Comparative Assessment of Stabilised Polybutadiene Binder under Accelerated Ageing

Luiz Felipe Cannaval Sbegue[1], Luciene Dias Villar[2]

ABSTRACT: Polybutadiene elastomers are versatile materials, being employed at several applications from rocket propellant binder to adhesives and sealants. The elastomers derived from hydroxyl-terminated polybutadiene are usually stabilised with antioxidants to prevent degradation. In this study, a comparative assessment among 2,2'-methylene-bis (4-methyl-6-*tert*-butylphenol) (AO2246), 2,6-di-*tert*-butyl-4-methylphenol (BHT), *p*-phenylenediamine (*p*PDA), and triphenylphosphine (TPP) regarding stabilisation of hydroxyl-terminated polybutadiene binder under accelerated ageing (six months at 65 °C) was carried out. Evaluation of antioxidants effectiveness was examined through Oxidation Induction Time, sol/gel extraction, swelling and mechanical testing, dynamic mechanical analysis, and mass variation measurement. AO2246 yielded the best performance, meanwhile BHT was poorly protective. TPP acted as prooxidant, causing a severe degradation of the binder, and *p*PDA was not manageable to be assessed due to the lower curing degree of the resulted polyurethane.

KEYWORDS: Ageing, Antioxidant, HTPB propellants, Stabilisers.

INTRODUCTION

Despite the ongoing trend into development of energetic polymeric materials, hydroxyl-terminated polybutadiene (HTPB) elastomers are still widely used as polymeric binders for solid rocket propulsion due to the excellent mechanical properties they provide. Moreover, polyurethanes based on HTPB are commonly used as coatings, adhesives and sealants (Gupta and Adhikari 2003), which does make studies about stabilisation of HTPB elastomers of broad interest. In fact, HTPB sensitivity to oxidation through the olefinic double bonds is well known (Coquillat *et al.* 2007a, 2007b, 2007c), thus rendering a need for using stabilisers, namely antioxidants (AO), to trap the radical species and to avoid an undesired crosslinking (Désilets and Côté 2000).

In general, AO are classified as primary or secondary, depending upon their mechanisms of action. Primary AO act as H-atoms donators to free-radicals, meanwhile secondary AO act as hydroperoxide decomposers, both acting as to prevent propagation of chain reaction (Vulic *et al.* 2002). The use of primary and secondary AO in conjunction may create a synergy between these compounds (Vulic *et al.* 2002). The sterically hindered phenols and secondary aromatic amines are the most representative classes of primary AO. Among the secondary AO, phosphine and phosphonite compounds are regarded as the most effective.

Since n-phenyl-2-naphthylamine (PBNA) has been banned for its use in propellant formulation, due to carcinogenic effects (Chhabra *et al.* 1993), the development

1.Universidade de São Paulo – Escola de Engenharia de Lorena – Departamento de Engenharia de Materiais – Lorena/SP – Brazil. **2.**Departamento de Ciência e Tecnologia Aeroespacial – Instituto de Aeronáutica e Espaço – Divisão de Química – São José dos Campos/SP – Brazil.
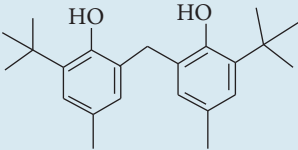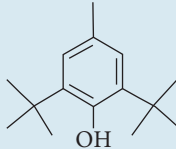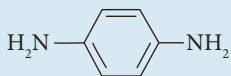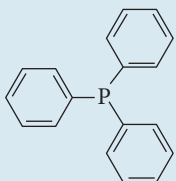
Author for correspondence: Luciene Dias Villar | Departamento de Ciência e Tecnologia Aeroespacial – Instituto de Aeronáutica e Espaço – Divisão de Química | Praça Marechal Eduardo Gomes, 50 – Vila das Acácias | CEP: 12.228-904 – São José dos Campos/SP – Brazil | Email: lucieneldv@iae.cta.br

of solid propellant technology has extensively relied on 2,2'-methylene-bis(4-methyl-6-*tert*-butylphenol), usually named as AO2246 for HTPB stabilisation (Coquillat *et al.* 2008). Despite of that, some studies (Celina *et al.* 2006; Désilets and Côté 2000) have pointed through a partly attachment of AO2246 to the polymeric HTPB network through the reaction with isocyanate. The practical consequence of this finding is the lower availability of this antioxidant to act as scavengers of radical species. Désilets and Côté (2000) also found that this attachment is dependent upon the [NCO]/[OH] ratio, being quite pronounced at ratios higher than the stoichiometric one.

