various derivatives. When such data are required, use of the HPLC method is recommended to complete the analysis.

In the development of rocket propellants, NMR can be used to select the formulations with the highest potential for long shelf life. This technique could also be used as an indicator of the state of degradation of the polymer network in a given solid rocket propellant to assure its reliability.

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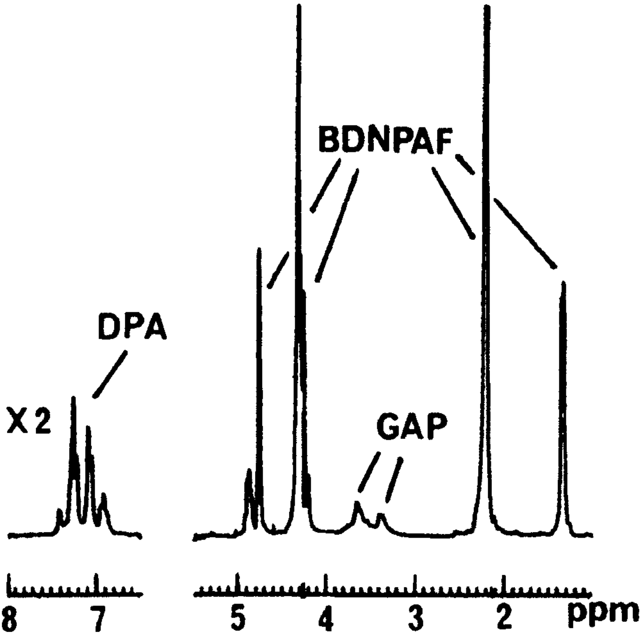

FIGURE 1 - ^1H NMR Spectra of an extracted propellant mixture

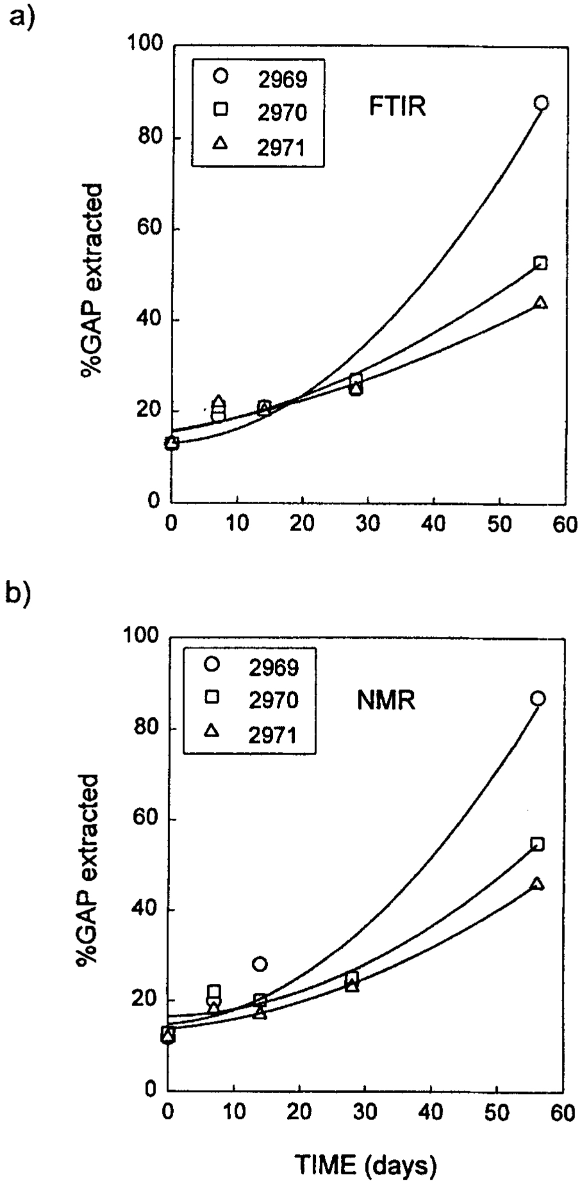

FIGURE 2 - Extractable fraction of the GAP polymer as a function of aging time at 80°C for formulations 2969, 2970 and 2971 as measured by a) FTIR and b) NMR method.

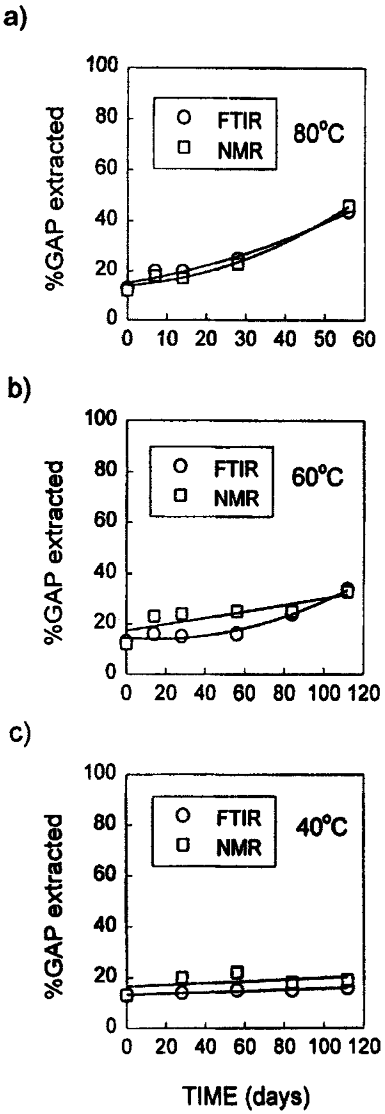

FIGURE 3 - Extractable fraction of the GAP polymer as a function of aging time at a) 80°C, b) 60°C and c) 40°C for formulation 2971 using both analytical methods.

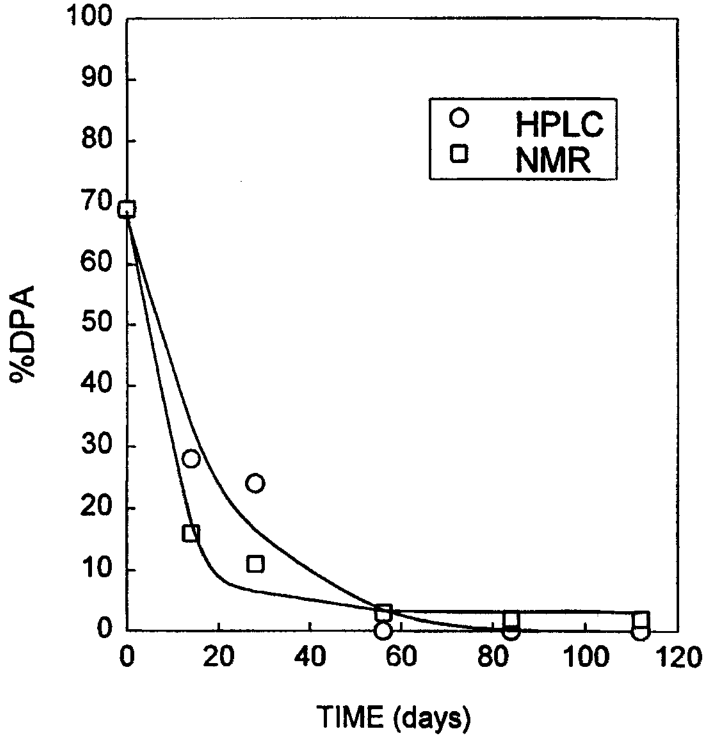

FIGURE 4 - DPA depletion as a function of aging time at 60°C for formulation 2971 as measured by HPLC and NMR methods.