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Synthesis and characterization of GAP/BAMO copolymers applied at high energetic composite propellants

Abstract: *The main objective of these studies was the synthesis and characterization of new energetic binders and their use in some propellant formulations. Following the working plan elaborated, the synthesis and characterization of the following compounds has been done successfully:*
- *GAP;*
- *energetic Monomer BAMO;*
- *energetic Binders;*
- *copolymer GAP/PolyBAMO.*

The scale up for the synthesis of copolymer GAP/PolyBAMO and PolyBAMO using GAP as initiator has been done and they were fully characterized by IR, (^{1}H, ^{13}C) NMR-spectroscopy, GPC, elemental analysis, OH-functionality, differential scanning calorimetry (DSC) and sensitivity tests (friction, impact). For this two scale up synthesis some propellant formulations were carried out and the results of mechanical and burning properties have been compared with GAP propellants.

Keywords: Energetic binders, PolyBAMO, Copolymer GAP/PolyBAMO, Propellants.

LIST OF SYMBOLS

ACE	Activated chain end
Al	Aluminium
AM	Activated monomer
AMMO	3-Azidomethyl-3-methyl oxetane
AP	Ammonium perchlorate
ARC	Accelerated rate calorimetry
BAM	Federal Institute for Materials Research and Testing in Germany (Bundesanstalt fuer Materialforschung und -pruefung)
BAMO	3,3-Bis-azidomethyl oxetane
BDNPF/A	Bisdinitropropylformal/acetal
BDO	Butanediol
BF_3O Et_2O	Boron trifluoride etherate
BF_3THF	Boron trifluoride tetrahydrofuran
BBrMO	Bisbromomethyl oxetane
BrMMO	3-Bromomethyl-3-methyl oxetane
BBrdiol	2,2-Bis(bromomethyl)-1,3-propanediol
BTTN	1,2,4-Butanetrioletrinitrate
CHN	Elemental analysis
CcGAP/PolyBAMO	Energetic copolymer from GAP and PolyBAMO
D	Polydispersity (dispersion broadness): Mw/Mn
DCM	Dichloromethane
DMA	Dimethylacetamide
DMF	Dimethylformamide
DMSO	Dimethylsulfoxide
DOA	Dioctyl adipate

DSC	Differential scanning calorimetry
D22	Dibutyltin dilaurate
ECH	Epichlorohydrin
GAP	Glycidylazidopolymer
GPC	Gel permeation chromatography
HDI	Hexamethylene diisocyanate
HMX	Ciclotetrametilene-tetranitramine
HTPB	Hydroxylterminated polybutadiene
IR	Infrared spectroscopy
Mw	Molecular weight (average weight)
Mn	Molecular weight (average number)
MP	Molecular weight at peak maximum
NaN3	Sodium azide
NCO	Isocyanate group
NMR	Nuclear magnetic resonance
N100	Isocyanate from Bayer Material Science – Desmodur® N-100
PECH	Polyepichlorohydrin
PolyAMMO	Polymer of 3-azidomethyl-3-methyl oxetane
PolyBAMO	Polymer of 3,3-bis-azidomethyl oxetane
PPG	Polypropyleneglycol
PS	Polystyrene
RDX	Cyclotrimetylenetrinitramine
SnCl4	Tin tetrachloride
TA	Themal analysis
TEOFF	Triethyl oxonium hexafluoro phosphate
TFBE	Trifluoride boron etherate
Tc	Critical temperature
THF	Tetrahydrofuran
Tg	Glass transition temperature
TG	Thermogravimetry
TLC	Tin layer chromatography
TMA	Thermomechanical analyzer
TMETN	Trimethylolethanetrinitrate
UV	Ultraviolet spectroscopy

INTRODUCTION

The use of energetic binders in formulation of cast-cured composite solid propellants has been presenting growing interest in the recent years. They are hydroxyl-terminated polyethers with azido or nitric groups polymers of low molecular weight that hold fuel and oxidizer compounds from the propellant. The OH groups from the propellant mixture react with the isocyanate groups forming a polyurethanic matrix that binds the solid propellant ingredients in a tough elastomeric three dimensional network structure capable of absorbing and dissipating energy.

In these new class of energetic binder, the polymer GAP showed to be very useful for high energetic rocket propellants (Provatas, 2000; Helmy, 1984). Together with energetic plasticizers, like nitrate esters, aliphatic nitro- and nitramine compounds, it offers high thermodynamic energy and performance with traditional oxidizers like ammonium perchlorate (Eisele, Zimdahl and Menke, 2002; Yoshio et al., 1994; Eishu and Yoshio, 1996), with nitramines (Menke and Eisele, 1997; Menke et al., 2002) and even with low energetic oxidizers, like ammonium nitrate (Menke, Böhnlein-Mauß and Schubert, 1996). Due to its positive heat of formation, good oxygen balance and high density, GAP opens the gate to high energetic composite propellants with much lower amount of solids and yet higher specific impulse and overall performance than traditional composite propellants based on AP/HTPB ingredients. With GAP, it is possible to formulate composite rocket propellants with higher energy, higher density and higher burning rates in connection to a significant reduced content of hydrogen chloride and chlorine in the exhaust. Consequently, it is pointing directly to high energetic chlorine reduced low pollution propellants for an eco-friendly environment. Due to its higher content of azido groups, PolyBAMO offers an enhanced kinetic and thermodynamic advantage for propellant application in comparison to GAP (Yoshio et al., 1994; Eishu and Yoshio, 1996). However, the high melting and glass transition point plus poor processability in comparison to GAP bring some disadvantages. Therefore, to overcome these drawbacks the copolymer GAP/PolyBAMO has been developed to produce a binder with similar properties, but higher energy content, which will be the binder of choice for the formulation of high energetic rocket propellants that will keep the advantages of AP/GAP formulations, and even improve their processability, glass transition points and mechanical properties. The objective of this study was to investigate the behavior of GAP/BAMO copolymers in propellant formulation with AP, AP/RDX 82 – 10, and a convenient energetic plasticizer, BDNPF/A, was chosen due to experiences with the AP/GAP propellants (Eisele, Zimdahl and Menke, 2002) and to keep a low mechanical and applicable sensitivity of the system.

The synthesis of the GAP/Poly BAMO binders was carried out by cationic copolymerization of epichlorohydrin and 3,3-bis(bromomethyl)oxetane (BBrMO), using butane-1,4-diol (BDO) as initiator and boron trifluoride etherate (BF_3OEt_2) as catalyst, followed by azidation with sodium azide and dimethylsulfoxide as solvent (DMSO). The polymerization can proceed by two different mechanisms: the activated monomer (AM) and the activated chain end (ACE).

AM mechanism involves successive additions of the protonated (activated) monomer to terminal hydroxyl groups of the initiator and after on the growing macromolecules (Elie, 1990).

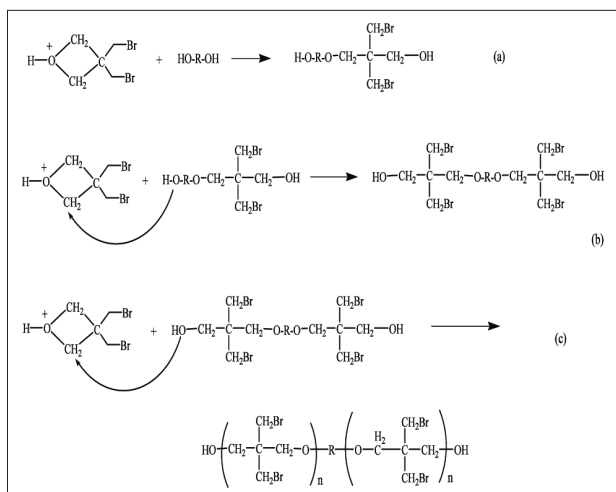Macromolecules growing by AM mechanism should have the structure shown in Fig. 1

Figure 1:   AM mechanism for polymerization of oxetane ring.

In the polymerization reactions that involve an ACE mechanism, a cationic oxonium ion is formed at the end of the chain and reacts with the incoming monomer molecules. The incoming molecules then acquire this cationic reactivity as they bond to the chain end to promote further chain growth (propagation). The polymerization proceeds in the presence of an initiator, present in a small quantity which is part of the propagation polymer chain (Kubisa et al., 2000).

