

Lifetime Prediction of Carboxyl-Terminated Polybutadiene (CTPB)

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SYNOPSIS

Carboxyl-terminated polybutadiene (CTPB) was subjected to temperature and humidity aging in order to estimate its useful lifetime as a solid propellant binder. CTPB samples were temperature aged from 1 week to 7 months at various temperatures ranging from 50 to 100°C. At various stages of temperature aging, viscosity of the samples were measured, end group analyses were performed, and the samples, after being crosslinked with MAPO, were mechanically tested. As far as mechanical properties are concerned, the ultimate tensile stress of the samples decreases with temperature aging and strain at break increases. End group analyses indicate that acid value of the samples decreases with aging and viscosity increases. The results of temperature aging were applied to an Arrhenius type time-temperature superposition relation and useful lifetime of CTPB as binder at 20°C was predicted to be around 10 years. The CTPB samples were also humidity-aged and the effects of humidity aging on mechanical properties were investigated. The results indicate that similar to temperature aging, ultimate tensile strength decreases and strain at break increases with aging. The effects of humidity aging, however, is much less pronounced in comparison to temperature aging.

INTRODUCTION

Carboxyl-terminated polybutadiene (CTPB) is a reactive liquid polymer which is mainly used in elastomer modified epoxy resins for applications such as structural adhesives, glass fiber reinforced composites, coatings, and electrical encapsulations.¹ It is also used in composite rocket propellants as a binder.

During long term storage, the chemical composition, the physical properties, and consequently the mechanical properties of CTPB may change. Particularly, long term storage leads to a decrease in mechanical properties, to disappearance of the terminal carboxyl functional groups, and to an increase in the polymer viscosity. Since the mechanical and ballistic properties of solid composite propellants are affected from the properties of the CTPB used

in their manufacture, lifetime expectations of CTPB during storage becomes an important issue.

Effects of long term storage on the properties of CTPB can be simulated by thermal aging. Previously, Okamoto² reported on thermal aging of CTPB. In the present investigation, a thermal aging study of this reactive liquid was conducted in the same temperature range as that used by Okamoto,² but at longer aging times and at specified humidity conditions. The effects of thermal aging on the mechanical properties of CTPB were also investigated in this work.

EXPERIMENTAL

CTPB used in this work was supplied by Thiokol Chemical Co. (HC 434). The properties of the untreated liquid polymer were determined before the aging studies and these properties are summarized in Table I.

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Table I The Properties of Untreated CTPB

Ultimate tensile strength	4.2×10^6 Pa
Strain at break	147%
Equivalent weight	2160 g
Number average molecular weight	3500
Functionality	1.623
Acid value	20.88 mg/g
Brookfield viscosity at 25°C	51.8 Pa s

In order to investigate the effects of aging on CTPB and resulting property changes, two types of conditioning were applied to CTPB samples:

1. Temperature conditioning
2. Humidity conditioning

For the temperature aging experiments, liquid polymer samples were placed in ovens at 50, 65, 75, 82, 90, and 100°C. Different samples were kept in the oven for different time intervals ranging from 1 week to 7 months. Each sample upon removal was tested as described below.

In order to investigate the effect of humidity on the mechanical properties of the CTPB, the polymer samples were placed in humidity chambers (Thermotron SM 32S). In these experiments a typical humidity cycle runs for 24 h. In such a cycle, the temperature was raised from 28 to 65°C in 2 h, then kept at 65°C for the following 6 h and finally it was gradually reduced back to 28°C with a rate of 2.3°C/h. The humidity in the chamber was raised to and kept at 95% for the period in which oven temperature was 65°C. In the remaining 16 h, while the temperature was being decreased to 28°C, the moisture in the chamber was above 85%. A schematical time-temperature diagram for the humidity cycle is depicted in Figure 1. After 1, 3, 10, and 30 cycles, CTPB samples were removed from the humidity chambers for testing.

Mechanical Testing

In order to apply mechanical testing, first a gel must be prepared from the liquid polymer. Consequently, some preliminary studies were needed to obtain optimum gelation conditions to be used for the preparation of samples for mechanical testing.

CTPB is a linear, difunctional molecule that requires the use of a polyfunctional crosslinking agent to achieve a gelatinous state. MAPO (tris-2 methyl azridinyl 1-1 phosphine oxide) has been used effectively as a curing agent for polymers containing car-

boxylic acid end groups. The determination of optimum MAPO/CTPB ratio is important, since this ratio directly influences the mechanical properties of the product gel.

