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Aging Studies on Carboxy Terminated Polybutadiene (CTPB) Binder and Propellant

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Aging studies on carboxy terminated polybutadiene (CTPB) and CTPB-based propellants have been carried out. The increase in the cross-link density during aging has been measured using a thermomechanical analyzer. During aging, a correlation has been shown between the cross-link density and the ignition temperature of the binder as well as of the propellant. The ignition temperature vs cross-link density results were found to show an opposite trend in CTPB and CTPB-based propellants, suggesting that the two ignition mechanisms are different.

Introduction

THE mechanism of aging in real propellant systems containing elastometric binders such as carboxy terminated polybutadiene (CTPB) and hydroxy terminated polybutadiene (HTPB) is not clearly understood. The available literature on the aging mechanism of CTPB/HTPB-based propellants is summarized here. Kuletz and Pakulak[1] have studied the accelerated aging of five cast composite propellants in the temperature range of 40-75°C to show that at the surface the binder undegoes change, while in the bulk it is the oxidizer. Schdelbaur[2] has found that CTPB-based propellants hardened during aging because of double-bond cross linking in the main chain. He suggested that $HClO_4$ and moisture acts as a cross-linking agent for double bonds. On the other hand, Mayers[3] explained CTPB propellant hardening as due to the cross linking caused by the oxidative attack of ammonium perchlorate (AP) on CTPB double bonds. The most thorough investigation so far available is by Layton,[4] who correlated the structure with the changes in mechanical properties in CTPB and HTPB propellants. He proposed that double bonds get cross linked with maximum percentage in the pendant vinyl group. He attributed the observed aging activation energy E of 5.7 kcal/mole at 24-66°C to the diffusion process.

Detailed investigations[5] on the aging of composite solid propellants have been carried out in this laboratory, and a mechanism has been proposed for the process of aging in propellants containing thermoplastic binders such as polystyrene and polymethyl-methacrylate. The present work is aimed at understanding the aging phenomenon of real propellant systems by choosing CTPB-based propellants for investigation.

Experimental Methods

CTPB-based binder was prepared by curing CTPB prepolymer (Butarez, CTL type II) with MAPO (trismethyl-aziridinyl phosphine oxide) and a bifunctional epoxy resin (GY 252). The mixture of the curing agent constitutes 16% by weight of the prepolymer and contains MAPO and epoxy resin in a 1:3 ratio. The thoroughly mixed slurry was cast in molds and cured at 80°C for 144 h so that a maximum degree of curing was attained in the solid product.

The propellant, containing 70% ammonium perchlorate (AP) and 30% binder, was cast as follows: CTPB prepolymer (23% by weight), Dioctyl Adipate (DOA) (2.7%), and lecithin (0.7%) were mixed well in a mortar, to which a mixture of curing agents (MAPO and epoxy resin present in the same proportion as in the neat binder) was added. The slurry was mixed well and AP was added in small portions. The mixing was continued until a homogeneous blend was obtained, and the curing was done exactly as it was for the binder.

Before the neat binder and the propellant samples were subjected to aging studies, experiments were conducted to ensure that the binder and the propellant were completely cured. The binder and the propellant slurry were separately kept at 80°C, and samples were taken periodically to estimate the gel content. Samples aged in air at 120 ± 1°C were also removed periodically to determine the gel portion and make other measurements.

Determination of Gel Content

Binder Samples

Rectangular pieces (weighing about 1 g) of the binder sample were swollen in toluene for 10 days to obain an equilibrium degree of swelling. The solution was filtered, the gel was washed repeatedly with toluene to remove the adhering sol portion, and then dried in a vacuum at 50°C for 24 h to obtain the constant weight of the gel.

Propellant Samples

Weighed propellant samples were pulverized and allowed to swell in toluene for a week. The solution was filtered, and the insoluble portion of the propellant was washed with toluene to remove the sol. It was washed with methanol and later with hot water (70°C) to remove the AP. To ensure complete removal of AP from the sample, washing with methanol and water was repeated until a constant weight was obtained. The error in the gel measurement was ±2%.

The results for both the binder and propellant samples are presented in Table 1.

