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The role of antioxidant on propellant binder reactivity during thermal aging

Abstract: *Thermal aging of hydroxy-terminated polybutadiene (HTPB) stabilized with 2,6-di(tert-butyl)hydroxytoluene (BHT) was carried out at 60ºC from 1 to 11 weeks. Samples of 200 mL were stored in sealed 500-mL Erlenmeyer flasks under atmospheric pressure or vacuum and periodically withdrawn for physical and chemical analysis, infrared spectroscopy characterization and measurement of HTPB/IPDI (isophorone diisocyanate) reactivity, expressed as pot life. Mechanical properties of the cured polyurethane, prepared from aged HTPB, were assayed by uniaxial tension tests. Despite the unchanged chemical structure, an increase in HTPB/IPDI binder reactivity was observed, being correlated with BHT depletion measured as color change (yellowing). Aging of HTPB showed no interference on mechanical properties of the cured polyurethane.*

Keywords: *Antioxidant, Composite propellant, HTPB propellant, Polyurethane resin, Storage.*

INTRODUCTION

Although there has been an increasing research effort into development of energetic polymer binders for solid rocket propulsion, hydroxy-terminated polybutadiene (HTPB) is still widely used in the formulation of composite propellant. This 1,3-butadiene homopolymer contains terminal and reactive hydroxyl groups, introduced during free radical polymerization by peroxide or azo compounds. During solid propellant processing, these hydroxyl groups react with a diisocyanate resulting in polyurethane, which acts as a binder for the solid particles of the propellant composition.

Due to the unsaturated character of the repeated unit, polybutadiene is known to be sensitive to oxidation, thus being usually supplied with the addition of stabilizers (Ninan *et al.*, 1996), namely antioxidants, especially hindered phenol compounds.

The mechanisms and kinetics of HTPB oxidation have been a matter of great concern since the 1960's. More recently, Coquillat *et al.* (2007a, b, c) have defended the occurrence of radical addition to double bonds and allylic methylene consumption, meanwhile Guyader *et al.* (2006) have emphasized the mechanism of epoxide formation during HTPB aging. In spite of this, both works agree that oxidation of HTPB is highly dependent on sample thickness and oxygen partial pressure, a condition hardly mentioned in previous studies (Hinney and Murphy, 1989; Pecsok *et al.*, 1976).

In one of these studies (Hinney and Murphy, 1989), the effect of HTPB aging over its reactivity with isocyanates was investigated by measuring the decrease in pot life, defined as the time necessary to reach a pre-established viscosity value. The authors attributed the increase in reactivity to the higher functionality derived from HTPB oxidation through a mechanism of hydroperoxide formation.

In our study, an assessment of the influence of usual storage conditions over aging of HTPB was carried out by submitting large samples (200 mL) of this resin, stabilized with the primary antioxidant BHT, to thermal aging under stagnated atmospheric pressure or under vacuum. Physical and chemical analysis, infrared spectroscopy and pot life measurement showed that, being diffusion-dependent, the observed increase of HTPB reactivity was not due to change in its chemical structure. Instead, an overview of the concerned literature indicated that it was related to BHT depletion and conversion into quinone derivatives, which may eventually react with isocyanates to graphitize into the polyurethane.

EXPERIMENTAL

Material

Samples of uncrosslinked HTPB (M_n = 2,900 g/mol) of predominant trans 1,4 structure (Takahashi and Diniz, 2002) were supplied by Petroflex (Brazil) containing 1% w/w of BHT (2,6-di(tert-butyl)hydroxytoluene, CA index name as 2,6-bis(1,1-dimethylethyl)-4-methyl-phenol). The material was maintained in tightly closed vessels at room temperature until they were used.

Aging conditions

Aging experiments were conducted on 200-mL samples of uncured liquid HTPB placed in sealed 500–mL Erlenmeyer flasks. Flasks were placed into forced circulating air oven at 60 ± 1°C and protected from day light exposition. Headspace of the flasks was kept either at atmospheric pressure or under 99% vacuum. Duplicated flasks were withdrawn after 1, 2, 4, 6, 9 and 11 weeks and placed for characterization at the same day of collection (pot life and physical and chemical analysis) or within a maximum of two days (mechanical properties). Samples were maintained in desiccators at room temperature until analyses were performed.

