Aging of HTPB/AP-Based Composite Solid Propellants, Depending on the NCO/OH and Triol/Diol Ratios

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ABSTRACT: Aging behavior of hydroxyl-terminated polybutadiene/ammonium perchlorate (HTPB/AP)-based composite solid propellants was studied as a function of crosslink density, which is predominantly determined by the molar ratio of diisocyanate to total hydroxyl (NCO/OH ratio) and the molar ratio of triol to diol (triol/diol ratio). For this purpose, 16 propellant samples with different compositions were prepared by changing the NCO/OH ratio as 0.81, 0.82, 0.83, and 0.85 for each triol/diol ratio of 0.07, 0.09, 0.11, and 0.13, and subjected to an accelerated aging at 65°C. The changes in the mechanical properties were monitored throughout the aging period. In the initial part of the aging period, a sharp increase in stress, modulus, and hardness values and a sharp decrease in strain values were observed for all the propellants. At further stages of aging, only slight changes were observed in the mechanical properties. Concerning the aging criterion as reduction in the strain capability more than the half of the initial value, the propellants with respective NCO/OH-triol/diol ratios of 0.81–0.09, 0.85–0.09, 0.81–0.13, 0.83–0.13, and 0.85–0.13 can be considered to be aged with time. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 79: 959–964, 2001

Key words: composite; propellant; mechanical properties; aging; HTPB; triol; diisocyanate

INTRODUCTION

Aging of the composite solid propellant is an important issue in rocket motor applications, as it determines the service life of a rocket motor. In essence, aging is defined as the deterioration of the solid propellant altering the performance characteristics of the solid rocket motors. Owing to the large surface area and chemical energy potential, the composite propellants are subjected to deterioration during handling, storage, and operation stages leading to changes in both the ballistic and mechanical properties.[1]

The extent of crosslink density in the binder matrix significantly affects not only the mechanical but also the aging properties of the composite propellant. The crosslink density can be adjusted by varying the amounts of the prepolymer diol (hydroxyl terminated polybutadiene, HTPB), curing agent (isophorone diisocyanate, IPDI), and the triols (triethanol amine, TEA). These are the main components making the network structure, the formation of which is practically completed at the end of curing period. In this respect, the equivalent ratios of the reacting species, namely

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NCO/OH ratio (or R value) and triol/diol ratio are useful tools to adjust the crosslink density and to obtain satisfactory mechanical and aging properties.

In composite propellants, aging occurs via oxidative crosslinking of the polymeric binder, migration of additives, and recrystallization of the oxidizer,[2,3] while the polyurethane (. . .—O—CO—NH—. . .) formation is practically completed within the curing period and, therefore, does not make any significant contribution to the aging of the propellant.[4] The migration of the plasticizer predominantly causes the hardening of the propellant layer and influences the layer adhesion.[5,6] The hardening of HTPB and CTPB (carboxy-terminated polybutadiene) based propellants during aging was attributed to the crosslinkage through the double bonds present in the main chain.[7] In this respect, it has been shown that the perchloric acid, $HClO_4$, generated from the decomposition of AP in a trace amount, catalyses the crosslinkage of the polymeric chains through the double bonds in the presence of moisture.[8]

In the preceding article,[9] we reported the changes in mechanical properties of hydroxyl-terminated polybutadiene/ammonium perchlorate (HTPB/AP)-based composite solid propellants during the curing period, depending on the variations in crosslink density, which is predominantly determined by the molar ratio of diisocyanate to total hydroxyl (NCO/OH ratio) and the molar ratio of triol to diol (triol/diol ratio). Here, we would like to report on the aging study of the same 16 propellants having various NCO/OH and triol/diol ratios at 65°C.