The effect of MAPO concentration on ultimate tensile stress and strength at break was studied.³ An optimum ratio of 4.5/95.5 (by weight) for MAPO/CTPB was found where the tensile stress is high and strain at break is almost constant. Following the optimization of MAPO content an optimum for curing time was also searched. It has been concluded that a minimum of five days are required for curing in order to achieve stable mechanical properties of the product which indicate the completeness of the curing reaction.³

In the actual mechanical testing experiments, samples containing 4.5% MAPO were prepared from aged liquids by mixing under vacuum and these samples were cured at 65°C for 7 days. At the end of the curing, the mechanical properties were tested in Instron machine at a crosshead speed of 5 cm/min at 25°C.

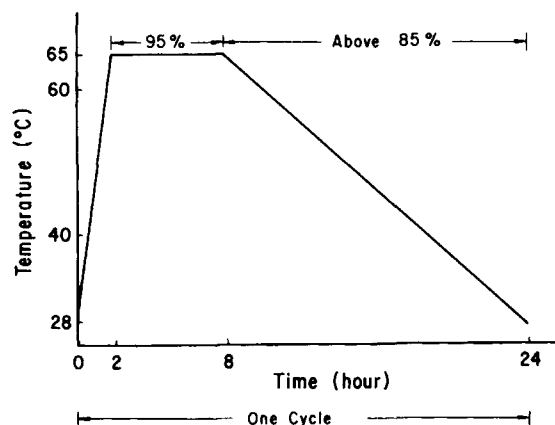
The reported experimental values are averages of five samples. The reproducibility of the data was within 5%.

End Group Analysis

A sample of 2–3 g of CTPB was dissolved in 100 mL mixture of toluene and isopropanol (60/40 by volume) and titrated with 0.1 N KOH in ethanol using thymol blue as indicator.

The acid values, that is milligram of COOH per gram of CTPB, were calculated by using the following relation:

$$\text{acid value} = (V_{\text{KOH}} N_{\text{KOH}} W_{\text{COOH}}) / m_{\text{CTPB}} \quad (1)$$

**Figure 1** Cycle in the humidity chamber.

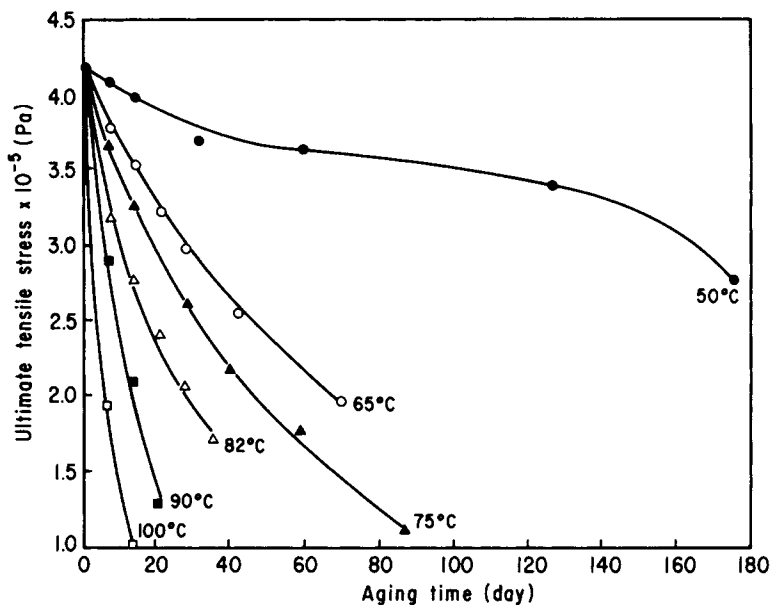


Figure 2 Ultimate tensile stress as a function of aging time.

where V is the volume of the KOH in milliliters which is consumed during titration, N is the normality of KOH, m is the weight of CTPB in grams and W is the formula weight of COOH group. The experiments were repeated with five samples and the reproducibility was found to be within 5%.

Viscosity Measurements

Viscosity measurements were performed in a Brookfield Synchro Lectric RVP model viscometer using spindle no. 4 at 25°C.