Since AO are used with the ultimate target to enhance long-term shelf life, the aim of this research was to conduct an assessment of the effectiveness of AO2246 to stabilise HTPB binder under accelerated ageing (six months at 65 °C) compared to other AO usually employed to stabilise polybutadiene, namely 2,6-di-*tert*-butyl-4-methylphenol (BHT), *p*-phenylenediamine (*p*PDA), and triphenylphosphine (TPP). Even thought it was not the main concern of this study, important findings were raised about the relationship between the chemical structure and the properties of unaged HTPB elastomers formulated with the AO investigated.

MATERIALS AND METHODS
MATERIALS

Uncrosslinked HTPB prepolymer, M_n 2,900 g/mol, of predominant trans 1,4 structure was supplied by Petroflex (Brazil) containing 1% w/w BHT. AO were used as received. BHT, *p*PDA, and TPP were supplied by Sigma-Aldrich, meanwhile AO2246 was supplied by Cyanox. Chemical name, structure and classification according to antioxidant mechanism of action are presented in Table 1. The preparation of HTPB elastomers was accomplished by reaction with diisocyanate of isophorone (IPDI, Veba Chemie) in the presence of ferric acetylacetonate (Fe(acac)$_3$, Merck), both of them used as supplied.

OIT MEASUREMENT IN HTPB PREPOLYMER

The assessment of antioxidant activity in the improvement of HTPB prepolymer oxidative resistance was carried out by measurement of Oxidation Induction Time (OIT). Samples of HTPB prepolymer added with 1% w/w AO were analysed. A control sample, without addition of AO, was also provided. OIT was measured in TA5008 (TA Instruments), DSC-Q1000 module. The samples were heated at 20 °C/min under nitrogen atmosphere up to 170 °C and kept in isothermal temperature for 5 min. Chamber atmosphere was changed afterwards to

Table 1. Chemical name, structure and classification of investigated antioxidants.

Acronym	Chemical name	Structural formulae	Classification
AO2246	2,2'-methylene-bis(4-methyl-6-*tert*-butyl-phenol)		Primary
BHT	2,6-di(*tert*-butyl)hydroxytoluene		Primary
*p*PDA	*p*-phenylenediamine		Primary
TPP	triphenylphosphine		Secondary

synthetic air. The time required to reveal the first oxidation peak after the change of nitrogen to synthetic air is assumed to be OIT at a constant temperature (ASTM D3895-14).

PREPARATION OF HTPB BINDER

Polyurethane binders were prepared from polymerization of HTPB with IPDI, using Fe(acac)$_3$ (0.012% w/w) as catalyst. Stoichiometric [NCO]/[OH] ratio was used. Formulations were prepared containing 1% w/w AO. A control formulation (CF), without addition of AO, was also prepared. Sheets of 2 mm thickness were cast and cured for seven days at 50 °C.

THERMAL AGEING ASSAY

Thermal ageing of the HTPB binders were carried out in type IIB forced ventilation ovens (ASTM E145-11) under atmospheric pressure and relative humidity (RH) less than 20%. The formulations were aged in separate ovens, in order to avoid cross-contamination by AO volatilisation. Ageing conditions were set up by following ASTM D3045-10 recommendations. The ageing assay was carried out at 65 °C having withdrawn after zero, one, two, four, and six months of storage.

The evaluation of antioxidant performance during thermal ageing was achieved by submitting withdrawn samples to sol/gel extraction, swelling and mechanical testing, dynamical mechanical analysis (DMA), as well as measurement of mass changes. Strands of HTPB binders were hanging inside the oven and used for DMA (Fig. 1a), sol/gel extraction, swelling and mechanical testing (Fig. 1b). Specimens for hardness and mass variation measurements were stored at the bottom of the oven (Figs. 1c and 1d, respectively).
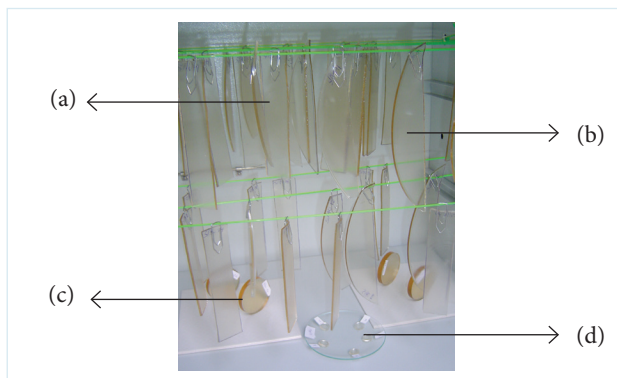

Figure 1. Storage of HTPB binders inside type IIB forced ventilation oven during accelerated ageing. (a) Strand for DMA; (b) Strand for sol/gel extraction, swelling and mechanical testing; (c) Specimen for hardness measurement; (d) Traveller for mass measurement.