Measurment of Cross-Link Densities of Binder Samples

Cluff's Compression Modules Analyzer (CMA) Technique

Toluene-swollen samples of the binder were placed below the bottom plate of the plunger along with the solvent. Weights (50-1000 g) were placed on the top tray and the deflection from the zero reading was noted for different weights. The force F (in dynes) corresponding to the deflection h was plotted as shown in Fig. 1 for the unaged binder. The slope s of the line was used to calculate an ef-

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Table 1 Data on the variation in gel content during curing and aging, ignition temperature and penetration temperature of the binder and propellant with storage time

Curing time at 80°C, h	Gel content of binder, %	Penetration temperature of binder, °C	Ignition temperature of binder, °C	Gel content of binder from propellant, %	Ignition temperature of propellant, °C
7½	44.10	–	–	–	–
5¾	–	–	–	32.53	–
19	74.36	–	–	–	–
18	–	–	–	72.94	–
24	63.38	–	–	67.46	–
48	65.25	–	–	77.68	–
72	79.07	–	–	78.37	–
96	84.02	–	–	83.69	–
144	79.88	–	–	84.09	–
164	77.00	–	–	81.01	–
Aging time at 120°C, days					
0	79.00	137.5	280±1	81.01	347±2
4	85.30	170.0	295±1	82.27	328±2
8	88.20	210.0	308±1	83.09	318±2
12	90.30	225.0	340±1	86.56	314±2
16	93.60	225.0	344±1	98.97	312±2

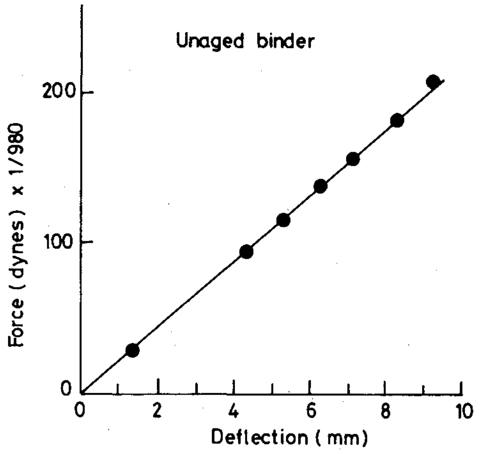


Fig. 1 Compression stress strain curves of swollon CTPB binder by CMA.

fective network concentration (V_e/V) from the following equation:

$$V_e/V = h_0 s/3A_0RT \qquad (1)$$

where A_0 is the cross-sectional area of the bottom plate of the plunger (the sample completely covers the plunger surface) and h_0 is the thickness of the unswollen samples. The results on V_e/V are presented in Table 2.

Measurement by Thermomechanical Analyzer (TMA)

In the present work a Dupont 943 TMA provided with a penetration probe was used. The experimental operation was carried out according to manufacturer's instructions. An unswollen binder sample of about 0.5 mm thickness was placed on the sample holder below the plunger, and the extent of penetration obtained by applying the force was recorded. Figure 2 shows a plot of $\Delta l/l$ (where l is the initial thickness and Δl is the decrease in the thickness of the sample) vs force (in grams). V_e/V was calculated as follows:

$$V_e/V = \frac{F/A}{RT[\alpha - (1/\alpha^2)]} \qquad (2)$$

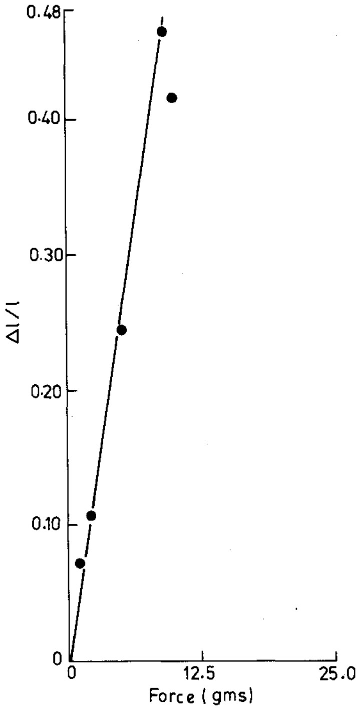


Fig. 2 Plot showing variation of $\Delta l/l$ with force for the unaged binder.

where F is the force (dynes), A the area of the probe (cm^2), R the gas constant (J/K/mole), and $\alpha = 1 + \epsilon$, where ϵ (penetration ratio) $= \Delta 1/1$. α is calculated from the slope of the $\Delta 1/1$ vs F plot. The results are presented in Table 2.

Measurement of Penetration Temperature of Binder Samples by TMA

The penetration temperatures were recorded by TMA at a heating rate of 10°C/min. The results are presented in Table 1. The penetration temperatures were calculated from the dynamic TMA plots, as shown in Fig. 3. A plot of penetration temperature of the binder samples as a function of storage time is given in Fig. 4.