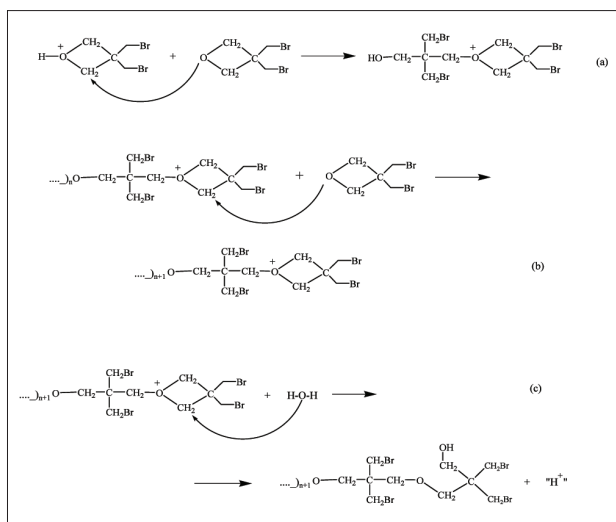Macromolecules growing by ACE mechanism should have the structure shown in Fig. 2.

Figure 2:   ACE mechanism for polymerization of oxetane ring.

The HO- groups are formed by reaction of the first protonated monomer molecule with an oxygen atom of another oxetane ring (a), while the tail groups are formed by deactivation of the cyclic tertiary oxonium ion. When the deactivating agent is water, the OH group is the end group of the final product.

EXPERIMENTAL

^{1}H-NMR, ^{13}C-NMR analysis were conducted on a 300 MHz Bruker MSL-300 spectrometer. The proton and carbon chemical shifts were recorded in ppm and calibrated on the solvents as internal standard. Infrared analyses were conducted on a Nicolet SX 5 spectrometer. Gel permeation chromatography was conducted on a water's gel permeation chromatography equipped with four ultrastyragel columns (100 Å, 500 Å, 1000 Å and 10000 Å), a refractive index detector and a Datamodule 730. THF was used as the mobile phase. The GPC was calibrated with a set of well characterized (i.e., M_n, M_w are well known) polystyrene and polypropylene standards (narrow standards), and thus the number average molecular weight (M_n) and weight average molecular weight (M_w) are reported relative to polystyrene and polypropylene. Differential scanning calorimetry (DSC) was carried out by a TA instrument Q 1000 using aluminium pans. Scans were carried out on each sample, at scan rates of 5°C/min, under argon flux, in the 40-450°C range. Thermogravimetric analysis (TGA) was performed by a TA Q500 apparatus, with a scan rate of 10°C/min, under nitrogen flux, in the 30-530°C range. OH group titration was carried out by standard ASTM procedure (Biedron, Kubisa and Penczek, 1991).

Solvents were purchased from Aldrich®, Fluka® or Merck & Co., Inc., according to the required purity, price and availability. DCM (Dichloromethane) was dried on P_2O_5 and distilled at atmospheric pressure (39°C); ECH (Epichlorohydrin) was dried on $MgSO_4$ and distilled at atmospheric pressure (116°C); BBrMO (3,3-bis (bromomethyl) oxetane) was distilled at 10 mmHg, 98°C; BDO (1,4 butanediol) was distilled at 7 mmHg, 103°C.

CoPolymerization ECH/BBrMO

A solution of butane-1,4-diol (1.8 g, 19.97 mmol) and $BF_3.Et_2O$ (5.76 g, 39.94 mmol) in anhydrous methylene chloride (300 mL) was stirred at 25°C for 2 hours under argon in a reaction calorimeter (RC1, Mettler–Toledo, Inc.). During this period of time, the first calibration of the heating measuring system was executed and the complex $BF_3.Et_2O$-BDO was formed. The reaction mixture was kept at 25°C and a solution of 3,3-bis-(bromomethyl) oxetane (60.55 g, 257.7 mmol) and epichlorohydrin (69.34 g, 749.4 mmol) in methylene chloride (300 mL) was added within a period of 2 hours with a controlled flow of 2.5 mL/min, and during this operation the heat of the reaction was measured. When the addition was complete, the reaction was left stirring for an additional hour for the second calibration of the reaction calorimeter system and then the reaction mixture was left standing overnight at room temperature. Solvent was evaporated

(vacuum/room temperature) and two times 150 mL of water were added and intensively mixed for quenching. Then the polymer was washed two times with 125 mL of a water/methanol 50/50 %vol mixture. Then it was dissolved in DCM, dried with magnesium sulphate, and the solvent was evaporated on a rotary evaporator; finally, it was dried under high vacuum at 70°C. The aspect of the material is a clear high viscous substance.

Analysis

GPC: number average molecular weight (M_n) 1134; weight average molecular weight (M_w) 1356; Polydispersity (Disp) 1.20; ^{1}H NMR (CDCl$_3$) δ 1.58-1.63 (m, 4H, BDO), 3.35-3.95 (m, overlapping protons from BBrMO and PECH); ^{13}C NMR (CDCl$_3$) δ 37.05 (Poly BBrMO, CH$_2$Br), 44.17 (PECH, CH$_2$Cl), 45.47 (Poly BBrMO), 68.85 (BDO), 69.64 (PECH), 70.06-73.42 (signals for CH and CH$_2$ of PECH and Poly BBrMO), 77.88 (Poly BBrMO), 79.44 (PECH).

The heat of reaction was 78 kJ/mol.

Azidation of CoPolymer ECH/BBrMO

CoPolymer ECH/BBrMO (126.7 g) was added to a round bottom flask with 500 mL of DMSO and heated to 120°C. To this mixture, sodium azide (119.1 g) was added and left stirring for 18 hours. Then it was cooled to room temperature and slowly added to 1.25 L of water with stirring and ice-water bath. The polymer was recovered, dissolved in about 100 mL of DCM and filtered to a clear solution free from sodium salts. The final purification was carried out by reprecipitation in pentane (450 mL). The recovered polymer was finally dried under high vacuum at 70°C to give a high viscous yellow and clear compound.

Analysis

GPC: number average molecular weight (M_n) 1383; weight average molecular weight (M_w) 1646; Polydispersity (Disp) 1.19; Equivalent Weight (titration) 1087, Hydroxyl functionality 1.27; ^{1}H NMR (CDCl$_3$) δ 1.59-1.63 (m, 4H, BDO), 3.15-3.90 (m, overlapping protons from BAMO and GAP); ^{13}C NMR (CDCl$_3$) δ 45.26 (BAMO), 50.76 (BDO), 51.71, 51.38 (BAMO and GAP), 68.91 (BDO), 69.79 (GAP), 70.65 (BAMO), 78.23 (GAP); IR(neat) 2873, 2089, 1445, 1277, 1103, 902; CHN. C, 36.96; H, 5.54; N, 43.32; Calc. C, 36.4; H, 5.04; N, 44.47.

DSC (on Peak): exothermic decomposition at 244.70°C (+2570 J/g).

Synthesis of monomer 3,3-bis (bromomethyl) oxetane (BBrMO)

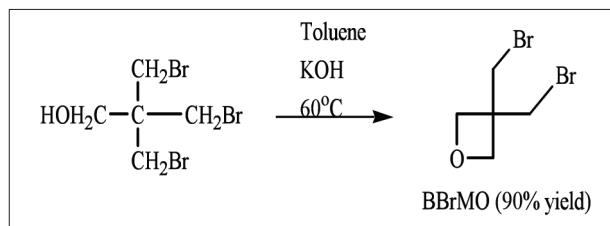3,3-bis(bromomethyl)oxetane (BBrMO) was synthesized as shown in Fig. 3.

Figure 3:   Synthesis of BBrMO.

The synthetic process started from the available tribromo-neopentyl alcohol supplied as free sample from the American Brom, Inc. of New York Company. However, we should emphasize that the compound is not easily ready available. Tribromo-neopentyl alcohol was then converted into the corresponding BBrMO in a reaction with toluene and potassium hydroxide in an improved method from one described in literature (US Patent 5,663,289, 1997; Bednarek, Kubisa and Penczek, 2001). The process previously described by other authors has always used tetrabutylammonium bromide as phase transfer catalyst for the synthesis. However, we could prove in our studies that the product can be obtained at a high purity (99%) and higher yield without the use of the catalyst. Since catalyst normally dictates the high cost of a chemical process, a significant reduction on the cost will be achieved with more environmentally friendly conditions.

Synthesis of copolymer GAP/Poly BAMO

As stated above, the synthesis of the GAP/Poly BAMO copolymer was performed by cationic polymerization of halogenated monomers using butane-1,4-diol as initiator and boron trifluoride etherate (BF$_3$OEt$_2$) as catalyst, followed by azidation with sodium azide in dimethylsulfoxide (DMSO) medium. The reaction steps are outlined in Fig. 4.

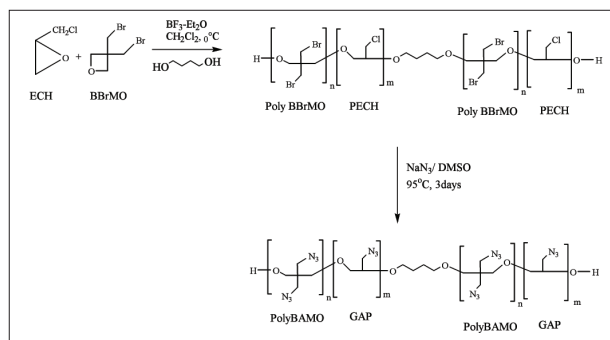Figure 4:   Synthesis of copolymer GAP/PolyBAMO. Butanediol has been used as initiator and therefore the copolymers should be difunctional.