EXPERIMENTAL

Materials

HTPB (RM-45, average molecular weight of 2700 g/mol, functionality of 1.93, with antioxidant additive of 0.1% by weight, ARCO Chemical Company, Philadelphia, PA), isophorone diisocyanate, IPDI (Fluka AG, Leverkusen, Germany), dioctyl adipate, DOA (Nursan Polimer Kimya A.S., Istanbul, Turkey), triethanol amine, TEA (Merck, Darmstadt, Germany), Tepanol (Dynamar, HX-878, 3M, Cottage Grove, MN), crystalline ammonium perchlorate, AP (average particle size of 200 μm, SNPE, Paris, France), aluminum powder (average particle size of 10.4 μm, ALCAN TOYO, Maitland, FL), and iron(III) oxide (average particle diameter of less than 1 μm, BASF, Ludwigshafen, Germany) were used as purchased. In addition to the coarse AP, fine AP particles with the average particle diameter of 10 μm were obtained by grinding the coarse ones in a laboratory mill (Alpine, Type 160 Z).

Preparation of Propellant Samples

In the formulation of the propellants with 87% solid loading, the sizes, distributions, and the amounts of solids, as well as the amount and the characteristics of the bonding agent were kept constant throughout the study to observe the effect of the binder matrix on the tensile properties of the propellants. For this purpose, 16 propellant samples with different compositions were prepared by changing the NCO/OH ratio as 0.81, 0.82, 0.83, and 0.85 for each triol/diol ratios of 0.07, 0.09, 0.11, and 0.13. In all experiments, 3 kg of propellant was produced in a stainless steel, 1 gallon, vertical blade, Baker Perkins mixer. The mixing was initiated by premixing the liquid components of HTPB, DOA, TEA, and Tepanol at 65°C for about 10 min. Then, the solid ingredients of iron(III) oxide, aluminium, and coarse AP were added and continued mixing for 30 min. After pouring fine AP and further mixing for about 3 h, the curing agent IPDI was added and mixed for 15 min. Having finished the mixing process, the propellant mixture was cast into the preheated, Teflon-coated molds in vacuum and then left to cure at 65°C for 7 days. The samples were left to age at the same temperature for about 300 days.

Methods of Testing

The mechanical properties (uniaxial tensile properties) of the propellants were tested on Hewlett Packard Instron tester (model 1185, by JANAF procedure) every 30 days during the aging period of 300 days following the curing. Prior to the each testing, specimens were conditioned at 25°C for a day. The aged samples were tested for their mechanical properties (tensile strength, elongation at maximum stress, initial modulus) at room temperature with a crosshead speed of 50 mm/min.

The hardness of the propellants was measured by using Zwick Shore A tester according to the ASTM D 2240.[10] The needle of the tester was inserted into the specimen, and hardness values were read after waiting for 15 s.

Error Analysis

During the aging studies, the mechanical properties of a propellant for predefined period of time were determined by using two to three specimens, because the study was designed to proceed for a long period of time with only 3 kg of propellant. In error analysis, because the number of specimens was not enough to predict the standard deviation of the result of each test from the average value, the data obtained throughout the aging period for each single propellant formulation were pooled to improve the reliability of standard deviation. The pooled standard deviation, s_p, is used to perform several sets of analyses, for example, on different days, or on different samples with slightly different compositions rather than relying on a single set of data to describe the precision of a method.[11] This method is applicable if the samples have similar compositions and have been analyzed in identical way. Having followed such a method, the maximum standard deviations for stress, strain, and modulus were found to be ± 0.04 MPa, $\pm 7.0\%$, and ± 0.61 MPa, respectively. On the other hand, because the hardness measurements were performed for at least five different points on the surface of the propellant, standard deviations of these results were calculated by using the classical method and found to be ± 7 in the worst case.

RESULTS AND DISCUSSION

Aging of the propellant is generally pronounced when it loses the desired mechanical, ballistic, or thermal characteristics with time after being cured. In the present study, the aging behavior of the HTPB/AP-based composite solid rocket propellants was investigated by monitoring the changes in mechanical properties. Following the curing period, the propellants were subjected to an accelerated aging at 65°C and their mechanical properties were tested.