Table 2 Measurement of the cross-link densities (V_e/V) by CMA and TMA

Storage time, days	V_e/V, moles/cm^3 (by TMA)	V_e/V, moles/cm^3 (by CMA)
0	7.9×10^{-6}	1.0×10^{-4}
8	15.3×10^{-6}	5.4×10^{-4}
12	24.0×10^{-6}	6.4×10^{-4}
16	33.5×10^{-6}	8.6×10^{-4}
20	34.0×10^{-6}	5.2×10^{-4}

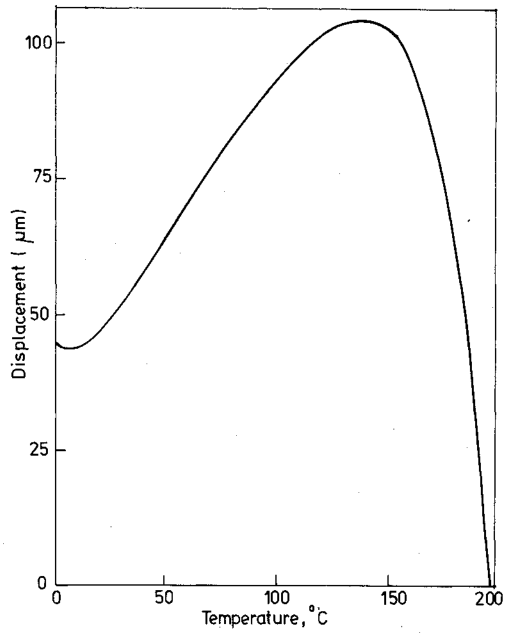


Fig. 3 Typical TMA plot of unaged binder.

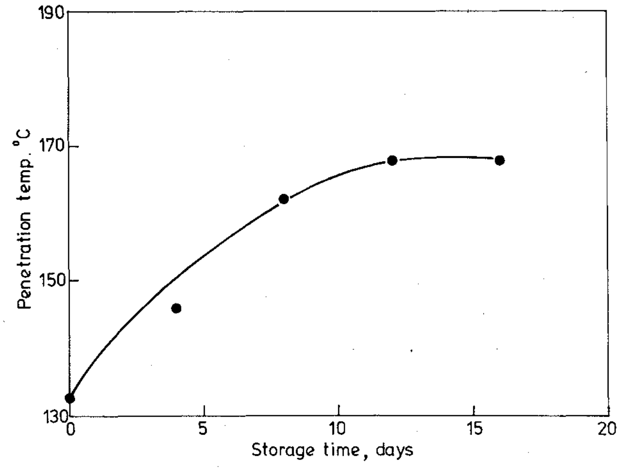


Fig. 4 Plot of penetration temperature of binder vs storage time.

Measurement of Ignition Temperatures

Binder Samples

The measurements were carried out using an ignition apparatus[6] based on the DTA principle, where a heating rate of 170°C/min and a constant oxygen flux (0.0001 g/cm^2·s) were employed. The T and ΔT outputs from the chromel-alumel thermocouple were connected to a strip-chart recorder. At the time of ignition a visual flame could be seen, and both the T and ΔT traces showed abrupt changes. The exact temperature, with an accuracy of ±1°C, could be obtained from T and ΔT traces of the polymer and was designated the ignition temperature.

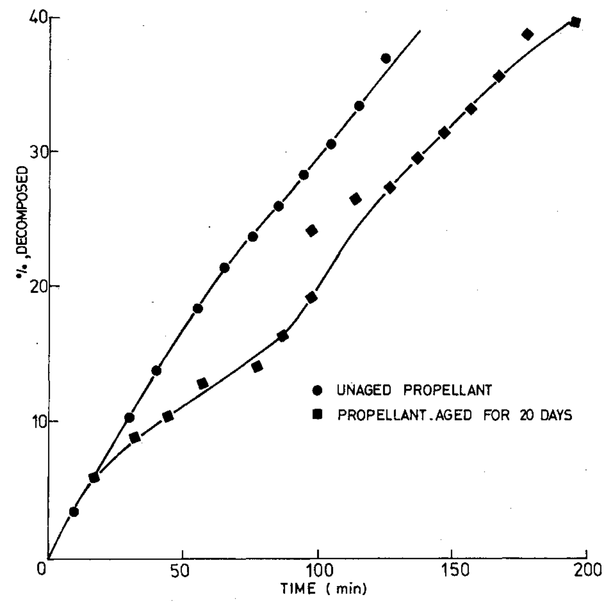


Fig. 5 Isothermal TG plots of propellant samples at 270±1°C.

