Fine-Tuning the Mechanical Properties of Hydroxyl-Terminated Polybutadiene/Ammonium Perchlorate-Based Composite Solid Propellants by Varying the NCO/OH and Triol/Diol Ratios

ÖZGÜR HOCAOĞLU,[1] TÜLAY ÖZBELGE,[2] FIKRET PEKEL,[1] SAIM ÖZKAR[3]

[1] Tübitak-Sage, PK 16 Mamak, 06261 Ankara, Turkey

[2] Department of Chemical Engineering, Middle East Technical University, 06531 Ankara, Turkey

[3] Department of Chemistry, Middle East Technical University, 06531 Ankara, Turkey

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ABSTRACT: Changes in the mechanical properties of hydroxyl-terminated polybutadiene/ammonium perchlorate-based composite solid propellants were studied during the curing period with respect to variations in the crosslink density, which was predominantly determined by the equivalent ratio of diisocyanate to total hydroxyl (NCO/OH ratio) and the equivalent ratio of triol to diol (triol/diol ratio). For this purpose, 16 propellants were prepared in different compositions through changes in the NCO/OH ratios (0.81, 0.82, 0.83, and 0.85) for each triol/diol ratio (0.07, 0.09, 0.11, and 0.13) and were tested for their mechanical properties immediately after curing. The propellants with an NCO/OH ratio of 0.82 had minimum stress, modulus, and hardness with maximum strain capability, whereas the propellants with an NCO/OH ratio of 0.85 showed just the opposite behavior. Variations in the isocyanate level seemed to have more effect on the mechanical properties at higher triol/diol ratios. It was also concluded that the propellants with triol/diol–NCO/OH combinations of 0.11–0.83, 0.11–0.85, 0.13–0.81, 0.13–0.83, and 0.13–0.85 were not acceptable for upper stage case-bonded rocket applications because of either high tensile strength or high modulus. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 84: 2072–2079, 2002; DOI 10.1002/app.10605

Key words: composites; propellant; mechanical properties; curing; hydroxyl-terminated polybutadiene; triol; diisocyanate

INTRODUCTION

Solid propellant composed of oxidizing and reducing agents is the main propulsive source of the rocket motor. In a case-bonded configuration, solid propellant grains are subjected to a variety of stresses and strains due to the following: shrinkage during the cure process; differences in thermal expansion between the case material and the propellant; and transportation, storage, and flight.[1] A propellant grain should have sufficient tensile properties to withstand all these stresses and strains.[2] The mechanical properties of a propellant depend on the solid content, particle size, and particle size distribution in the solid part[3] and the bonding quality of the interphase between the solid particulates and the polymeric

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Correspondence to: S. Özkar (sozkar@mehtu.edu.tr).

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binder.[4] However, the mechanical properties are predominantly determined by the crosslink density in the binder matrix, which can be adjusted through variations in the relative amounts of the prepolymer diol, curing agent, and triol.[5] These three components react with one another to form a polyurethane network structure that makes the matrix looser or tighter at the end of the curing period. In this respect, the equivalent ratios of the reacting species, namely, the NCO/OH ratio (or R value) and the triol/diol ratio, are useful tools for adjusting the crosslink density and for obtaining satisfactory mechanical properties.[5] From a practical point of view, the mechanical properties must be fine-tuned by the NCO/OH and triol/diol ratios being varied in a narrow range so that the material will retain its processability for casting. This requires knowledge of the effect of NCO/OH and triol/diol ratios on the mechanical properties of the propellant.

Here we report the results of a study conducted to acquire such knowledge for a hydroxyl-terminated polybutadiene (HTPB)/ammonium perchlorate (AP)-based composite propellant containing HTPB as a diol, isophorone diisocyanate (IPDI) as a curative, and triethanol amine (TEA) as a triol. Sixteen propellants with an 87% solid loading (a rheological study gave the optimum solid loading of 87 wt % for the ingredients used)[6] were prepared in different compositions through changes in the NCO/OH ratios (0.81, 0.82, 0.83, and 0.85) for each triol/diol ratio (0.07, 0.09, 0.11, and 0.13) and were tested for their mechanical properties immediately after curing.