Curing of an HTPB-based composite propellant is due the reaction between isocyanates and diols giving the polyurethane network structure, and is known to be complete within 7 days, for example, at 65°C. Therefore, it is not expected to contribute to the aging. However, the excess amount of either isocyanate or hydroxyl groups may cause changes in mechanical properties during aging. Therefore, the effect of both the NCO/OH and triol/diol ratios on the aging characteristics was studied.

The aging behaviors of 16 propellants having various combination of NCO/OH ratio and triol/diol ratio are given in Figures 1–4. At first glance, one observes the presence of a general trend that

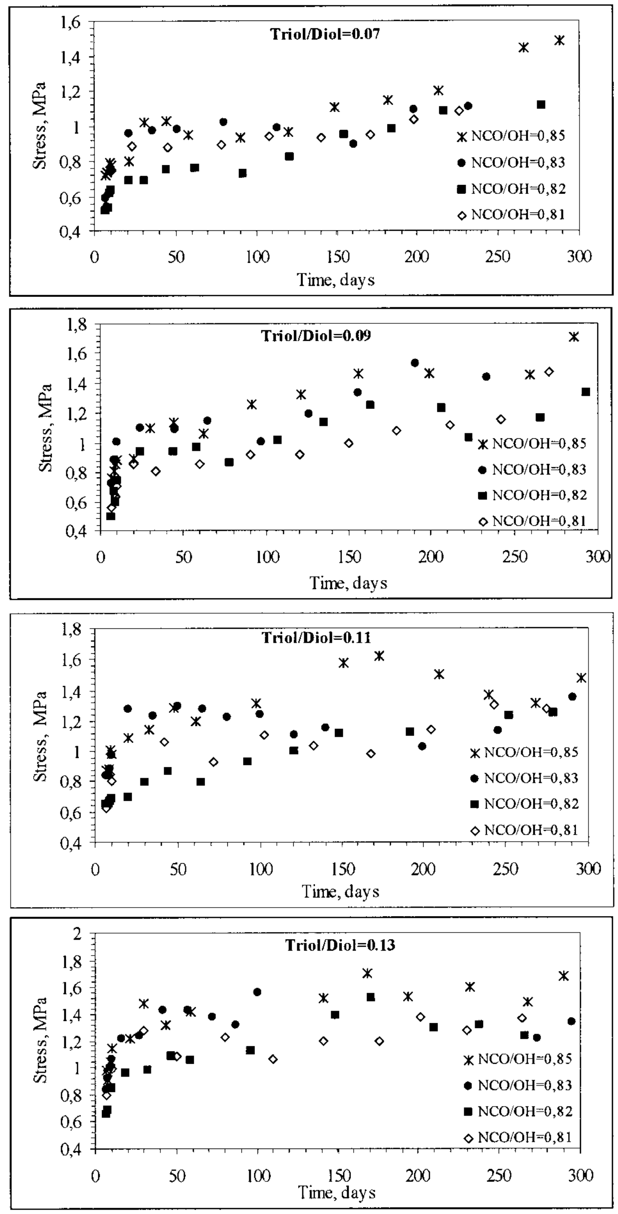

Figure 1 Change in stress with time and NCO/OH ratio for different triol/diol ratios.

the stress, modulus, and hardness values increase first sharply and then slightly, while strain values decreases in the same manner for all the propellants. However, the propellant with a higher NCO/OH or triol/diol ratio has higher values of stress, modulus, and hardness, and lower strain values throughout the aging period. Thus, the propellant having higher NCO/OH or triol/diol ratio is more likely to age and lose the properties with time. The sharp changes in the mechanical properties in the first days of aging pe-