Characterization

Determination of pot life was made by stoichiometric reaction of HTPB with IPDI (isophorone diisocyanate, CA index name as 5-isocyanato-1-(isocyanatomethyl)-1,3,3-trimethyl-cyclohexane) in the presence of 0.012% w/w of the catalyst ferric acetylacetonate (tris(2,4-pentanedionato-iron). The catalyst was blended with HTPB in a mechanical stirrer. The mixture was heated for bubble removal. After addition of IPDI, the mixture was manually stirred and immediately placed for viscosity measurement at 50°C. The time required to reach 20 Pa.s was considered as the pot life. At each sampling time, an unaged sample of HTPB was also analyzed for pot life as a control.

Yellowing of HTPB was measured by using a spectrometer in the visible region (PerkinElmer Lambda 3B UV/VIS). In preliminary tests, a range of wave length varying from 220 to 320 nm was evaluated. Maximum absorption was obtained at 295 nm. Samples were diluted in toluene (1:1) and analyzed in duplicate with toluene as the blank.

Determination of physical and chemical properties included: hydroxyl number (Takahashi *et al.*, 1996);

viscosity at 25°C measured in a small sample device (Brookfield LVDV-II+ with software Wingather 2.2) and humidity (Karl Fischer Metrohm 633).

Fourier transform infrared spectra (FT-IR) were collected by using a PerkinElmer Spectrum One spectrometer. HTPB was analyzed as thin films, while BHT was analyzed as potassium bromide pressed-pellet. Analyses were carried out under transmission mode at the following conditions: spectral range 4000 - 400 cm^{-1}; 40 scans and 4 cm^{-1} resolution.

Pot life and color change were evaluated by using the property retention index (PRI) as defined by ASTM D5870-95 (2003) for destructive tests. Determination of the PRI for each replicate exposed to aging, z_i, is defined by Eq. (1).

$$z_i = \frac{p_{i,x}}{p_0} \tag{1}$$

Where,

$P_{i,x}$: property of the i replicate at exposure time, x, and

p_0: initial value of the property.

Determination of the mean PRI, $\overline{Z}$, is defined by Eq. (2).

$$\overline{Z} = \frac{\sum_{i=1}^{n} z_i}{n} \tag{2}$$

Where,

z_i: PRI for each replicate exposed to aging;

n: number of replicates.

Mechanical properties

Samples of HTPB aged for 1, 5, 8 and 10 weeks were also used to prepare polyurethane samples with 2 mm thickness and compared with polyurethane prepared from unaged HTPB. Dumbbell specimens were assayed for uniaxial tension tests, according to ASTM D412-06a in a Zwick 1474 testing machine at 500 mm/min and 25°C. Hardness was measured in circular specimens with 70 mm thickness by following ASTM D2240-05.

RESULTS AND DISCUSSION

Physical and chemical properties of HTPB for the unaged condition are presented in Table 1, which are in accordance

with recommended specifications (MIL-H-85497-81) for application of HTPB in solid propellants. Some of the properties investigated have no specified limits.

In order to improve the comparison between both treatments (atmospheric pressure and vacuum), property retention index was applied to the processing property of pot life and to HTPB color changing (yellowing), as showed in Fig. 1. A remarkable decrease of pot life retention index was followed by a sigmoidal increase of color retention index during the course of the aging experiment (Fig. 1). A linear correlation between them is presented in Fig. 2, showing that the decrease in pot life is related to yellowing increase by a correlation factor of 0.90 and 0.94 for atmospheric pressure and vacuum, respectively.