SOL/GEL EXTRACTION

Solvent extraction was performed by using continuous Soxhlet extraction with chloroform (120 mL) for 24 h to determine sol/gel fractions. Samples of approximately 0.5 g of grounded HTPB elastomer were analysed in duplicate. Soluble fraction was submitted to evaporation in a rotary evaporator. Sol and gel fractions were dried at 60 °C until constant mass.

SWELLING TESTING

Swelling testing was performed by using HTPB binder discs (10 mm diameter, 2 mm thickness, 0.2 ± 0.02 g). Dried sample disks were placed, in triplicates, into chloroform at room temperature. Replicates were placed in separated vials, under occasionally agitation, until equilibrium was reached (approximately, seven days). The swollen sample disks were weighted ($m_{1,2}$) and placed to dry until constant mass (m_2). Molecular mass between chemical crosslinks (M_c) and crosslink density (ρ_e) was determined by Eqs. 1 and 2, respectively, following Flory-Rehner's equations (Flory and Rehner 1943).

$$M_c = -\frac{\rho_2 V_1 \left(v_2^{1/3} - v_2/2 \right)}{\ln(1 - v_2) + v_2 + \chi \cdot v_2^2} \tag{1}$$

$$\rho_e = \frac{\rho_2}{M_c} \tag{2}$$

where: ρ_2 is the density of the gel; V_1 is the molar volume of the solvent; v_2 is the volume fraction of the gel; χ is the Flory-Huggins interaction parameter between solvent and polymer.

In this study, ρ_2 was 0.84 g/mL, V_1 was 81.21 mL/mol, v_2 was calculated for each HTPB elastomer formulation, as defined in Eq. 3, and χ was 0.24 (Eroğlu 1998) for HTPB-chloroform pair at 45 °C. Hence, some loss of accuracy is expected due to the fact that, in the present study, swelling tests were performed at room temperature.

$$v_2 = \frac{1}{Q} = \left[1 + \frac{\rho_2}{\rho_1} \times \left(\frac{m_{1,2} - m_2}{m_2} \right) \right]^{-1} \tag{3}$$

where: Q is the swelling ratio by volume; ρ_1 is the density of the solvent at 25 °C (1.47 g/mL for chloroform).

MECHANICAL TESTING

Dumbbell-shaped specimens (ASTM D412-13 model C) were cut from the HTPB binder 2 mm-strands and assayed

for uniaxial tensile tests, according to ASTM D412-13, in a Zwick 1474 testing machine at 23 ± 2 °C, and a cross-head speed of 500 mm/min. Actual strain was measured with an optical extensometer. The initial modulus of elasticity (Young modulus) was defined as the secant modulus between 3 and 10% of elongation. Reported results are mean values of ten specimens. Hardness was measured in four specimens with 10 mm thickness (Fig. 1c) by using Zwick Shore A tester according to ASTM D2240-10.

DMA ANALYSIS

DMA measurements were carried out in flexion mode with single cantilever clamps by using a DMA-Q800 analyzer (TA Instruments). Specimens ($35 \times 11 \times 2$ mm) were cooled at −130 °C, with the aid of liquid nitrogen, and heated up to +80 °C at 3 °C/min. Tests were conducted at a frequency of 1 Hz and oscillation amplitude of 30 μm. The samples were analysed in duplicate, and the results were expressed as mean values.

MASS VARIATION

Discs of HTPB binders, with the same dimensions as the ones used for swelling test, were employed as travellers for gravimetrically measurement of mass change during thermal ageing (Fig. 1d). Measurements were made on a regular basis (once a week, usually), and, for each formulation, five travellers were used. Results are expressed as mean values.

RESULTS AND DISCUSSION
OIT OF HTPB PREPOLYMER

Thermal analysis to determine OIT is usually employed to verify the readiness of materials to degrade through oxidation. In this study, antioxidant performance was firstly assessed by measuring OIT in HTPB prepolymer samples added with 1% w/w AO. OIT values are presented in Table 2, which includes a control sample without the addition of any further antioxidant.

Due to stabilisation of HTPB prepolymer from its manufacturer by using 1% w/w BHT, samples were expected to have some residual content of this antioxidant, including the control sample. However, this would not interfere in the assessment of antioxidant activity, since the analysis was made on a comparison basis.