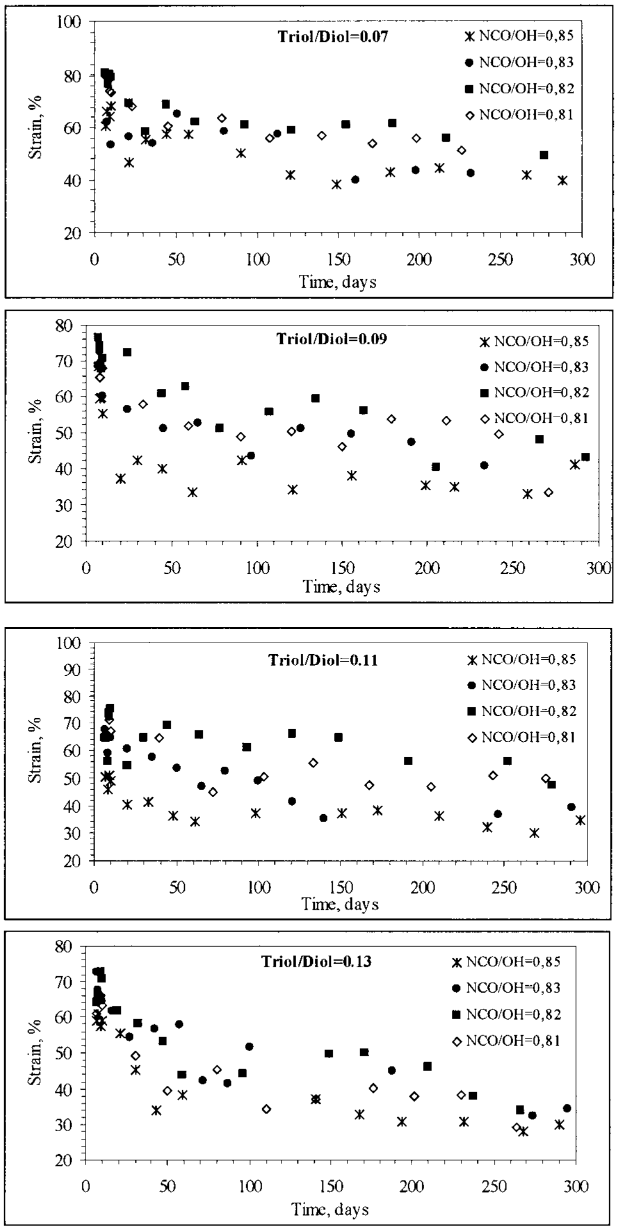

Figure 2 Change in strain with time and NCO/OH ratio for different triol/diol ratios.

riod are observed to be faster for the propellants having NCO/OH ratio of 0.85 or triol/diol ratio of 0.13 than those for the others. Consequently, high isocyanate content of the propellant or the high concentration of triol seems to be responsible for the rapid changes in mechanical properties during both curing and aging periods. The sudden changes in mechanical properties particularly of the propellant with higher NCO/OH ratios at a high triol/diol ratio cannot be attributed to the migration of plasticizer, which occurs essentially at the curing stage in the semicrosslinked propellant. The slight changes observed in the mechanical properties in the following days are most probably due to the low tendency of the propellants against deformation at very high crosslink density.

In the case of high OH content for the propellant having a low NCO/OH ratio, because the isocyanate was completely consumed during the curing reaction, the polymeric chains could be crosslinked through the C=C double bonds by