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RESULTS AND DISCUSSION

Under the conditions described in the experimental part, the polymerization reaction is expected to proceed mainly by an activated monomer mechanism (AMM), involving successive additions of the protonated (activated) monomer to the terminal hydroxyl groups of the growing macromolecules (Kubisa et al., 2000; US Patent 5,663,289, 1997; Bednarek, Kubisa and Penczek, 2001). This polymerization produces polymers of narrow polydispersity since all the chains at the reaction mixture are expected to grow at approximately the same rate. However, in practice, the presence of cyclic oligomers during the polymerization process is unavoidable. These cyclic oligomers are undesirable compounds as they contain no functionality and therefore do not participate in the cross-linking step, and their low molecular weight may interfere in the desirable mechanical properties of the final product.

In order to favor the AMM mechanism and thus limit the appearance of these cyclic oligomers, it is very important to keep the monomer concentration as low as possible during the polymerization (USPatent 5,313,000; Kubisa and Penczek, 1999; Biedron, Kubisa and Penczek, 1991; Penczek, 1988). Therefore, all synthesis were performed by slowly dropping the ECH and BBrMO monomers mixture (two hours dropping time was the minimum that guaranteed very precise isothermal conditions during all the reaction time).

The ratio of the monomers was selected considering that the binder must be completely non-crystalline in order to be used in casting propellant formulations. Based on preliminary investigations, using different molar ratios of the halogenated monomers, all polymerizations were carried out with the following molar ratios: ECH/BBrMO = 75/25 (corresponding to a theoretical nitrogen content equal to 45.2% by weight); $(ECH+BBrMO)/BF_3OEt_2 = 25/1$ and $BF_3OEt_2/BDO = 2/1$.

However, the exact composition of the copolymer was determined by ^{13}C-NMR. The structure of the compound is shown in Fig. 5.
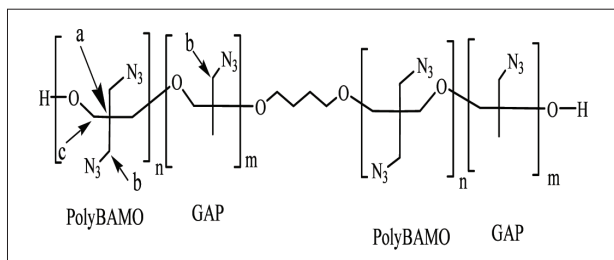

Figure 5:   Structure of copolymer GAP/PolyBAMO.

The IR spectra gave a first confirmation of the copolymer structure. In Figure 6, the spectra of the unreacted monomers mixture, of the halogenated copolymer and of the azido copolymers are reported. The comparison between the first two spectra shows that the C-O-C symmetrical stretching is shifted from 987 cm^{-1} to 1125 cm^{-1}, due to the opening of the heterocyclic rings of the monomers. The two peaks at 1277 and 2108 cm^{-1}, corresponding to the symmetrical and the asymmetrical stretching of N$_3$ groups, respectively, show the presence of the azido group in the third spectrum. The substitution of chlorine groups is confirmed by the complete disappearance of the CH$_2$Cl peak at 746 cm^{-1}, while the same cannot be done for bromine groups because the band at 605 cm^{-1}, corresponding to the C-Br bond, is not detectable even in the spectrum before azidation (Oliveira et al., 2006; 2007).
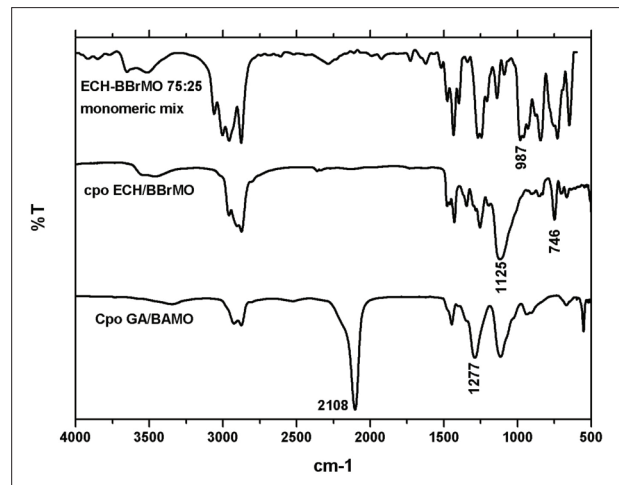

Figure 6:   Infrared spectra of ECH/BBrMO=75/25, molar ratio, mixture of un-reacted monomers, and of the corresponding copolymer before and after azidation.

However, the presence of bromine groups and their complete displacement after azidation has been confirmed by ^{13}C-NMR analysis (disappearance of the peak at 36 ppm from the spectra of the halogenated copolymers). The NMR analysis was used to determine the real composition of the synthesized copolymers.

The ^{13}C NMR spectrum is shown in Fig. 7. The signal at 44.3 is attributed to C quaternary (a) of polyBAMO unity. The signals that appear at 49.5-51.8 and 52.5-53.2 are attributed to CH$_2$N$_3$ of polyBAMO and GAP units (b). The intensities and integration of these carbon signals that are giving in Fig. 6 were a:b = 5.7:29.80. The ratio of CH$_2$N$_3$ is 2:1 PolyBAMO:GAP. According to this ratio, 5.7 of signal a was multiplied by 2 for PolyBAMO units and the difference to signal b was attributed to GAP units. Therefore, the molar ratio observed in ^{13}C NMR for GAP/

PolyBAMO was 62.4% GAP/29.8%PolyBAMO. This composition gives approximately 16% of PolyBAMO, higher than the initial planned one. Since PECH is more likely to form oligomers during polymerization reactions, this difference can be explained due to the partial consumption of ECH monomers to cyclic oligomers, which were partially removed during purification.

An attempt to use NMR technique to do end-group analysis has also been done. For this purpose, the hydroxyl end groups were converted into ester ones by reaction with acetyl chloride. Spectra of acetylated and non acetylated polymers are shown in Fig. 8.

The signals at 53.2-52.5 that correspond to CH_2N_3 were shifted upper field and overlapped with the other signals at 51.8-49.5. This shifting indicates that these CH_2N_3 groups are next to the $-(C=O)CH_3$ group introduced by the acetylation of the hydroxyl end groups. Because in GAP the CH_2N_3 groups at the end of the chains are in
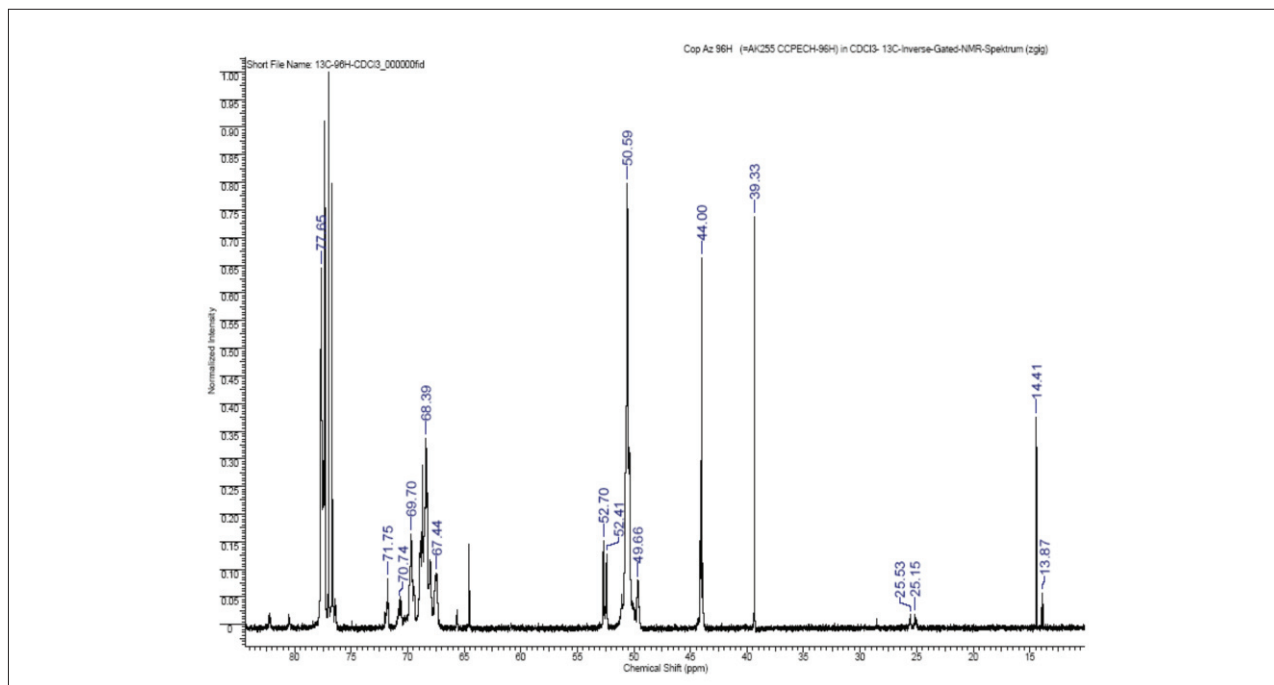

Figure 7: ^{13} C NMR for CcGAP.