OIT results showed greater stabilisation activity for AO2246 (Table 2), with a time span of 96 min to appear the first oxidation peak. This performance was followed by pPDA and TPP, with 35.6

and 16.76 min, respectively. BHT showed a lower performance, with only 3.6 min, just a little higher than the control sample (2.79 min). The delay observed in the control sample to initiate oxidation has demonstrated that BHT residual content in HTPB prepolymer was significant, thus additional BHT resulted in only a slight improvement of stabilisation around 30%.

From the OIT results, the most promising decreasing order of antioxidant performance to prevent oxidation of HTPB was AO2246 >> pPDA > TPP > BHT. Since TPP is a secondary antioxidant, it is likely that some synergetic effect has occurred with the residual BHT present in HTPB prepolymer. In spite of this, the primary antioxidants AO2246 and pPDA presented higher OIT values.

Table 2. OIT values for HTPB prepolymer in the presence of the investigated antioxidants.

Sample	OIT (min)
HTPB (control)	2.79 ± 0.08
HTPB + AO2246	96 ± 2
HTPB + BHT	3.6 ± 0.6
HTPB + pPDA	35.6 ± 0.6
HTPB + TPP	16.76 ± 0.08

UNAGED HTPB BINDER

HTPB binder containing pPDA resulted in a very soft material, unable to be properly extracted from the mould. Similar result was obtained by increasing the [NCO]/[OH] ratio from 1.0 to 1.25 in order to take into account the reaction between pPDA and IPDI. The formation of short-chain polyurethanes from pPDA/IPDI reaction is prone to be the most likely reason for the softening behaviour observed. In fact, it is well known that the reaction between isocyanates and primary aryl amines presents comparable relative rates to primary hydroxyl groups (Szycher 1999). Since the elastomer obtained was not able to be assayed by the tests employed in this study, pPDA was excluded from the further characterization of unaged HTPB binders.

Tables 3 and 4 summarise the results obtained for sol/gel extractions, swelling testing, mechanical testing and DMA for unaged HTPB elastomers. Mean values were evaluated by one-way Analysis of Variance (ANOVA). When appropriate, Tukey's test was applied for comparison between the means. In Tables 3 and 4, identical letters placed after mean values indicate no significant difference at 95% confidence level.

Table 3. Sol/gel fractions and swelling testing parameters for unaged HTPB binders.

AO	Soxhlet extraction			Swelling testing	
	Sol fraction (%)	Gel fraction (%)	Sol-Gel Recovery (%)	M_c (g/mol)	ρ_e (mol/mL × 10⁻⁴)
CF	8.5 ± 0.2	83.6 ± 0.4	92.1	4,500a ± 50	1.86a ± 0.02
AO2246	9.5 ± 0.7	83.3 ± 0.7	92.8	6,200c ± 300	1.37c ± 0.07
BHT	8.0 ± 0.6	84.7 ± 0.3	92.7	5,370b ± 50	1.56b ± 0.01
TPP	9.2 ± 0.2	82.9 ± 0.2	92.1	5,680d ± 20	1.48d ± 0.01

Table 4. Mechanical property at rupture and dynamic mechanical property for unaged HTPB binders.

AO	Mechanical property at rupture			Dynamic mechanical property	
	σ_r (MPa)	ε_r (%)	E (MPa)	E' at −125 °C (MPa)	T_g (max E") (°C)
CF	1.37a ± 0.06	280ac ± 20	1.80a ± 0.03	3,450 ± 150	−74.2 ± 0.3
AO2246	1.2b ± 0.1	290a ± 40	1.56c ± 0.05	3,420 ± 30	−73.7 ± 0.1
BHT	1.14b ± 0.08	200b ± 30	1.78ab ± 0.02	3,430 ± 90	−73.7 ± 0.1
TPP	1.19b ± 0.06	230bc ± 30	1.73b ± 0.02	3,540 ± 30	−73.2 ± 0.4

σ_r: Strength at rupture; ε_r: Elongation at rupture; E: Young modulus; E: Storage modulus; T_g: Glass transition temperature; E": Loss modulus.

Sol/gel analysis presented a recovery around 90% (Table 3), which can be considered a quite satisfactory recovery for a gravimetric analysis. From ANOVA, sol fraction resulted not significantly different for all the formulations studied at 95% confidence level (Table 3). Similar behaviour was observed for gel fraction. Sol/gel extraction showed that the chemical structure of unaged HTPB elastomers was dominated by gel (approximately 80%).