RESULTS AND DISCUSSION

Effects of Thermal Aging

Effects of thermal aging on mechanical properties of the CTPB are shown in Figures 2 and 3. These results show that the ultimate tensile stress decreases and the strain at break increases with aging time. The rate of decrease in ultimate tensile stress and the rate of increase in strain at break increases as the aging temperature increases. It is proposed that the change in mechanical properties stems from the decrease of functional groups of the polymer

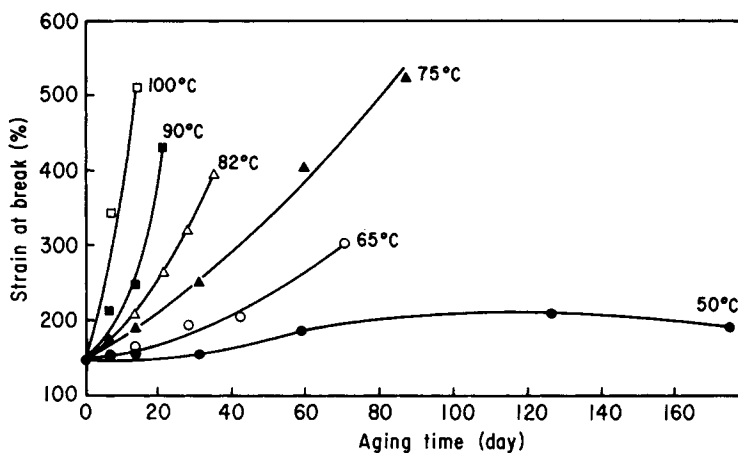
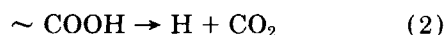


Figure 3 Strain at break as a function of aging time.

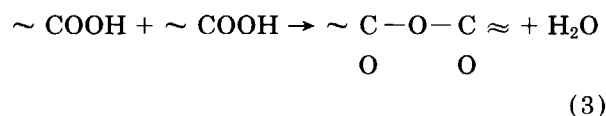
during aging. As the functional groups decrease, the number of crosslinks in the polymer network also decreases and the linear bonds become longer in the reaction of CTPB with MAPO causing a decrease in the ultimate tensile stress and an increase in the strain at break. It is also highly probable that the concentration of loose ends increase as a result of limited reactivities of such groups during thermal degradation.

Figure 4 shows the acid value versus aging time at six different aging temperatures. As the aging time and temperature increase, the acid value decreases. This means that functionality decreases as aging time and temperature increases. The rate of decrease in the acid value is higher at higher aging temperatures.

A possible cause of disappearance of acid groups is a decarboxylation reaction²:



Another possible cause of decrease in acid groups is acid-anhydride formation reaction that occurs by dehydration²:



The disappearance of acid groups due to loss of CO_2 has been reported by several workers in the literature.⁴

Among the two mechanisms considered, the latter appears to be more applicable, since the viscosity increase accompanies a decrease in the acid value.

A quantitative mechanism however could not be established.

The effects of thermal aging on viscosity of CTPB is depicted in Figure 5. It can be concluded from the figure that there is an increase in the viscosity of CTPB during aging. Like other properties the rate of increase of viscosity is higher at higher aging temperatures. Similar results were reported by Okamoto.²

Loss of volatile material cannot be a major cause of slow, steady viscosity increase, because the loss of volatile materials occurs in the first 20 h of thermal aging, also the volatile material content of CTPB is lower than 1.0%.²

Kishore et al.⁵ attributes the additional increase in viscosity during aging to further crosslinking at the double bonds of CTPB molecules instead of at the COOH group. This result is qualitatively in agreement with the work of Layton.⁶ The results of a detailed FTIR work will help to clarify this point.⁷

Effect of Humidity Aging

During humidity aging studies, the samples underwent humidity cycles described earlier in the experimental section for different time intervals. To show the results of humidity aging on the properties of CTPB, the mechanical properties were depicted as a function of conditioning time in Figure 6. The results indicate that there is a decrease in the ultimate tensile stress and an increase in the strain at break point with an increase in conditioning time. When compared with thermal aging, it is seen that the various properties tested were less severely affected by humidity aging.