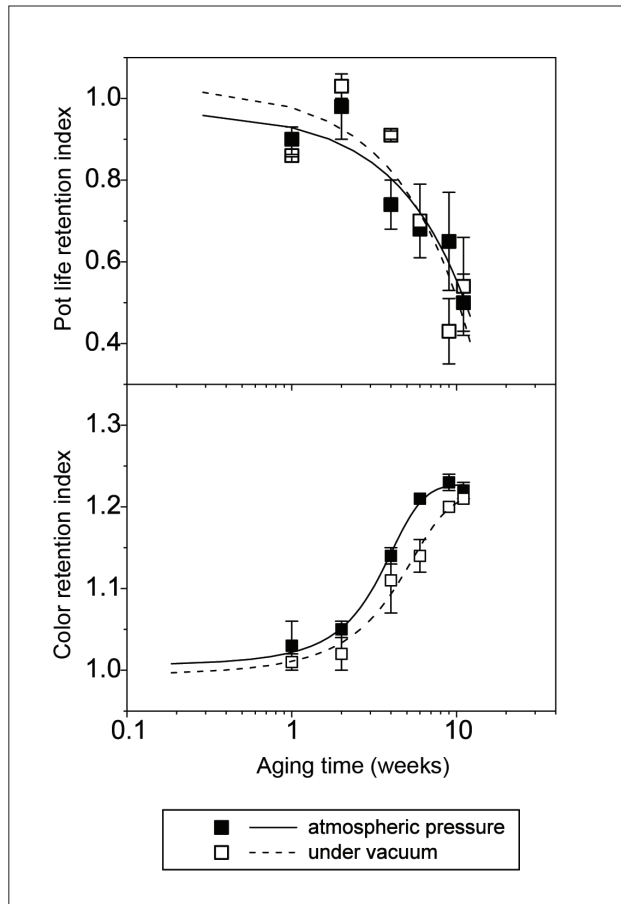Figure 2: Correlation between pot life and color change retention indexes.

Figure 1: Pot life and color change retention indexes as a function of aging time.

The values of hydroxyl number, viscosity and humidity are presented in Fig. 3. Dashed lines represent upper (UL) and lower (LL) limits (Table 1). Although some fluctuations can be observed, the investigated properties were kept under the specified limits and showed no significant variations throughout the aging assay.
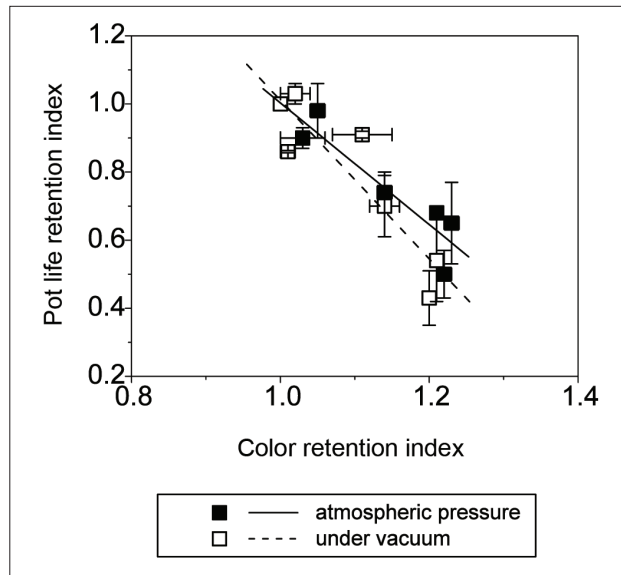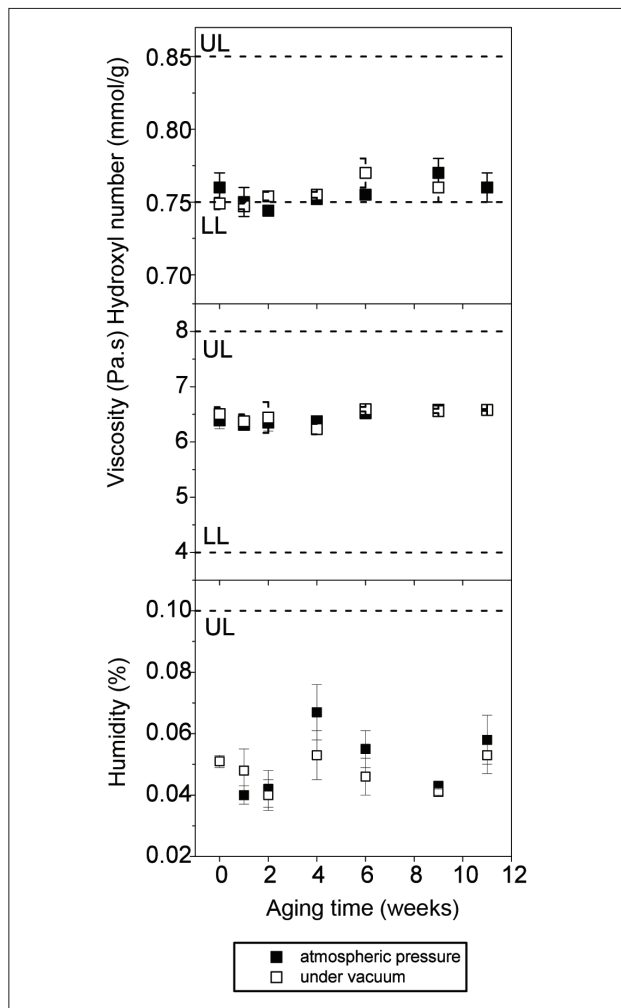