On the other hand, swelling tests have pointed through a great difference in crosslink architecture of the gel fraction for HTPB elastomers prepared with different AO. The results showed a steady increase in crosslink density for the elastomers in the following sequence: AO2246 < TPP < BHT < CF (Table 3). As a consequence, decrease in molecular mass between chemical crosslinks (M_c) followed the opposite sequence. In general, when formulating a HTPB binder, there is little concern about the possible effects that AO may have over the gel structure which is going to be formed. However, these findings have shown that, although the sol/gel fractions of these formulations can be not significantly different, their chemical structure may have some expressive variations, which may interfere in the mechanical behaviour of the binders.

Actually, in agreement with the swelling results, HTPB binder containing AO2246 presented the lowest stiffness among the formulations evaluated, as shown by the values obtained for Young modulus and elongation at rupture (Table 4). As indicated by the Tukey's test, the other formulations presented some similarities in mechanical results, depending on the property

considered. From DMA results, values of storage modulus (E') at −125 °C and glass transition temperature (T_g) obtained from E" (loss modulus) peak have presented no significant difference at 95% confidence level for all the elastomeric binders studied. Thus, it seems that the gel structure of stabilised HTPB is more sensitive to the loads applied during unaxial stress-strain testing than to the loads under DMA testing.

AGED HTPB BINDER

Samples of HTPB binders withdrawn during accelerated ageing were submitted to Soxhlet extraction and swelling testing with the aim of evaluating the possible changes on their structure. For conciseness reasons, only sol fraction (Fig. 2) and crosslink density (Fig. 3) are presented, since gel fraction and molecular mass between chemical crosslinks are data complementary to the ones provided herein.

Sol fraction presented a continuous decrease during thermal ageing for all the formulations studied (Fig. 2). In addition, formulations containing AO2246 and TPP have presented the highest (6.0%) and the lowest (4.7%) ultimate sol content, respectively.

Crosslink density may be defined as the number of chain segments between the covalent or ionic bonds present in the polymeric chains. Higher crosslink density means higher interlacing, thus resulting in lower mobility. As unaged material, CF has presented the highest crosslink density, meanwhile AO2246 has presented the lowest value (Table 3). After ageing, AO2246 has not presented significant change in

the crosslink density (Fig. 3). BHT and CF have, otherwise, shown exponential increase, after a lag phase of approximately two months. On the other hand, TPP followed an asymptotically increase from the early beginning of the thermal ageing. After six months, samples containing BHT, TPP or without AO (CF) became very brittle, and, hence, it was not possible to continue the swelling testing due to the loss of accuracy.

Sol/gel analysis and swelling testing have indicated that the most important changes in the chemical structure of polybutadiene binders have occurred in gel fraction, due to the major increase in crosslink density of HTPB chains. Changes in sol fraction also indicate that some loosely chains, such as low molecular mass polyurethane and unreacted HTPB prepolymer, may have been linked to gel fraction, thus decreasing the sol content. The most remarkable changes have occurred for binders containing TPP, followed by CF and BHT. Being a secondary antioxidant, TPP was expected to behave synergistically with
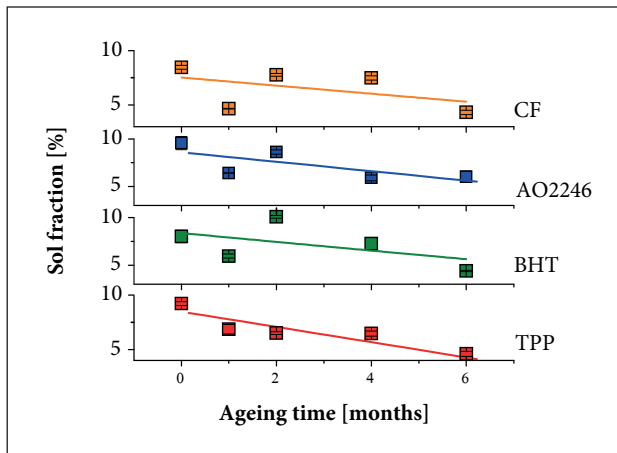
residual BHT from HTPB prepolymer, which, nevertheless, was not observed, despite the predictions obtained from OIT results (Table 2). As a matter of fact, Pauquet *et al.* (1993) have pointed out limitations of OIT predictions for secondary AO, when results are extrapolated to long-term stabilisation.

Ageing of the formulation containing AO2246 has shown little effect on the mechanical properties (Figs. 4 to 6), with a smooth tendency of elongation decrease and modulus increase. On the other hand, the other formulations were not able to be evaluated during the entire ageing assay due to the high level of stiffness reached by the samples. TPP presented the worst scenario, being not able to be mechanically tested after the first month of accelerated ageing. BHT and CF were assayed up to the second month, which corresponds to the lag phase observed before exponential increase in crosslink density (Fig. 3).