EXPERIMENTAL

Materials

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

Preparation of the Propellant Samples

To investigate the effects of the binder matrix on the tensile properties of the propellants, we kept constant the sizes, distributions, and amounts of solids, as well as the amounts and characteristics of the bonding agent, in the formulation of the propellants with an 87% solid loading[6] throughout the study. For this purpose, 16 propellant samples with different compositions were prepared through changes in the NCO/OH ratio (0.81, 0.82, 0.83, and 0.85) for each triol/diol ratio (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 (Saginaw, MI) mixer. The mixing was initiated by premixing of the liquid components (HTPB, DOA, TEA, and Tepanol) at 65°C for about 10 min. Then, the solid ingredients (iron(III) oxide, aluminum, and coarse AP) were added, and mixing continued for a while. After the pouring of fine AP and further mixing for about 3 h, the curing agent IPDI was added and mixed for a sufficient period of time. With the mixing process finished, the propellant mixture was cast into preheated, Teflon-coated molds *in vacuo* and left to cure at 65°C for 7 days.

Testing Methods

Uniaxial tensile testing of the propellants was carried out with a Hewlett–Packard Instron (Highwaycomb-bucks, England) tester model 1185 by the Joint Army National Navy Airforce (JANAF) procedure.[7] Before the testing, the specimens were conditioned at 25°C for 40 h. The cured samples were tested for their mechanical properties (tensile strength, elongation at maximum stress, and initial modulus) at room temperature with a crosshead speed of 50 mm/min. For each measurement, four samples were tested.

The hardness of the propellant was measured with a Zwick (Ulm, Germany) Shore A tester according to ASTM Standard D 2240.[8] The needle of the tester was inserted into the specimen, and the hardness values were read after 15 s.

Error Analysis

The mechanical properties of a cured propellant sample were determined with four specimens because of the limitation of the sample amount. In

Table I Mechanical Properties of Propellants with Various NCO/OH and Triol/Diol Ratios

NCO/OH Ratio	Triol/Diol Ratio	Ultimate Stress (MPa)	Strain at Maximum Stress (%)	Initial Modulus (MPa)	Hardness (Shore A)
0.81	0.07	0.60	79.7	1.86	48
	0.09	0.56	68.7	1.88	41
	0.11	0.63	65.7	2.45	53
	0.13	0.79	61.0	3.33	58
0.82	0.07	0.52	80.7	1.63	38
	0.09	0.49	76.7	1.37	39
	0.11	0.65	64.4	2.56	53
	0.13	0.66	64.0	2.45	46
0.83	0.07	0.59	80.3	1.99	51
	0.09	0.73	68.8	2.39	55
	0.11	0.84	67.6	3.21	58
	0.13	0.84	72.5	2.85	55
0.85	0.07	0.72	60.6	2.96	47
	0.09	0.77	68.6	2.50	59
	0.11	0.87	50.5	4.47	63
	0.13	0.98	58.9	3.92	58

error analysis, because the number of specimens was not high enough for prediction of the standard deviation of the result of each test from the average value, the data obtained throughout the study were pooled for improved reliability of the standard deviation. We used the pooled standard deviation to perform several sets of analyses, for example, on different samples with slightly different compositions, rather than relying on a single set of data to describe the precision of a method.[9] This method is applicable if the samples have similar compositions and have been analyzed in an identical way. Having followed this method, we found that the maximum standard deviations for stress, strain, and modulus were ±0.03 MPa, ±3.7%, and ±0.38 MPa, respectively. However, 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 with the classical method and found to be ±2 in the worst case.