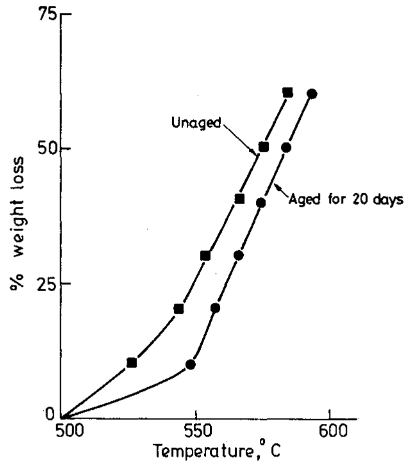


Fig. 6 Dynamic TG plots of unaged and aged binder samples.

Propellant Samples

The measurements were carried out in a DTA assembly[7] in air with a heating rate of 10°C/min. The results are presented in Table 1.

Thermogravimetric (TG) Studies

The thermal degradation of propellant samples (atmosphere air and sample weight 20 mg) was carried out in an assembly, described elsewhere,[8] at 270±1°C. The TG plots are shown in Fig. 5. Dynamic TG runs on the binder samples with a heating rate of 10°C/min were carried out in an N_2 atmosphere using a Stanton Redcroft thermobalance. The TG plots are given in Fig. 6.

Results and Discussion

The results of the measurements of gel content, cross-link density, ignition temperature, and penetration temperature of the binder and propellant are discussed below.

Gel Content

The results of the variation of the gel content with curing and aging time are shown in Fig. 7 and Table 1. It may be seen in Fig. 7 that the gel content initially increases exponentially with time and then remains constant.

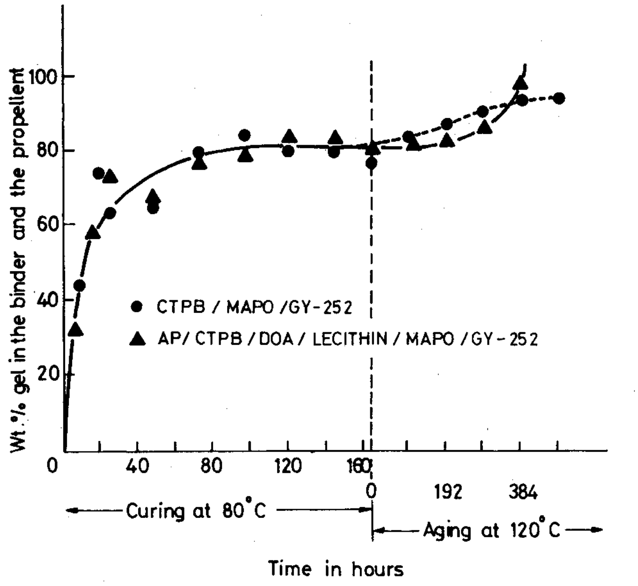


Fig. 7 Variation of gel content with curing and aging time.

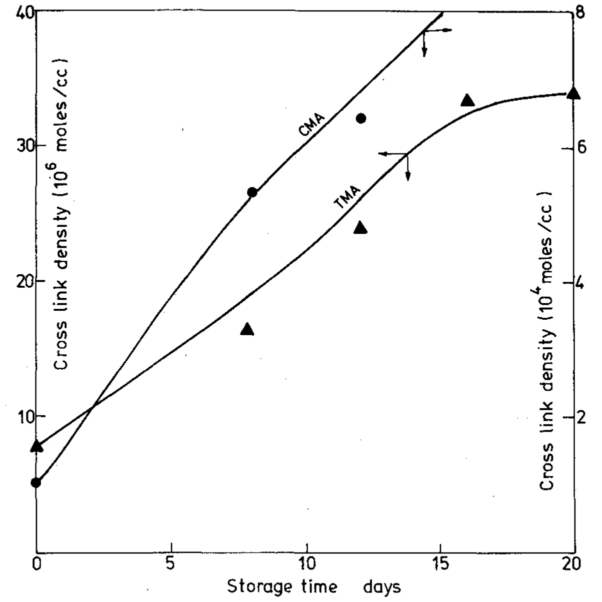
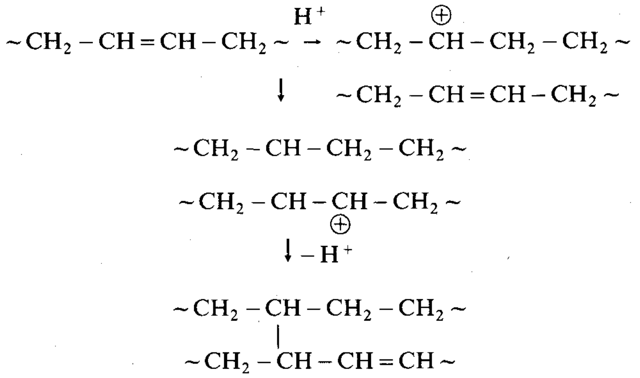