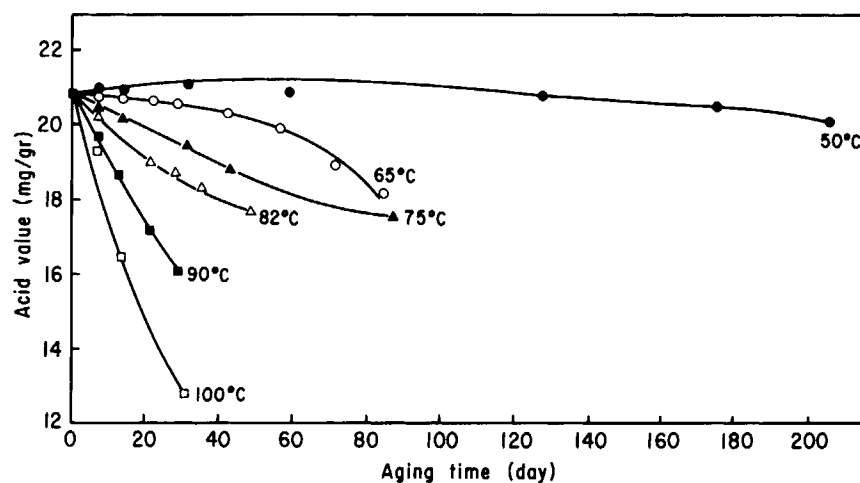


Figure 4 Acid value as a function of aging time.

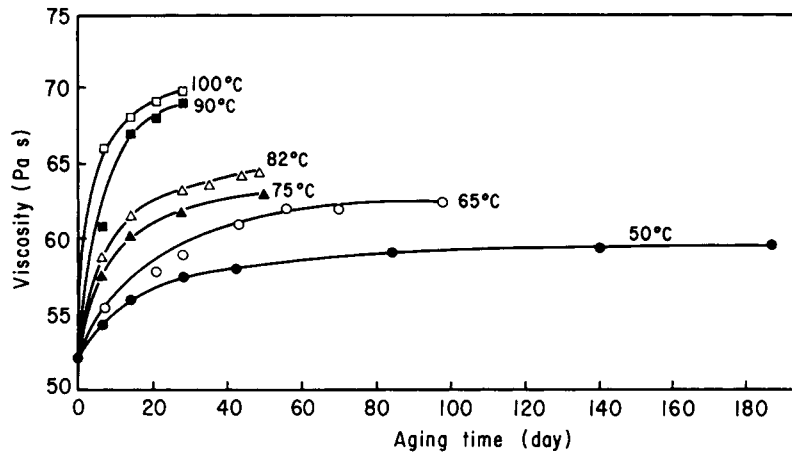


Figure 5 Polymer viscosity as function of aging time.

Lifetime Prediction

The knowledge of the useful life of a polymer is of fundamental importance to its application. Like many other polymers, the physical and chemical properties of CTPB is altered with time, and this affects the performance of the products manufactured from CTPB. Since this material is used as a prepolymer for composite rocket propellants, deterioration of its properties with time becomes cru-

cially important for the performance of the rocket. Therefore, a realistic estimate of the useful lifetime of CTPB is necessary.

The ultimate tensile stress of the composite material prepared from the unaged CTPB is 4.2 kg/cm^2 .³ According to the military standards, no polymeric binder can be used in the production of a propellant which has an ultimate tensile stress value less than 3.0 kg/cm^2 .⁸ The starting tensile stress values of the samples considered in this study are considerably higher than this limiting value and it takes a very long period of time for this value to decrease to the specified limit under normal storage temperatures. As a result, in the present study, to accelerate the decay in ultimate tensile stress, the samples were stored at elevated temperatures and the results are extrapolated to normal storage temperatures using the principle of time-temperature superposition.

An Arrhenius-like relation is used in the present work to predict the lifetime of CTPB. This technique is widely used in propellant industry.⁹ The method is based on a concept of "half-lifetime" defined as the time necessary to elapse for a specified reduction in a set of selected properties of the polymer. The time-temperature superposition is believed to follow an Arrhenius relationship,

$$t = t_0 \exp(E/RT) \quad (4)$$

where E is the activation energy of the degradation process, generally accepted to be constant, t is the lifetime, R is the gas constant, T is the aging temperature, and t_0 is the preexponential factor.