Following mechanical characterisation of the aged binders, hardness measurements indicated an asymptotically increase
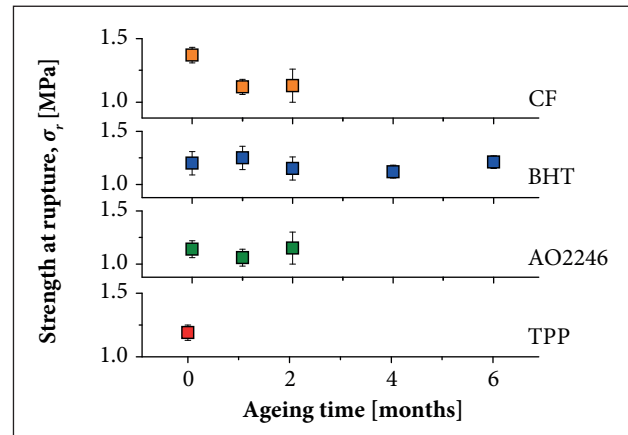

Figure 2. Sol fraction of HTPB binder under accelerated ageing.
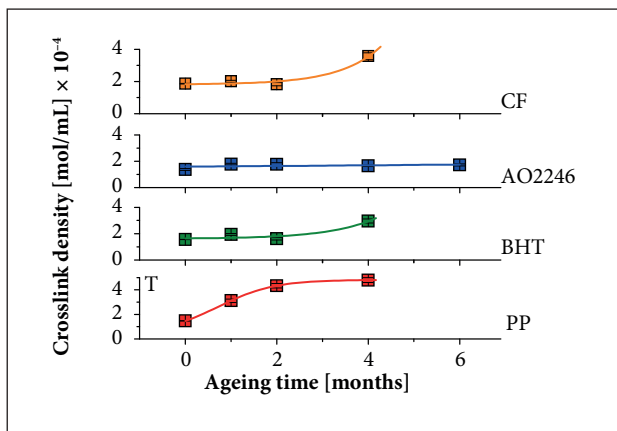
Figure 3. Crosslink density of HTPB binder under accelerated ageing.

Figure 4. Strength at rupture of HTPB binder under accelerated ageing.
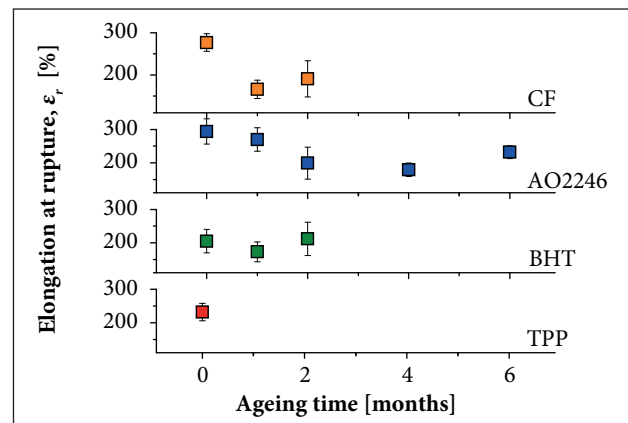

Figure 5. Elongation at rupture of HTPB binder under accelerated ageing.

for TPP from the early beginning of the ageing assay (Fig. 7). A tendency of hardness increase was very low pronounced for BHT and control, being not significant for AO2246 (Fig. 7).

Aged samples withdrawn after six months were also submitted to DMA. However, only AO2246 was able to be assayed, due to the high level of degradation observed for other samples, as reported for mechanical testing (Figs. 3 to 6). Storage modulus (E') of AO2246 resulted in 3,430 ± 30 MPa, meanwhile T_g resulted in −72.6 ± 0.1 °C. By applying mean comparison, only T_g showed to be significantly different from the initial value (Table 4) at 95% confidence level. The change to a slightly higher T_g indicates that some degree of crosslink did occur in the presence of AO2246, although it cannot be realized by the measurement of crosslink density, as shown in Fig. 3.