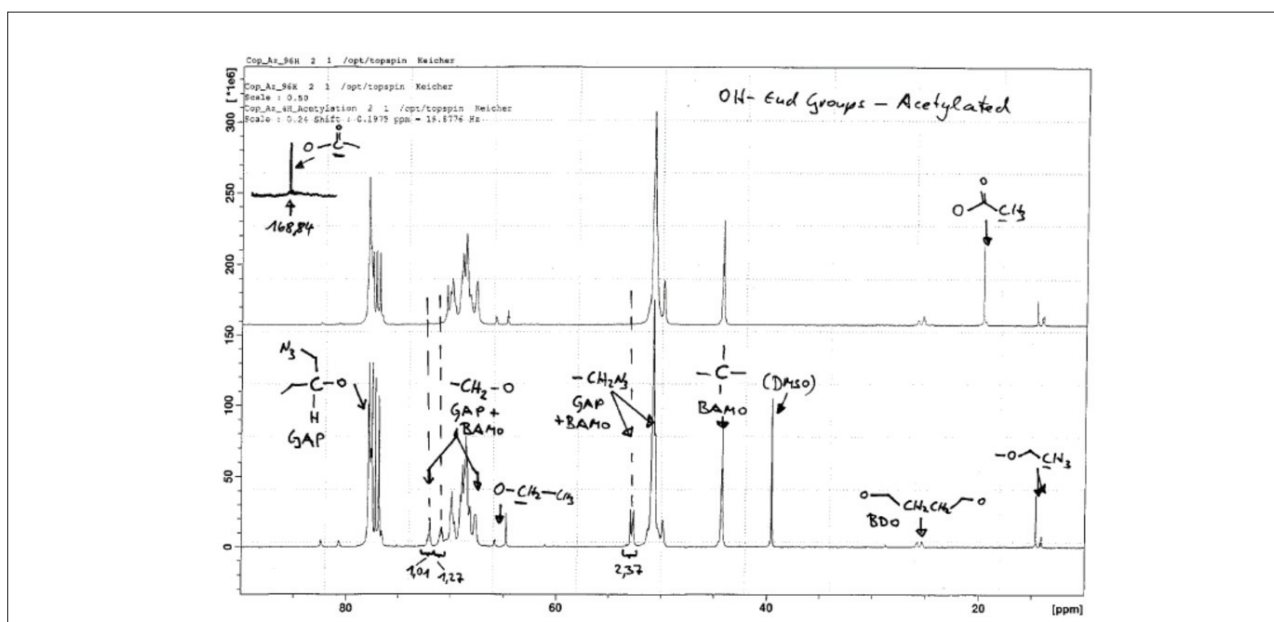Figure 8: ^{13} C spectra for Acetylated CcGAP.

β-position to the secondary hydroxyl groups, unlike BAMO, in which the CH_2N_3 groups are separated by one more CH_2-group, it is more likely that the shifted CH_2N_3 groups belong to GAP end units (Lieber et al.,1963).

The signals at 72.5-70.6 that correspond to CH_2O are also shifted upper field overlapping with the other signals at 70.6-67.4. This indicates that this terminal unit belongs to Poly-BAMO.

The signals at 26.4-25.1 are due to the CH_2 group in the $OCH_2CH_2CH_2CH_2O$ units, coming from butane-1,4-diol (BDO), used as initiator.

Considering that each sequence of macromolecule has one BDO and at least one or two OH terminal group, the intensity of the signals should be in the same proportion. However, the integration of the signals BDO: CH_2O: CH_2N_3 are: 0.66:3.17:3.30, which differs from the value expected from the AMM mechanism, which should lead to one BDO molecule per chain. Therefore, the presence of a mechanism of propagation alternative and contemporary to AMM must be hypothesized. This is reasonable, also considering that the chosen starting ratio BF_3OEt_2:BDO is 2:1 and a chain transfer reaction with unreacted ether groups of BF_3OEt_2, leading to O-CH_2CH_3 end-groups, may occur. This is compatible with the weak signals at 65.5-64.6 ppm and 14.4-13.9 ppm, assigned to O-CH_2CH_3 and O-CH_2CH_3, respectively.

From the spectrum of the acetylated copolymer, the amount of hydroxyl end groups and OCH_2CH_3 end groups is calculated from the integrals of the signals at 19.51 ppm O(C=O)CH_3 and signals at 14.40, 13.84 ppm OCH_2CH_3. Assuming that OH and OCH_2CH_3 are the only existing end groups in the copolymer, there are 74% of OH and 26% of OCH_2CH_3 end groups. The integral values of CH_2 from the initiator BDO at 25.63, 25.14 ppm give only 9.5% mol of BDO when it is compared with the integral values of the end groups (OH and OCH_2CH_3). This value for BDO is too small, which confirms again that some alternative mechanism can operate in this polymerisation.

The molecular weights of the copolymers were evaluated by GPC analysis and the hydroxyl terminal functionalities, responsible for the peak around 3400 cm^{-1} (Fig. 2), were measured by titration. The GPC is shown in Fig. 9. The curve is bimodal and the left peak, corresponding to lower molecular weights, should belong to cyclic oligomers, while the right one should belong to the linear chains. A deconvolution analysis of the curves leads to an estimated content of cyclic oligomers varying in the range of 6-11% by weight. Combining the GPC analysis and the OH group titration, the degree of functionality relative to the
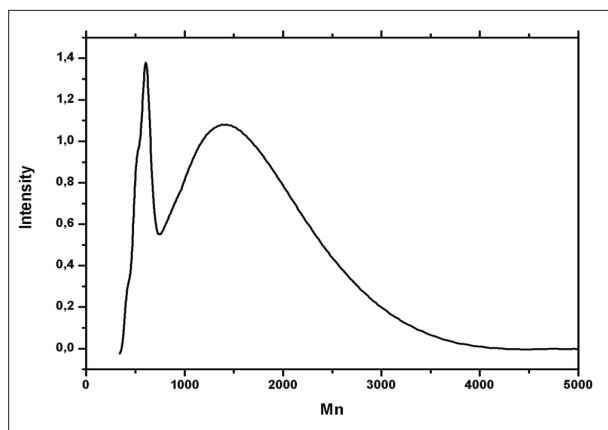

Figure 9:   GPC analysis of copolymer.

linear chains could be estimated. However, it should be emphasized that the GPC was calibrated with polystyrene standards (since a copolymer standard was not available) and this can lead to significant errors in the absolute values.

The low value of the polydispersity confirms that AMM, even if it is not the only mechanism involved, should be the prevailing one.

Since thermal decomposition of the propellant binders is a very important and crucial parameter for the combustion of the composite solid propellant, DSC and TGA analysis were performed for all the copolymers. At DSC, all the curves presented a main single exothermic peak between 244-245°C that can be associated to the decomposition of the azide groups to give nitrogen molecules. Considering that the same peak for GAP homopolymer corresponds to an energy release of 2240 J/g, the values obtained for the copolymers can be compared with those expected, based on the composition estimated with NMR.

In fact, the experimental values are a little bit higher but quite close to the expected ones. This small difference can be explained by the TGA (Fig. 10) that, in correspondence with the same phenomena, shows a sharp weight loss of around 40-45%, with respect to the total. Again, this value is higher than that corresponding to nitrogen release alone, but at those temperatures, the phenomenon is superposed to an incipient degradation of the polymer chains, as it can be seen from the TGA curve that after the sharp step does not level, but, instead, shows a gradual weight loss. In any case, both DSC and TGA confirm that the copolymers start to decompose/degrade at high temperatures, thus showing a satisfactory thermal stability.