The aging times corresponding to 3.0 kg/cm^2 ultimate tensile stress at each aging temperature were

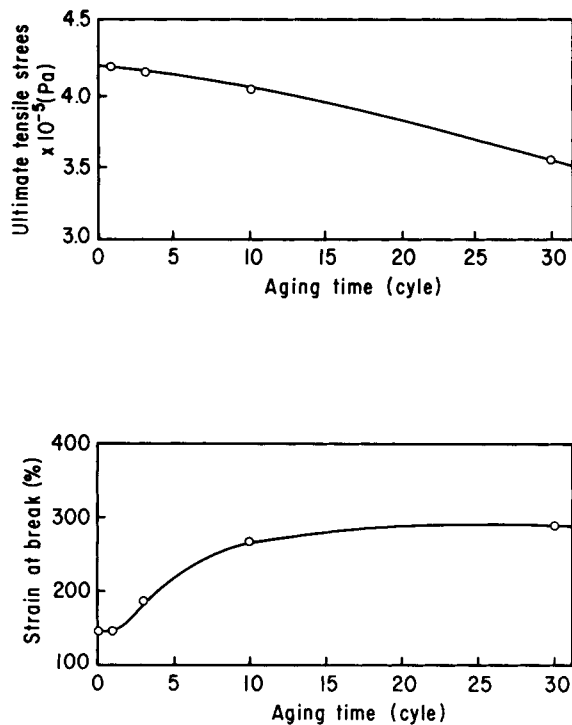


Figure 6 Ultimate tensile stress and strain as a function of aging time after humidity conditioning.

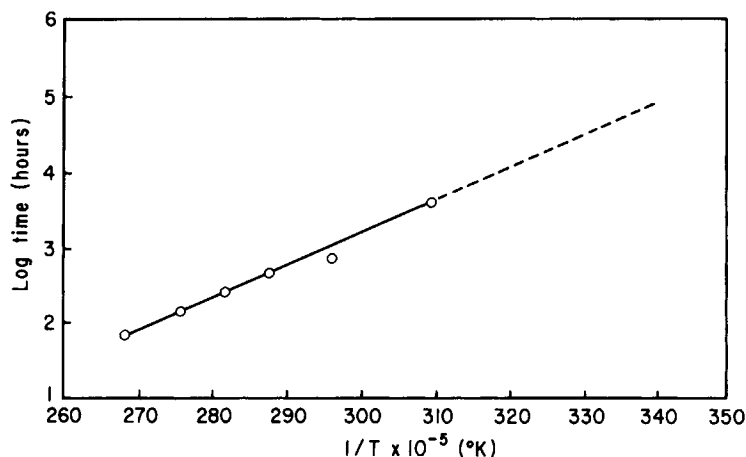


Figure 7 Life time prediction using ultimate tensile stress values.

read from Figure 2. Then according to eq. (5), the logarithm of aging time was plotted as a function of the reciprocal of the aging temperature. The resulting line was then extrapolated to the normal storage temperature of 20°C, and the corresponding life time was determined to be 10.17 years as can be seen from Figure 7. The linearity of the plot can be taken as a justification of the assumption made for eq. (5), namely, constancy of the activation energy in the temperature interval studied.

The same technique was also applied to other properties to predict the respective life times. For this purpose the average values of strain at break, acid value, and viscosity corresponding to 3.0 kg/cm² ultimate tensile stress were read from Figures 3, 4, 5, respectively at six different aging temperatures and these readings were again plotted according to eq. (5). The lifetime of CTPB according to strain at break, the acid value, and viscosity were found to be 9.72, 10.17, and 9.72, respectively. From these results we can say that CTPB polymer used in the present study fulfills its elastomeric properties as a solid rocket fuel when stored for a period of ten years at room temperature.

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REFERENCES

1. R. S. Drake, D. R. Egan, and W. T. Murphy, *Am. Chem. Soc. Org. Coating Appl. Polym. Sci. Proc.*, **46**, 392 (1982).
2. Y. Okamoto, *Polym. Eng. Sci.*, **23**, 222 (1983).
3. TUBITAK SAGE Technical Bulletin No. 1, 1987.
4. D. M. French and L. Rosborough, *J. Appl. Polym. Sci.*, **10**, 273 (1966).
5. K. Kishore, V. R. Pai Verneker, V. Gayathri, K. R. Shubna, and K. Sridhara, *J. Spacecraft*, **20**, 371 (1983).
6. L. H. Layton, AFRPL-TR-74-16, 1974.
7. N. Koc, R. Ozturk, and O. Guven, to appear.
8. A. M. Ball, Engineering Design Handbook Series, Solid Propellants Part I, U.S. Army Material Command, U.S. Gov. Printing Office, Washington, DC, 1963.
9. A. Ram, O. Zilber, and S. Kenig, *Polym. Eng. Sci.*, **25**, 535 (1985).

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