Measurement of net gain or loss of mass by using traveller specimens resulted in the behaviour described in Fig. 8, where m_0 corresponds to initial traveller mass and m, to the mass at ageing time t. At the beginning of the ageing assay, all the
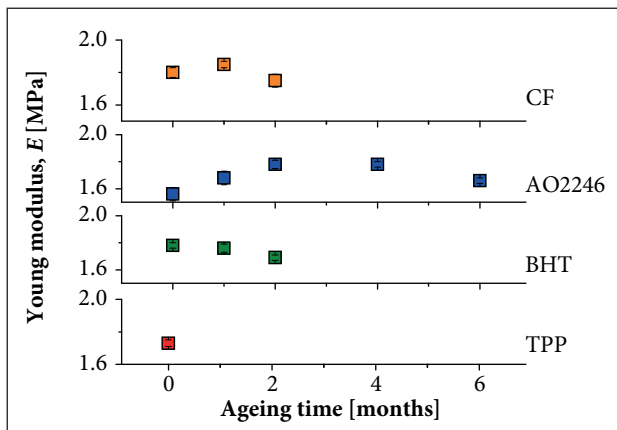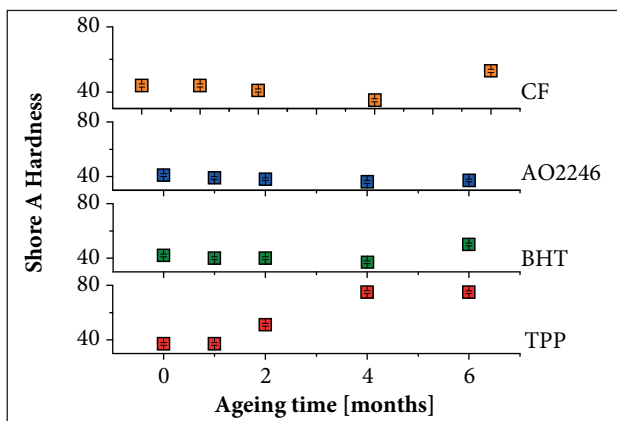
formulations showed some loss of mass, which can be attributed to volatilisation of AO, and it was more pronounced for the formulation containing BHT, due to lower molar mass. Gain of mass due to the oxidation of the HTPB backbone was readily noticed for TPP formulation, followed by control and BHT samples. In the presence of AO2246, there was no expressive gain of mass throughout the assay.

With no shadow of doubt, the results from mechanical testing, DMA and mass variation have pointed to a negligible effect of ageing on AO2246 formulation, and, in opposite, a very significant effect on TPP. Although some loss of mass at the beginning of ageing assay indicates that unattached AO2246 was lost by volatilisation, the remained content of this antioxidant was very effective in protect HTPB binder against oxidation.

On the other hand, although TPP was reported earlier (Hinney and Murphy 1989) to efficiently avoid HTPB prepolymer oxidation, thus preventing its increase in functionality, this antioxidant was not suited for HTPB binder protection. In fact, TPP has acted as a prooxidant, promoting a fast loss of mechanical properties and an expressive gain of mass by oxygen uptake through oxidation.

Finally, the results from BHT formulation suggested that this antioxidant may be used for stabilisation of HTPB binder. Although, if used previously for stabilisation of BHT prepolymer, the additional protective effect may be negligible. In fact, loss of BHT through volatilisation was more expressive than the observed for CF (Fig. 8). In addition, it was expected that BHT would have a reduced performance compared to AO2246, due to the presence of only one active hydroxyl group and to the lower molar mass, thus being more susceptible to volatilisation.
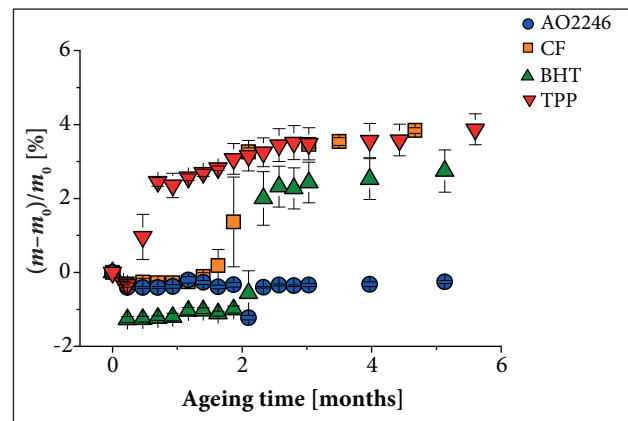

Figure 6. Young modulus of HTPB binder under accelerated ageing.

Figure 7. Hardness of HTPB binder under accelerated ageing.

Figure 8. Mass variation of HTPB binder under accelerated ageing.