Figure 3: Physical and chemical properties of HTPB as a function of aging time.

Table 1: Physical and chemical properties of unaged HTPB and recommended specifications

Physical and chemical property	HTPB unaged	MIL-H 85497-81 type I
Hydroxyl number (m mol/g)	0.75 ± 0.01	0.75 to 0.85
Humidity (%)	0.05 ± 0.02	0.10 max.
Acid number (mg KOH/g)	0.16 ± 0.01	ns
Viscosity (Pa.s, 25°C)	6.8 ± 0.1	4.0 to 8.0
Refraction index (ηd)	1.516 ± 0.001 (20°C)	ns
Density (20°C)	0.902 ± 0.001	ns

ns: not specified.

Table 2: Mechanical properties of cured polyurethane obtained from aged and unaged HTPB

Aging time (weeks)	Mechanical properties		
	Tensile strength [MPa]	Tensile modulus [MPa]	Hardness [ShA]
0	1.3 ± 0.1	2.1 ± 0.1	41 ± 1
1	1.3 ± 0.1	2.1 ± 0.1	40 ± 1
5	1.4 ± 0.1	2.0 ± 0.1	41 ± 1
8	1.2 ± 0.1	2.1 ± 0.1	40 ± 2
10	1.3 ± 0.1	2.3 ± 0.1	43 ± 1

Infrared spectra were obtained on samples of HTPB exposed to 0, 1, 2, 4, 6, 9, and 11 weeks under thermal aging at both pressure conditions. For practical reasons, only the first and the last exposure time spectra are presented in Fig. 4. Aged and unaged HTPB
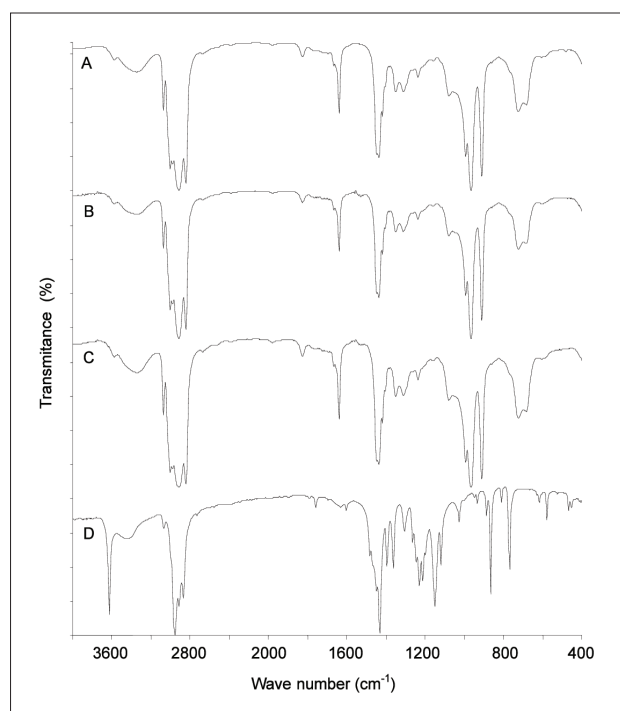