Fig. 8 Plots of cross-link density by CMA and TMA vs storage time.

The constancy of the gel content starts after about 100 h of curing. Even after 144 h (up to 168 h) the gel content maintains a constant value, suggesting that the propellant has completely cured. The gel content during the curing of the neat binder and the binder in the propellant mix fall on the same curve (Fig. 7), suggesting that the process of curing remains unaltered in the presence of AP. Curing reactions in thermoplastic prepolymers such as polystyrene and the corresponding polystyrene/AP (25%/75%) have been studied,[9] and the changes in the viscosity average molecular weight with time indicate that the nature of the curing reactions are simialr for both the neat prepolymer and the prepolymer in the propellant. Prolonged curing of the CTPB binder and the propellant beyond 168 h was avoided to insure that they did not start aging at this temperature.

Percentage gel contents of the binder and propellant samples during aging are also presented in Fig. 7 and Table 1. It may be seen that the gel content, after remaining constant for 100-160 h at 80°C, shows significant increase with time when the propellant is subjected to aging at 120°C. This additional increase in gel content during aging is attributed to further cross linking at the double bonds and not at the COOH. This result is qualitatively in accordance with the work reported by Layton.[10] It may be noted that there is an increase in the gel content of about 14% in the neat binder and 20% in the propellant binder. Even allowing for the errors involved in the gel estimation, the increase in the gel content in the neat binder is still less. This increase can be attributed to the cross linking of polymer chain ends containing no COOH groups (which form a small portion of the binder) through the double bonds at the aging temperature. The difference in the extent of the gel content of the neat binder and propellant binder under identical conditions suggest that either the mechanism of cross linking and/or the rate is different in the two cases.

In case the mechanisms are different, one can envisage a proton-transfer mechanism and a free-radical mechanism. In the case of the neat binder it has to be a free-radical cross linking, but it may not be in the propellant. Schdelbaur[2] has shown that $HClO_4$ in the presence of moisture is a good cross-linking agent for the double bonds. It has also been shown in this laboratory[11] that the aging of composite solid propellants is through a proton transfer in the AP, which will produce $HClO_4$. The cross-linking process through a proton transfer can be visualized as follows:



$$\sim CH_2-CH=CH-CH_2\sim \xrightarrow{H^+} \sim CH_2-\overset{\oplus}{C}H-CH_2-CH_2\sim$$

$$\downarrow \quad \sim CH_2-CH=CH-CH_2\sim$$

$$\begin{array}{c} \sim CH_2-CH-CH_2-CH_2\sim \\ \sim CH_2-CH-\underset{\oplus}{C}H-CH_2\sim \\ \downarrow -H^+ \\ \sim CH_2-CH-CH_2-CH_2\sim \\ | \\ \sim CH_2-CH-CH=CH\sim \end{array}$$

Thus, the most favorable cross-linking process in the propellant would be the proton-transfer mechanism, as compared to the free-radical mechanism. It may be noted that the activation energy for the proton-transfer process[11] (~13 kcal/mole) is much lower than the anticipated activation energy for a thermally initiated free-radical process.

Cross-Link Density

The gel content measurements give only a qualitative idea about the extent of cross linking. The precise parameter, which indicates the extent of cross linking in the polymers, is the "cross-link density" or the V_e/V. The cross-link densities obtained by both the CMA and TMA methods are given in Table 2. Figue 8 represents a plot of cross-link densities vs storage time. The order of cross-link density values obtained from CMA and TMA differ. This difference may be attributed to 1) solvent-swollen samples are used in CMA, whereas unswollen samples are used in TMA; and 2) the range of load employed in CMA and TMA are quite different. In CMA, up to a 1000 g load was used and in TMA up to 50 g was employed. The superiority of CMA or TMA cannot be settled at this stage, but it is likely that TMA gives more precise data. It is evident from Table 2 that there is a continuous increase in the cross-link densities of the binder sample during aging.