The C, H, N analysis is in Table 1, which showed the nitrogen content of the copolymers in comparison with GAP.
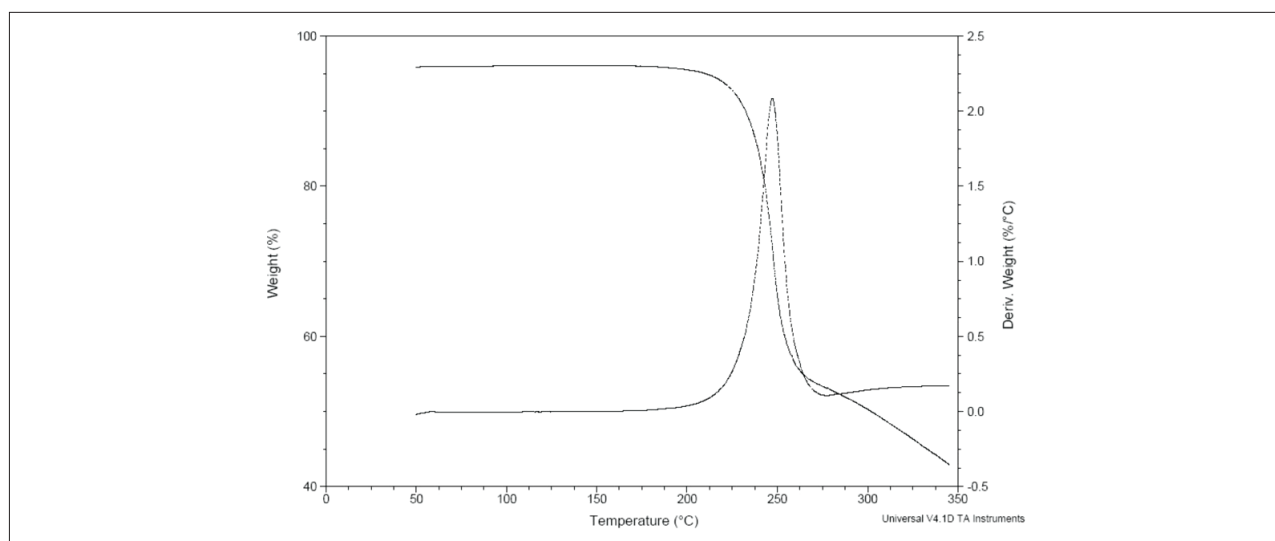
Figure 10: Thermogravimetric curve and its derivative vs temperature for the copolymer.

Table 1:   C, H, N content of the copolymers

Product	C	H	N
	%	%	%
GAP	34.72	4.93	38.51
Cc GAP/PolyBAMO	36.96	5.54	43.92

As it was wished and expected, the copolymers have higher energy content compared to GAP alone.

Test of the binder in propellant formulation

Several studies have been done over the past years to develop high energy binders to provide better performance than the common binder HTPB in the propellant formulations.

It is well known that GAP has been employed as an energetic binder as well as energetic plasticizer to increase the burn rate, specific impulse etc., in ammonium nitrate, nitramide, nitramine and perchlorate propellant systems due to its positive heat of formation and high density (ASTM E222-94). Another good advantage to be pointed is the eco-friendly environment, that leads to chlorine reduced low pollution propellants.

However, the use of GAP as an energetic binder or as plasticizer with HTPB has not been so successful, as it results in propellants with poor mechanical properties. The literature (Provatas, 2000) has reported that the critical temperature (Tc), at which the binder begins to loose its elastomeric properties under motor operations, is around -30°C, which is considered very high.

This temperature is lowered down by adding plasticizer, but this technique has some limitations as the mechanical properties required for rocket motor operations limit the maximum ratio of GAP:Plasticizer to 1:1.

Therefore, to overcome these problems energetic binders of copolymers of GAP and PolyBAMO has been suggested in this study. The higher energy content of GAP/PolyBAMO may contribute also to an enhanced performance of the resulting propellant.

The copolymer GAP/PolyBAMO has been initially synthesized, at Fraunhofer-Institut fur Chemische Technologie (ICT), in Germany, as part of the cooperation program between ICT and the Chemistry Division (AQI) of IAE (Space Aeronautical Institute). At ICT, this copolymer was tested in propellant formulation. The synthesis of the copolymer was repeated at the synthesis laboratory of Chemistry Division of IAE, and it was tested in a typical composite propellant formulation.

Test of the copolymer at the Fraunhofer-Institut fur Chemische Technologie (ICT)

The copolymer GAP/PolyBAMO -AK 264 was used for the propellant formulation at ICT and compared with the results obtained from the traditional HTPB composite propellant.

In principle, this new energetic binder will allow formulations of smokeless propellants with high specific impulse and comparatively low solid loading. Rocket propellant formulations with a specific impulse Isp $\geq$ 2450 Ns/kg at 1000 psi are possible with RDX/GAP/TMETN/BTTN ingredients.

Table 2 shows a standard AP/HTPB propellant formulation and also the properties of this propellant that can be used

Table 2: AP/HTPB Composite Propellant AP 1092 for comparison with AP/GAP/BAMO propellant

Ingredients	Density (g/cm³)	AP 1092
Solid loading		**86**%
AP 192 um mps	1.95	48%
AP 45 um mps	1.95	24%
AP 4,9 um with 0,7% Petro®	1.94	13%
Burning modifiers		
Iron-III-oxide 6 m²/g	5.24	0.7%
Zircon carbide 2 um	6.73	0.3
Plasticizer		
Diisooctyladipat DOA	0.925	3.5
Antioxidant		
Irganox 565	1.09	0.2
HTPB Prepolymer		
R 45 M eq = 1288	0.9	9.36
Bonding agent		
HX 878 eq = 200	1.1	0.16
Isocyanate		
IPDI eq = 111	1.05	0.78
Curing Catalyst		
Triphenylbismut TPB		200ppm
Properties		
Theoretical Density (ρ)		1.693g/cm³
Energetic solids		85ma%
Total solids volumetric		74.17% vol%
Total Binder		14ma%
Plasticizer p. o. B.		25.00ma%
R=NCO/OH		0.87eq
Specific Impulse (Isp)		2410Ns/kg
Specific Impulse (Isp)		245.7s
Volumetric Specific Impulse (Isp*ρ)		4080Ns/dm³
Characteristic Velocity C*		1498m/s
Temperatur of Combustion Tc		2916K
Kappa (Cp/Cv)		1.216
Casting viscosity EOM		136Pas
Friction sensitivity		48N
Impact sensitivity		10Nm
Flash temperature 20°/min		256°C
Dutch test 8-72 hours, 105°C		0%
Vacuum stability 40 hours/100°C		0.05mL/g
Max. tensile strength		1.02N/mm²
Elongation at break		25%
E-Modulus		8.97N/mm²
Burning rate (2MPa)		8.8mm/s
Burning rate (4MPa)		11.6mm/s
Burning rate (7MPa)		14.5mm/s
Burning rate (10MPa)		16.6mm/s
Burning rate (13MPa)		18.7mm/s
Burning rate (18MPa)		21.8mm/s
Burning rate (25MPa)		26.6mm/s
Calculated pressure exponent (2 to 25MPa)		0.43

for comparison with the new energetic binder ones that are proposed in this study. Thermodynamic properties were calculated for the expansion ratio of 70:1, the mechanical properties were experimentally obtained at 20°C and rate of 50 mm/min and the burning rates values were obtained at different pressure as indicated (p in MPa) Mechanical properties 20°C/50 mm/min.

With the energetic binder synthesized at ICT, three propellant formulations (GAP 03, 05b and 07) have been performed, and the composition, physical and mechanical properties were compared to equal formulations with GAP alone (GAP 02, 04a, 09 and 10), as shown in Table 3.

All three formulations with the new binder and GAP diol is endowed with a higher specific impulse than the AP/ HTPB propellant. The propellants have been targeted to a maximum of specific impulse, usually accompanied by an oxygen balance between $-5\% \leq O_2 \leq 0\%$. The maximum between 2450 Ns/kg $\leq$ Isp $\leq$ 2500 Ns/kg is reached for AP/GAP/BDNPF/A formulations between 70-75% energetic solids depending on the amount of plasticizer and the incorporation of nitramines like RDX and HMX. The addition of 10 - 15% of RDX gives a 1% higher Isp compared to the formulations without nitramine.

Processing and mechanical properties

Contrary to AP/HTPB propellants with 85% of energetic solids, the AP/GAP/PolyBAMO formulations are easier for casting and process. With about 50% of BDNPF/A plasticizer, the propellants GAP 03 and 05b with the new binder present excellent casting viscosity; even propellant GAP 07 with 76.6% of energetic solids and without plasticizer reflects good processing. The higher softness of the GAP/PolyBAMO propellants compared to those with pure GAP diol may have its reason from plasticizing parts within the new product. Further optimization on the ratio of curing agent and the amount of plasticizer will be necessary if the polymer binder is produced in a larger scale.

Similar results are obtained for the mechanical properties of AP/GAP and AP/GAP/PolyBAMO propellants. Further optimization and the addition of a suitable bonding agent appear to be necessary for both types of propellant formulations. The AP/GAP propellants should be equipped with a higher tensile strength, a better elongation and a reduced modulus.