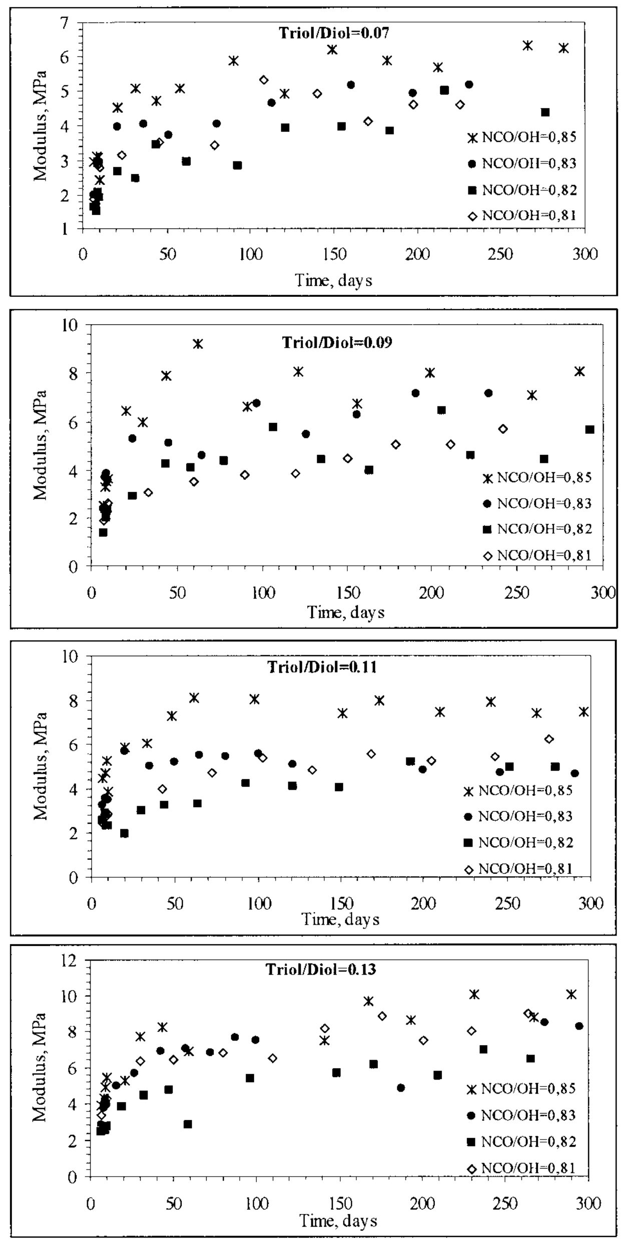

Figure 3 Change in modulus with time and NCO/OH ratio for different triol/diol ratios.

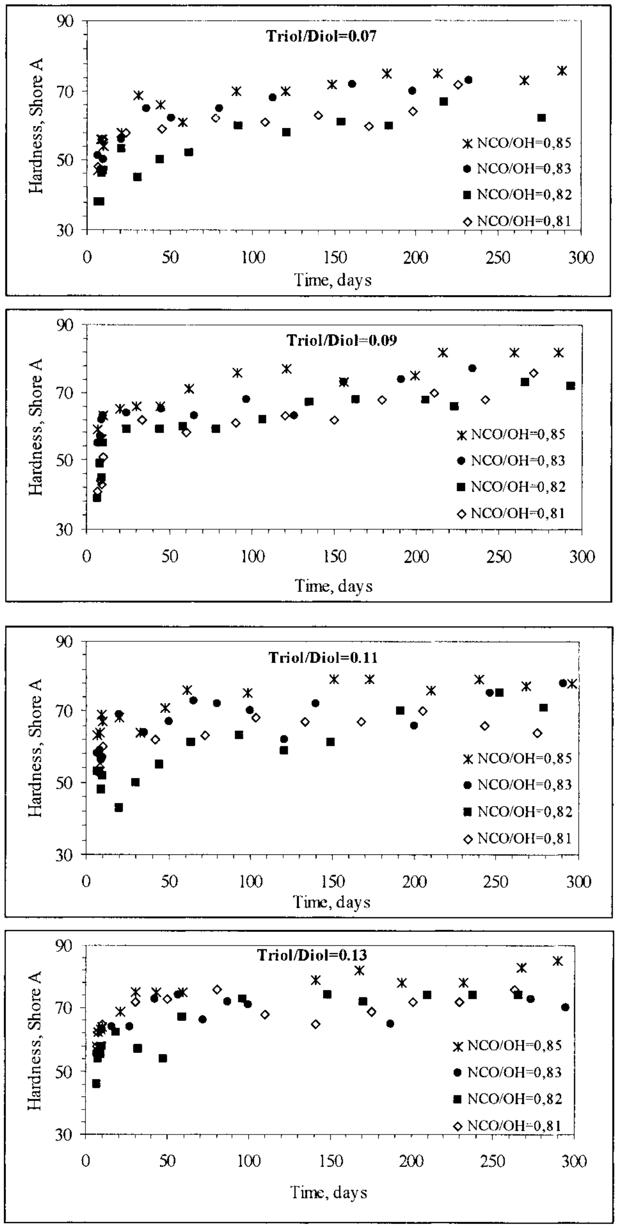

Figure 4 Change in hardness with time and NCO/OH ratio for different triol/diol ratios.