Penetration Temperature of the Binder

It can be seen that the penetration temperature of binder sample increases with the storage time (Table 1). Penetration temperature is analogous to the softening temperature of the polymers. During aging, as a result of continuous cross linking in the polymer backbone, the structure of the cross-

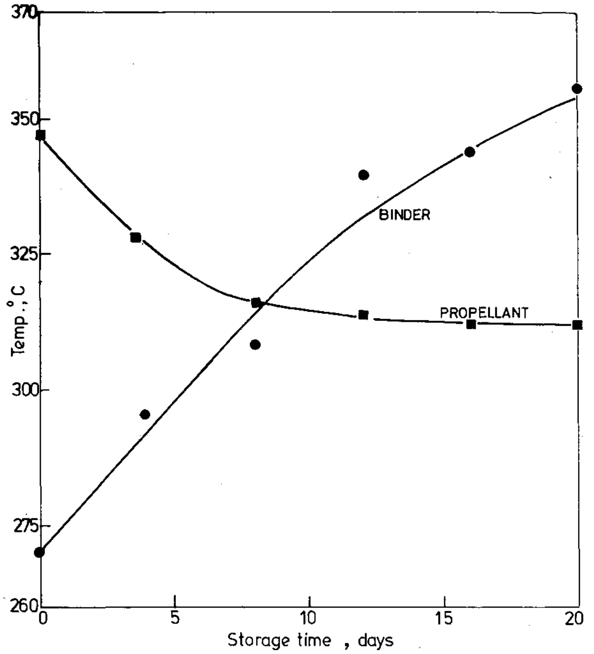


Fig. 9 Plot of ignition temperatures of propellant and binder as a fucntion of storage time.

linked binder becomes compact and rigid, making the penetration more and more difficult. Hence, the penetration temperature increases during aging. Comparison of columns 2 and 3 in Table 1 presents some interesting features. The gel content shows a marginal increase; on the other hand, the penetration temperature shows a drastic increase. This suggests that the increase in the cross-link density need not necessarily increase the gel content, particularly when all of the end groups are cross linked and further cross linking is through the double bonds within the network.

All the above-mentioned facts support the occurrence of thermal cross linking in the CTPB binder during aging. The thermal cross linking in polybutadiene has been studied before,[12] wherein a qualitative mechanism based on a free-radical process has been proposed.

Ignition Temperature of Binder and Propellant Samples

Ignition temperatures of the binder and propellant samples are given in Table 1, and a plot of the same as a function of the storage time is given in Fig. 9. It can be seen that the ignition temperature of the binder increases with storage time, whereas a reverse trend is obtained for the propellant samples, an interesting and an intriguing observation.

It is known that polymer ignition is generally governed by the gas-phase reactions.[13,14] This would then suggest that a polymer having a higher rate of gasification ignites at a lower temperature and has a lower ignition delay as compared to one where the rate of gasification is less. In addition, the degree of cross linking in the polymer affects main chain scission prior to gasification. The activation energy for the main chain scission of a highly cross-linked polymer is greater than that of a less cross-linked polymer.[11] Hence, binders with a higher extent of cross linking (aged samples) should have lower rates of gasification compared to those with a lower amount of cross linking.

To confirm this view, dynamic TG measurements (heating rate of 10°C/min) were carried out for aged (20 days stored) and unaged binder samples (Fig. 2). It can be clearly seen that the degradation rate is faster for the unaged binder, thus supporting the desensitization in the observed ignition temperatures of the binder samples during aging. The observation that the ignition temperature of the binder increases and that of the propellant decreases with aging time suggests that the rate-controlling mechanisms of the two are quite different.

Conclusions

The following conclusions can be derived from the work presented in this paper:

1) The measurement of the gel content during the curing of neat CTPB and CTPB present in the propellant formulation has shown that the mechanism of curing CTPB remains the same in both cases. It has been observed in both cases that curing at 80°C is completed after 100 h.

2) When the cured propellant is aged at 120°C, the gel content increases further because of further cross linking at the double bonds. This additional cross linking occurs in the neat binder via a free-radical mechanism, but in the propellant similar cross linking is controlled by proton transfer.

3) Ignition temperatures of the neat binder in oxygen and of the propellant show an opposite trend as a function of aging time at 120°C. This shows that the ignition mechanisms of the binder and the propellant are quite different.

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