Glass transition points

The glass transition points have been determined by DSC and TMA. Both values are outlined in Table 3. For

Table 3: AP/GAP/BAMO propellants in comparison to AP/GAP propellants

Ingredients	Density / Units	O₂ balance	Equivalent weight	GAP-02	GAP-03	GAP-04a	GAP-05b	GAP-07	GAP-09	GAP-10
	g/cm³	%	g	Mass (%)	Mass (%)	Mass (%)	Mass (%)	Mass (%)	Mass (%)	Mass (%)
AP 200 μm SNPE	1.95	34.04		40	40	42	42	43.2	43.6	42.4
AP 45 μm SNPE	1.95	34.04		20	20	21	21	21.6	21.8	21.2
AP 6,6 μm with 0,6%TCP	1.95	33.84		11	11			11.8	11.9	11.6
RDX 5 μm Dyno	1.816	-21.61				11.5	11.5			
GAP Diole (SNPE)	1.29	-118.26	1470	12.75	11.83	10.99	10.1	18.46	13.02	15.96
Gap/PolyBamo copolymer	1.29	-119.9	1021						1.78	2.19
N100	1.14	-200.58	192	1.75	2.67	1.51	2.4	4.34	7.4	6.05
BDNPF/A	1.39	-57.64		14	14	12.5	12.5			
Iron-III-oxide 240m²/g	5.24	10.02		0.5	0.5	0.5	0.5	0.6	0.5	0.6
Iron-III-oxide 6m²/g	5.24	10.02								
Zirconcarbide	6.73	-61.99								
Carbon	1.85	-266.41								
D22	drops			5	5	5	5	5	5	5
Total				100	100	100	100	100	100	100
Theoretical Density	g/cm³			1.724	1.721	1.737	1.734	1.739	1.749	1.744
O₂ balance propellant	%			-2.46	-3.41	-4.22	-5.12	-4.73	-3.49	-1.12
Total solids	mass (%)			71.5	71.5	75	75	77.2	77.8	75.8
R=NCO/OH value				1.05	1.20	1.05	1.26	1.25	1.05	1.05
Plasticizer in binder	%			49.12%	49.12%	50.00%	50.00%	0.00%	33.33%	25.00%
Properties	**Units**									
Specific Impulse	Ns/kg			2482	2478	2503	2499	2469	2504	2479
Specific Impulse	s			253.1	252.6	255,1	254.7	251.7	255.2	252.7
Volumetric Specific Impulse	Ns/dm³			4280	4266	4348	4334	4293	4380	4325
Characteristic Velocity C*	m/s			1496	1498	1512	1514	1503	1511	1490
Tc Combustion	K			3068	3067.5	3112	3108.8	3059	3110.5	3055.5
Viscosity before curing	Pas			72	48	96	72	408	224	186
Viscosity EOM	Pas			64	44	76	56	248	152	160
Surface Hardness	Shore A			60	20	53	20-25	65	70	78
Max. tensile strength	N/mm²			0,41	0,26	0,36	0,21	0.68	0.56	0.73
Elongation at max. tensile strength	%			7,8	24,4	13,1	37,4	12.8	7.6	4.8
Elongation at break	%			10,3	26,8	18,3	44,4	15.4	12.2	6.6
E-modulus	N/mm²			7,42	1,61	5,44	0,9	8.17	14.57	23.39
Tg (DSC)	°C			-48,3	-50,4		-50,5	-40,9	-44.4	-43.3
Tg (TMA)	°C			-49,85	-50,7		-51	-40.7	-43.8	
Impact sensitivity	Nm			6	5	5	5	5	5	5
Friction sensitivity	Nm			30	30	20	30	32	32	48
Chemical stability										
Ignition temperature 20°C/min	°C			212	213	208	209	200	207	206
Dutch test 8-72hours/105°C	% weight loss			0,17	0,14	0,16	0,15	0.14	0.14	0.22
Vacuum Stability 40hours/100°C	mL/g			0,3	0,29	0,34	0,31	0.36	0.3	0.3

formulations with equal amounts of plasticizer like GAP 03 and GAP 05b, the AP/GAP/PolyBAMO propellants with GAP/PolyBAMO copolymer (Tg = -50°C) show a clear advantage over those of AP/GAP formulations like GAP 02 (Tg = -48°C). As shown in Figs. 11 and 12, the copolymer GAP/PolyBAMO with -54.3°C already shows a lower glass transition point than GAP diol – here it is GAP OP 2A 653 from SNPE with -49.3°C.

Chemical stability and sensitivity

Although the values of Dutch test, vacuum stability and deflagration point represent only the results of short term tests; the chemical stability of both AP/GAP and

AP/GAP/PolyBAMO propellants appear convenient and quite sufficient for practical purpose. The limits for the Dutch test are 2% of mass loss within 8 - 72 h heating at 105°C and the limits for vacuum stability are 1.2 mL/g gas evolution within 40 hours heating at 100°C. Both terms have been fulfilled within a good margin.

Sensitivity values have been determined only by impact and friction sensitivity, as it was outlined above for the monomers and copolymers. The determined reaction limits of Friction Test (BAM) hammer and friction apparatus are within a convenient scope for application if they are compared to those of AP/HTPB rocket propellants, which were determined by the same operator.
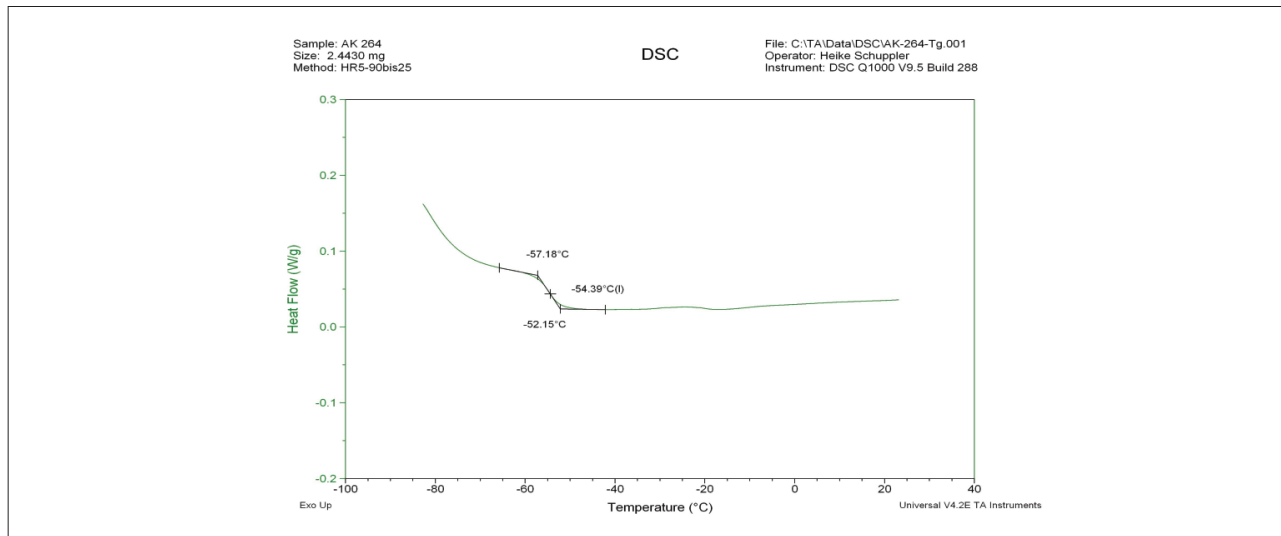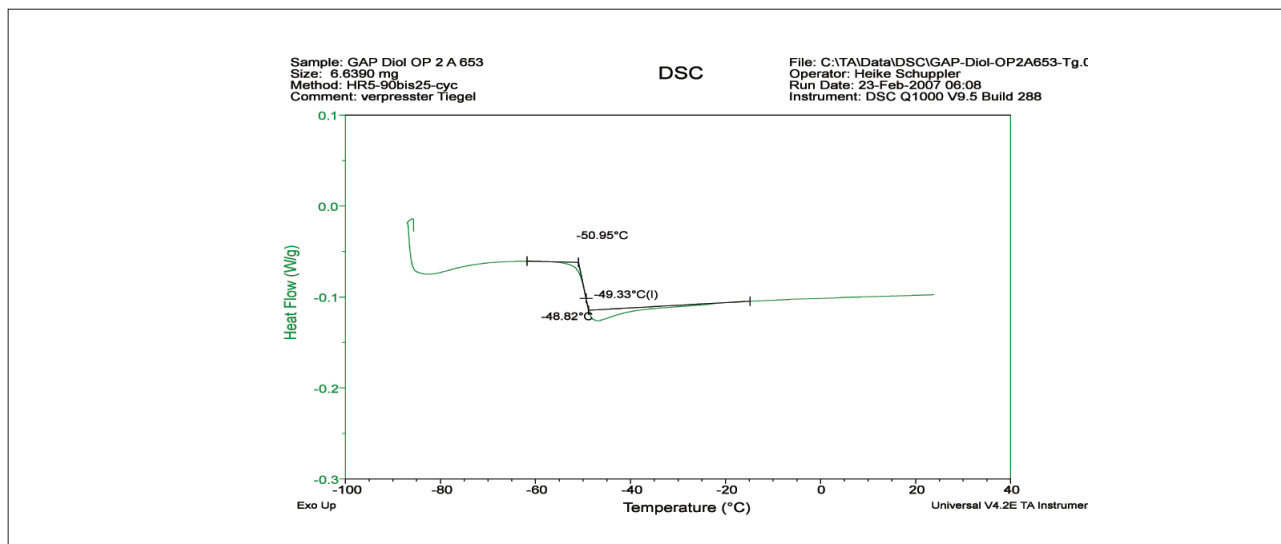

Figure 11: Glass transition of GAP/PolyBAMO copolymer.