Figure 4: Infrared spectra of aged and unaged HTPB and BHT antioxidant. A: unaged HTPB; B: aged HTPB under atmospheric pressure for 11 weeks; C: aged HTPB under vacuum for 11 weeks; D: BHT.

samples presented similar spectra for both atmosphere conditions investigated. Increase in the absorption at the region of 3394 cm^{-1}(νOH), which could account for increase in functionality, was not observed. Additionally, the absorption at the region of 1639 cm^{-1} (νC=C olefinic) remained unchanged, indicating no radical addition to double bonds up to the detection level of this technique. The absence of absorptions at the regions around 1740-1800 cm^{-1} (νC=O) and 830-1000 cm^{-1} (νOO) in the aged samples also indicates no built-up of carbonyl or hydroperoxide groups. A BHT spectrum was also included in Fig. 4. Due to its low concentration (1%) on HTPB, peaks of BHT or its quinone derivatives were not apparent in HTPB spectra.

In order to verify if the change in reactivity of the binder system could interfere in the mechanical properties of the cured polyurethane, properties of tensile strength, Young modulus and hardness (Shore A) of the HTPB/IPDI polyurethanes were assayed. They showed not to be changed with the aging of HTPB (Table 2).

Although the readily oxidative nature of HTPB is well established, Coquillat *et al.* (2007 a, b, c) and Guyader *et al.* (2006) have demonstrated its dependency on oxygen diffusion. Considering the aging testing conditions of this study, which used large samples (200 mL) exposed to mild temperature, without shaking the flasks, oxygen diffusion was quite difficult even at atmospheric pressure. In these conditions, oxidation of HTPB backbone may have hardly occurred as pointed by the

results of physical and chemical properties, especially hydroxyl number (Fig. 1), and by infrared spectra (Fig. 4). It is important to state that the dark condition of aging and the analysis of aged samples had minimized any effect of UV light in the results presented (Fig. 1 and 3).

The unchanged values of humidity (Fig. 3) indicated that the reactivity increase cannot be attributed to the reaction between IPDI and any absorbed atmospheric humidity.

In addition, the occurrence of HTPB homopolymerization or oxidative cross-linking during aging could not be verified, respectively, by the results of viscosity of uncured HTPB (Fig. 3) or by any change in the mechanical properties of the cured polyurethane (Table 2).

On the other hand, the correlation between pot life decrease and color change (Fig. 2) indicated that the well-known yellowing of hindered phenol antioxidants (Vulic *et al*., 2002), even in the absence of oxygen (Bangee *et al*., 1995), may be related to the apparent change in HTPB reactivity, which was observed independently of the oxygen partial pressure. In fact, some studies (Celina *et al*., 2006; Désilets and Côté, 2006; Shanina, Zaikov and Mukmeneva, 1996) have demonstrated that quinone derivatives from hindered phenol antioxidants react quite readily with isocyanates and graphitize into HTPB backbone. Based on this literature evidence, our results indicate that the apparent increase of the HTPB/IPDI binder reactivity is due to a side-reaction between BHT quinone derivatives and IPDI.

CONCLUSION

The observed increase of reactivity after thermal aging of HTPB was correlated to antioxidant depletion and quinone by-products formation, which was assigned the role to react with IPDI, thus resulting in the observed pot life decrease. No experimental evidence was obtained in order to correlate the change in reactivity with change in chemical structure of HTPB.

ACKNOWLEDGMENTS

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