free radical mechanism, although the antioxidant, 2,2′-methylene-bis-(4-methyl-6-*tert*-butylphenol), added into HTPB to prevent the crosslinking through free radical mechanism, does not perform its job completely. Thus, crosslinking obviously proceeds by a free radical mechanism, which contains the following steps;[12] a chain scission at the weakest CH_2—CH_2 bond in a polydiene chain accompanied by a shift to terminal vinyl groups, formation of peroxy radiacal by oxygen attack, the chain propagation forming the active binder radical with hydroperoxide, crosslinking of two chain radicals, and termination reaction by the antioxidant.

In addition to the free radical mechanism, the enhancement in the crosslink density might be attained by crosslinking of the C=C double bonds of the main polyurethane chain through a proton transfer mechanism,[b,8c] in which perchloric acid, $HClO_4$, generated from the decomposition of ammonium perchlorate, acts as protonic initiator for the crosslinking reaction between the C=C double bonds of two polymeric chains. In this case, the bonding quality of the interphase between the polymeric binder matrix and the ammonium perchlorate particles seems to be important. The bonding agent used in the propellant should be effective enough to protect the binder from decomposition products of ammonium perchlorate because a good bonding agent may also be an aging inhibitor.[4] The most favorable crosslinking process in the HTPB/AP-based composite propellants would be the proton transfer mechanism, compared to the free radical mechanism. It may be noted that the activation energy of a proton transfer mechanism (~13 kcal/mol) is much lower than the anticipated activation energy for a thermally initiated free-radical mechanism.[8]

Although the requirements for the mechanical properties of composite solid rocket propellants are usually determined by the design of the rocket motor, and therefore, can vary depending on the designed motor, the propellants formulated with high NCO/OH and triol/diol ratios do not seem to be useful. It was found that the simultaneous use of high values for both ratios in propellant formulations yields a brittle composite material with higher stress, modulus, hardness, and lower strain capability. The loss in strain capability could be regarded as a reliable aging criterion in such a way that, generally, the critical storage time is defined as the time to produce an associated decrease in the initial strain at maximum stress by a factor of 0.5.[13] Thus, the propellants having a strain of less than the half of the initial value could be considered as the aged ones and having lost their mechanical properties and, therefore, could not be used further. In this sense, the propellants with respective NCO/OH-triol/diol ratios of 0.81–0.09, 0.85–0.09, 0.81–0.13, 0.83–0.13, and 0.85–0.13 were found to be the aged ones at the end of certain periods of time.

CONCLUSION

From the investigation of the effects of NCO/OH and triol/diol ratios on the aging of the HTPB/AP-based propellants, following points can be concluded:

(1) the stress, modulus, and hardness values increase first sharply and then slightly while strain values decreases in the same manner for all the propellants.
(2) The propellant with a higher NCO/OH or triol/diol ratio has higher values of stress, modulus, and hardness, and lower strain values throughout the aging period.
(3) The sharp changes in the mechanical properties in the first days of the aging period are observed to be faster for the propellants having an NCO/OH ratio of 0.85 or a triol/diol ratio of 0.13 than those for the others.
(4) The propellants having respective NCO/OH-triol/diol ratios of 0.81–0.09, 0.85–0.09, 0.81–0.13, 0.83–0.13, and 0.85–0.13 can be considered to be aged and, therefore, cannot be used further.

The results of this parametric investigation can readily be used in the design of composite propellants having suitable characteristics required for a particular rocket application.

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