CONCLUSION

The main objective of this investigation was to compare the effectiveness of AO2246, a phenolic hindered antioxidant, with those of BHT, *p*PDA, and TPP in the stabilisation of HTPB binders for solid rocket propellants. In order to estimate the readiness of the investigated AO to prevent HTPB oxidation, the measurement of OIT was carried out, and the results revealed as the most promising decreasing order of antioxidant performance to be AO2246 >> *p*PDA > TPP > BHT. Otherwise, a more complete evaluation has confirmed OIT results only partially. Hence, in the presence of AO2246, HTPB binder presented the lower crosslink density, sol fraction decrease, mechanical and thermo-mechanical (DMA) changes and mass (loss/gain) variations. *p*PDA has to be withdrawn from this study, since its reaction with isocyanate (IPDI) resulted in a very soft material, unable to be assayed. Finally, the relative order between TPP and BHT was proved to be the opposite envisaged by OIT results. In fact, BHT showed to be an alternative antioxidant for HTPB stabilisation, meanwhile TPP has actually acted as a prooxidant additive.

The findings described herein raised an important point about using analysis of one component, in this case, HTPB prepolymer, to predict the ageing behaviour of a formulation containing this component, as in the HTPB binder. Being a more complex system, AO proved to have interactions with the HTPB backbone and with the curing agent, thus resulting in a different comparative performance of stabilisation. In addition, these interactions may, eventually, interfere with mechanical properties of the resulted HTPB binders.

ACKNOWLEDGEMENTS

REFERENCES

Celina M, Elliot JMS, Winters ST, Assink RA, Minier LM (2006) Correlation of antioxidant depletion and mechanical performance during thermal degradation of an HTPB elastomer. Polym Degrad and Stabil 91(8):1870–1879. doi: 10.1016/j.polymdegradstab.2005.11.006

Chhabra JS, Athar J, Agrawal JP, Singh H (1993) Comparative study of various antioxidants for HTPB prepolymer. Plast Rub Compos Process Appl 20:305-310.

Coquillat M, Verdu J, Colin X, Audouin L, Celina M (2008) A kinetic evaluation of the thermal oxidation of a phenol stabilised polybutadiene. Polym Degrad Stabil 93 (9):1689–1694. doi: 10.1016/j.polymdegradstab.2008.05.031

Coquillat M, Verdu J, Colin X, Audouin L, Nevière R (2007a) Thermal oxidation of polybutadiene. Part 1: effect of temperature, oxygen pressure and sample thickness on the thermal oxidation of hydroxyl-terminated polybutadiene. Polym Degrad Stabil 92(7):1326–1333. doi: 10.1016/j.polymdegradstab.2007.03.020

Coquillat M, Verdu J, Colin X, Audouin L, Nevière R (2007b) Thermal oxidation of polybutadiene. Part 2: mechanistic and kinetic schemes for additive-free non crosslinked polybutadiene. Polym Degrad Stabil 92(7):1334–1342. doi: 10.1016/j.polymdegradstab.2007.03.019

Coquillat M, Verdu J, Colin X, Audouin L, Nevière R (2007c) Thermal oxidation of polybutadiene. Part 3: molar mass changes of additive-free non crosslinked polybutadiene. Polym Degrad Stabil 92(7):1343–1349. doi: 10.1016/j.polymdegradstab.2007.03.018

Désilets S, Côté S (2000) Chemical bond between stabilizers and HTPB binders in propellants. Propell Explos Pyrotech 25(4):186–190. doi: 10.1002/1521-4087(200009)25:4<186::AID-PREP186>3.0.CO;2-B

Eroğlu MS (1998) Characterization of the network structure of hydroxyl terminated poly(butadiene) elastomers prepared by different reactive systems. J Appl Polym Sci 70(6):1129–1135. doi: 10.1002/(SICI)1097-4628(19981107)70:6<1129::AID-APP9>3.0.CO;2-Q

Flory PJ, Rehner J (1943) Statistical mechanics of swelling of crosslinked polymer networks. Chem Phys 11:521-526.

Gupta T, Adhikari B (2003) Thermal degradation and stability of HTPB-based polyurethane and polyurethaneureas. Thermochim Acta 402(1-2):169–181. doi: 10.1016/S0040-6031(02)00571-3

Hinney HR, Murphy JR (1989) Suppression of reactivity changes in PolyBD R-45M resin. Paper presented at ICT 1989. Proceedings of the 20th International Annual Conference of Fraunhofer ICT; Karlsruhe, Germany.

Pauquet JR, Todesco RV, Drake WO (1993) Limitations and applications of oxidative induction time (OIT) to quality control of polyolefins. Paper presented at IWCS 1993. Proceedings of the International Wire and Cable Symposium; Saint Louis, USA.

Szycher M (1999) Szycher's handbook of polyurethanes. Boca Raton: CRC Press.

Vulic I, Vitarelli G, Zenner JM (2002) Structure-property relationships: phenolic antioxidants with high efficiency and low colour contribution. Polym Degrad Stabil 78(1):27–34. doi: 10.1016/S0141-3910(02)00115-5