Figure 12: Glass transition of GAP diol OP2A 653.

Burning behaviour

The burning behaviour was determined by Crawford Bomb tests. Burning rates were determined on coated propellant strands with 5 mm x 5 mm cross section and 50 mm measuring distance.

The burning rate was calculated using the expression (Eq.1):

$$r = Ap^n \quad \text{or} \quad \ln r = n \ln p + \ln A \tag{1}$$

Where p is the pressure, n is the pressure exponent and A is the burn rate constant (for propellants with n ≤ 1 and explosives with n ≤ 1). Practicable values for rocket propellants are n ≤ 0.6, and the more convenient values for TMP propellants are n ≤ 0.5. The values for AP/HTPB composite propellants are usually in the range between 0.3 ≤ n ≤ 0.5.

The burning behaviour of the reference AP/HTPB propellant formulation AP 1092 is presented in Fig. 13.
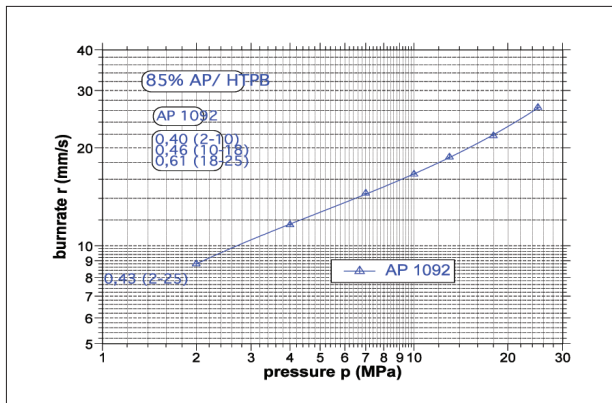

Figure 13: Burn rate versus pressure diagram for AP 1092.

The burning behaviour of the propellant formulations for GAP/PolyBAMO copolymer, comparatively with GAP, accordingly with the formulations from Table 3, is graphically presented in Figs. 14 to 18. Burn rates and pressure exponents are outlined in Table 4.

Propellants with 11 - 12% RDX 5μ like GAP 04a, 05b and 09 clearly differ in burn rates with 16 - 19 mm/s at 10 MPa compared to propellants with AP 6 μ like GAP 02, 03, 07 and 10 with 23 to 31 mm/s at 10 MPa. An increase of burn rates at lower pressures is also observed for propellants with reduced amount of plasticizer BDNPF/A. The azido polymer GAP and GAP/PolyBAMO favour burn rate increase and overall performance of the formulation compared to traditional AP/HTPB propellants. Propellants with GAP/ PolyBAMO copolymer, GAP 03 and 07 are endowed
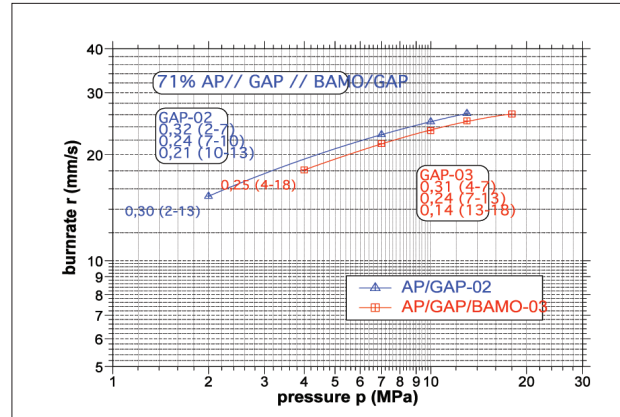

Figure 14: Burning behaviour of the AP/GAP propellant GAP-Com-02 and the AP/GAP/PolyBAMO propellant GAP-Com-03.
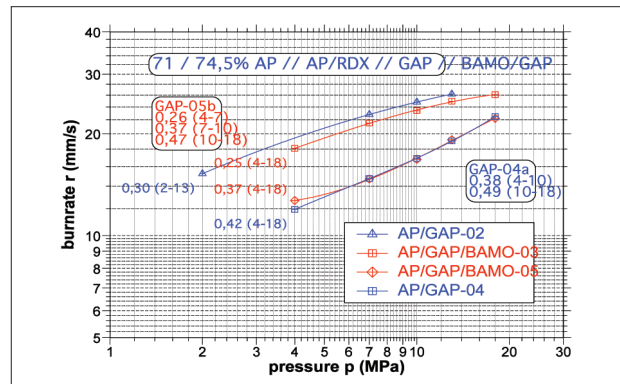

Figure 15: Burning behaviour of the AP/GAP and AP/GAP/ PolyBAMO propellant 02 and 03 in comparison to the AP/RDX/GAP and AP/RDX/GAP/BAMO propellants 04a and 05b.
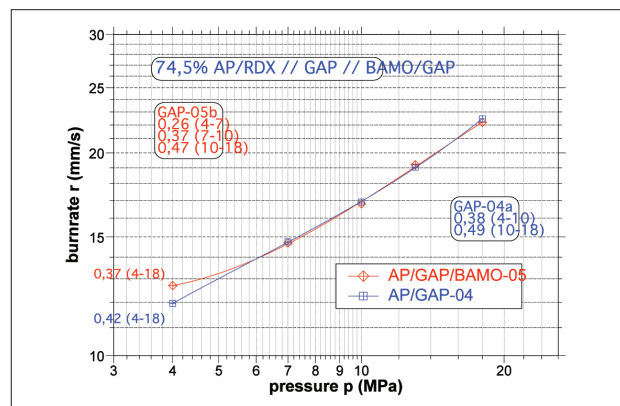

Figure 16: Burning behaviour of the AP/RDX/GAP propellant GAP 04a and the AP/RDX/GAP/BAMO propellant with Gap/PolyBamo copolymer: GAP 05b.

with a beneficial reduction of pressure exponents. A slight advantage in pressure exponents can be observed for the AP 6 μ in comparison to those with RDX 5 μ. Nevertheless, all propellant formulations exhibit quite
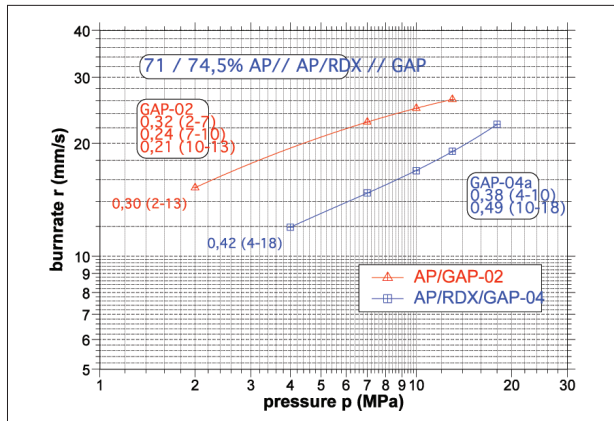
Figure 17: Burning behaviour of the AP/GAP propellant GAP 02 in comparison to the AP/RDX/GAP propellant GAP 04a.
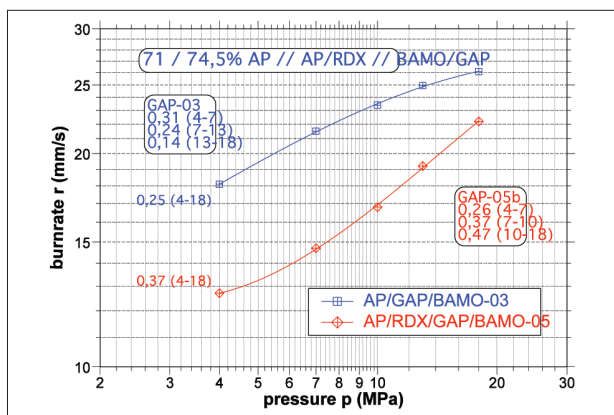

Figure 18: Burning behaviour of the AP/GAP/BAMO propellant GAP 03 in comparison with AP/RDX/GAP/PolyBAMO propellant GAP 05b.

convenient burning behaviour, which may be brought to good use in rocket motor applications. Figures 14 to 18 refer to the burning behaviour of composite propellants using AP and GAP/PolyBAMO copolymer (mixtures of AP/GAP/BDNPFA and AP/GAP/PolyBAMO/BDNPF/A), determined by Crawford measurements at 23 - 24°C.

Test of the copolymer at the Chemistry Division of IAE

The synthesis of the copolymer GAP/PolyBAMO was reproduced at the Synthesis Laboratory and then tested in a typical formulation of composite propellant at the Propellant Research Laboratory of Chemistry Division.

Curing test of the copolymer

Before the use in propellant formulation, the copolymer was submitted to a curing test, using a tri-functional isocyanate (Desmodur® N 100, Bayer Material Science), the same one that has been used at ICT. For comparison reasons, curing tests with N100 were also done with the pre-polymers HTPB and GAP. Dibutyltin dilaurate (DBTDL - D22) was used as catalyst for all three curing reactions, the same catalyst used in the tests at ICT (as it can be seen at Table 4). Two drops of the catalyst were used for each 5 g of the pre-polymer.

Initially, in the tests, a NCO/OH ratio of 1:1 for all the three pre-polymers was used, and the curing agent was

Table 4:   Burning rates and pressure exponents of propellant formulations for Gap/PolyBAMO copolymer comparatively with GAP

Burning rate	Units	GAP-02	GAP-03	GAP-04a	GAP-05b	GAP-07	GAP-09	GAP-10
Burning rate (2MPa)	mm/s	15.2						
Burning rate (4MPa)	mm/s		18.13	11.95	12.15	23.9	13.9	23
Burning rate (7MPa)	mm/s	22.8	21.5	14.75	14.62	27	16.8	27.8
Burning rate (10MPa)	mm/s	24.75	23.4	16.9	16.81	29	19	31.5
Burning rate (13MPa)	mm/s	26.2	24.95	19.05	19.22	30.5	21.7	32.5
Burning rate (18MPa)	mm/s		26.1	22.47	22.18	34	26	33.8
Pressure exponents								
n1		0.32 (2-7)	0.31 (4-7)	0.38 (4-10)	0.35 (4-7)	0.22 (4-7)	0.34 (4-7)	0.34 (4-10)
n2		0.24 (7-10)	0.24 (7-13)	0.49 (10-18)	0.37 (7-10)	0.20 (7-13)	0.53 (7-18)	0.12 (10-18)
n3		0.21 (10-13)	0.14 (13-18)		0.47 (10-18)	0.33 (13-18)		
n average		0.30 (2-13)	0.25 (4-18)	0.42 (4-18)	0.40 (4-18)	0.23 (4-18)	0.41 (4-18)	0.26 (4-18)

adjusted according to the OH equivalent of each pre-polymer. After heating at 60°C for 24 hours, it was observed the curing of HTPB and the GAP pre-polymers with a hardness of 42 Shore A. However, the mixture containing the copolymers GAP/PolyBAMO resulted in a softer stick polymer. Therefore, as an attempted to solve the problem, a value of 1.55 for the ratio of NCO/OH was used, which is the same used at the formulations tests at ICT (Table 4). As a result, it was possible to increase the hardness of the polymer; however, still with lower value than the ones for HTPB and GAP. Nevertheless, it was the value used for testing GAP/PolyBAMO copolymer in propellant formulation.

Test of GAP/PolyBAMO copolymer in propellant formulation

The propellant formulation at the Chemistry Division of IAE using GAP/PolyBAMO copolymer was carried out based on the results obtained in ICT (Table 4). Due to the small amount of copolymer available for the test, only 1 kg of propellant was processed, which is presented in Table 5. Since some components like RDX and AP 6 μm were not available in internal market, they were excluded from the formulation. The energetic plasticizer, BDNPF/A, was replaced by DOA, and AP 200 μm was replaced by AP 400 μm. However, the percentage of solids (77.5%) for the propellant formulation was the same as the one used in ICT.

Table 5: Composite propellant formulation containing GAP/Poly BAMO tested at AQI/IAE

Component	%	Mass (g)
GAP/Poly BAMO	14.56	145.6
DOA	4.5	45.0
Fe_2O_3	0.5	5.0
AP 400 μm	54.0	540.0
AP 30 μm	23.0	230.0
N 100	3.44	34.4
DBTDL	-----	40 drops

For safety reasons, the propellant formulation was processed using a helicone mixer (one gallon) located at the explosive pilot plant of Defense System Division – Explosive department (ASC-XPQ) at IAE. Then, the mixture was loaded in 2 moulds measuring 125 x 125 x 10 mm, and left curing at 60°C for 192 hours. During the processing, the mixture had an aspect of low viscosity before the addition of the curing agent, but it was not possible to measure precisely the value of it, due to the small amount of available propellant. After the addition of the curing agent, the substances were mixed for 10 minutes and loaded into the moulds. During the loading, the viscosity rapidly increased, which brought difficulty to finish the operation. This behavior was attributed to the excess of DBTDL (curing catalyst) that was used. Therefore, for future formulations, it is recommended the use of lower quantity of catalyst in order to extend the pot life of the mixture.

The propellant was cured at 60°C for 192 hours. The measured hardness was 45 Shore A and it is an intermediate value between the ones obtained at ICT: 20 Shore A for formulations containing BDNPF/A, and 65 Shore A for formulations without plasticizer.

The mechanical properties of the propellant samples were measured at the Mechanical Properties Laboratory (PPM) of the Chemistry Division. Stress and strength properties were measured and gave a value of 0.2 MPa and 10% of elongation. Despite being low values, they are similar to the results obtained in some formulations that were carried out at ICT, especially the ones containing BDNPF/A (Table 4). The fragility of the propellant observed in the test performed at AQI can be attributed mainly due to the presence of bubbles in the propellant. This bubbles appeared for technical reason since it was not possible to cast the propellant under vacuum. Nevertheless, both values – one from AQI and other from ICT – are low, which shows a propellant with fragile mechanical properties for being used in rockets, especially the big sized ones. Klaus Menke, phD, from ICT (Eisele, Zimdahl and Menke, 2002), has already mentioned that the low values can also be due to the mono functional molecules which might be present at the copolymer that can disturb the cross linking process of the polymeric matrix, which is in agreement with the results obtained in the curing tests of the copolymer (item Curing test of the copolymer). Klaus Menke also suggested that the mechanical properties of the propellant can be improved by a previous reaction of the copolymer with an excess of diisocyanate (for example, HDI), which leads to a new copolymer with isocyanate terminal groups. Another alternative to improve the mechanical properties of the propellant could be executed with the use of a bonding agent that is regularly used in HTPB propellant formulation.

The propellant processed at AQI was also tested in burning rate at Crawford Bomb and have presented values around 20 mm/s, which are similar to the ones obtained at ICT. However, under the narrow range of pressure in which the samples were tested (4 to 6 MPa), the value of the exponent of the pressure (n) is very low (close to zero). Some formulations tested at ICT also presented low values of n (0.12 to 0.20), with an increase on the

values of pressure. The low values of n can be considered an advantage in some specific propellant formulation. However, this burning behavior with low value of n should be better evaluated in future work, especially using a wider range of pressure.

CONCLUSIONS

Random copolymers of GAP/PolyBAMO with nominal composition 75/25 were synthesized to produce a material which has been tested as energetic binder in some formulations of solid rocket propellant. The synthetic route started with the synthesis of the halogenated polymeric precursor and then by its azidation. The introduction of PolyBAMO units in the GAP chain has the advantage of an increase in the azide groups and, consequently, in the energetic content of the material, but with a limited value that preserves the amorphous morphology of the polymer. The operating conditions and the catalytic system were chosen in order to favour a living character of the polymerization and the formation of hydroxyl-terminated chains. However, the characterization of the final product showed that the addition of monomeric units followed also some alternative ways which led to the formation of cyclic oligomers, of non-hydroxylic end groups and to a not very small polydispersity index. Although the measurements of GPC has been done without an appropriate standard, the calculated average number of OH groups for each chain resulted coherent with the value estimated from NMR analysis. The preliminary curing tests showed a promising elastomeric rubber with very good mechanical properties. Samples of the copolymer have been tested at ICT (Germany) and at the Chemistry Division of IAE, and a comparative analysis has been carried out. The first results showed that the copolymer has good potential to be used as binder in propellant formulations, which will lead to a propellant with high specific impulse. However, lots of work still need to be done till a specific propellant formulation containing the new energetic copolymer be ready for use in reality at a flying rocket motor.

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