RESULTS AND DISCUSSION

The mechanical properties of the HTPB/AP-based composite solid propellants were investigated with respect to the crosslink density of the polymeric binder in terms of the NCO/OH and triol/diol ratios. These ratios were varied through simultaneous changes in the amounts of TEA, IPDI, and HTPB. The relevant combinations of NCO/OH and triol/diol ratios used in the formulation of the propellants are listed in Table I. The selection of the NCO/OH ratio range was based on a previous study in which the optimum mechanical properties for HTPB/AP-based composite propellants were obtained when the NCO/OH ratio was within a range of 0.8–0.9.[1] Because the mechanical properties were very sensitive to the NCO/OH ratio, the range for this value had to be narrowed within 0.81–0.85 for the HTPB/AP-based propellants used in this study. The curing period was determined to be 7 days at 65°C for all of the propellants on the basis of the tensile strength, modulus, and hardness of the sample in the course of the curing reaction. Furthermore, the curing kinetics of the HTPB–IPDI mixtures were studied in bulk by quantitative FTIR spectroscopy, which confirmed the curing period of 7 days at 65°C.[10]

Mechanical Properties Depending on the NCO/OH Ratio

The tensile properties of a composite propellant depend on the characteristics of the polymeric binder matrix due to the changes in the crosslink density, which is strongly affected by the NCO/OH ratio. The variations in the mechanical properties of propellants with the NCO/OH ratio at the end of the curing period are shown in Figures 1–4 for different triol/diol ratios. All the

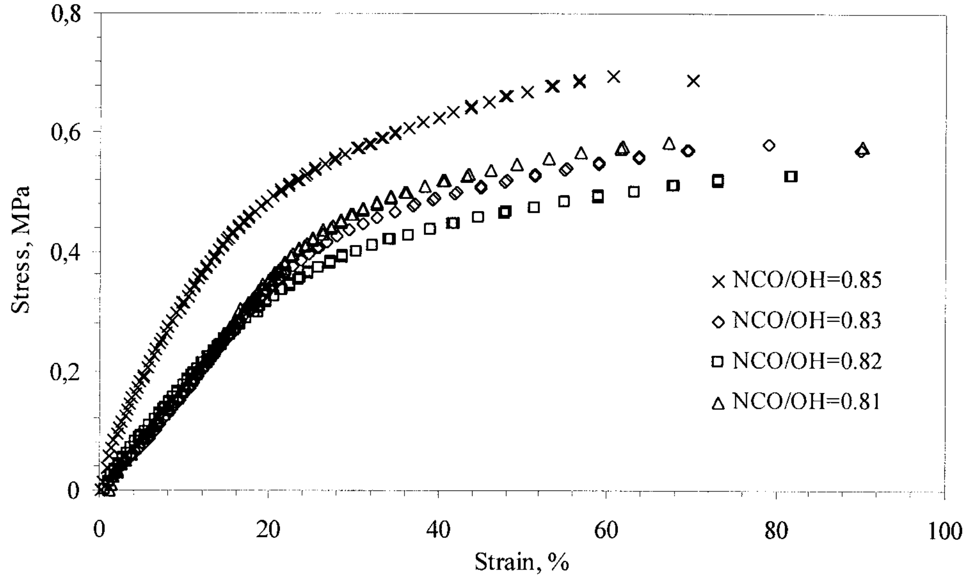

Figure 1 Stress–strain diagrams for the propellants with a triol/diol ratio of 0.07.

values for the mechanical properties listed in Table I were obtained as averages of four specimens. A careful inspection of the results given in Table I indicates that the stress, modulus, and hardness values first decrease with the NCO/OH ratio, reaching a minimum at an NCO/OH ratio of 0.82, and then start to increase for the propellants with triol/diol ratios of 0.07, 0.09, and 0.13, whereas for the propellants with a triol/diol ratio of 0.11, a regular increase is observed with the increasing NCO/OH ratio. Although only slight variations are observed in the mechanical properties as a result of the narrow range for the NCO/OH ratio, some meaningful conclusions can be obtained, for example, from the evaluation of strain values recorded at maximum stress. The strain capability of propellants is maximum at an NCO/OH ratio of 0.82 for the propellants with triol/diol ratios of 0.07 and 0.09. However, maximum strain capability is obtained at an NCO/OH ratio of 0.83 for the propellants with triol/diol ratios of 0.11 and 0.13.

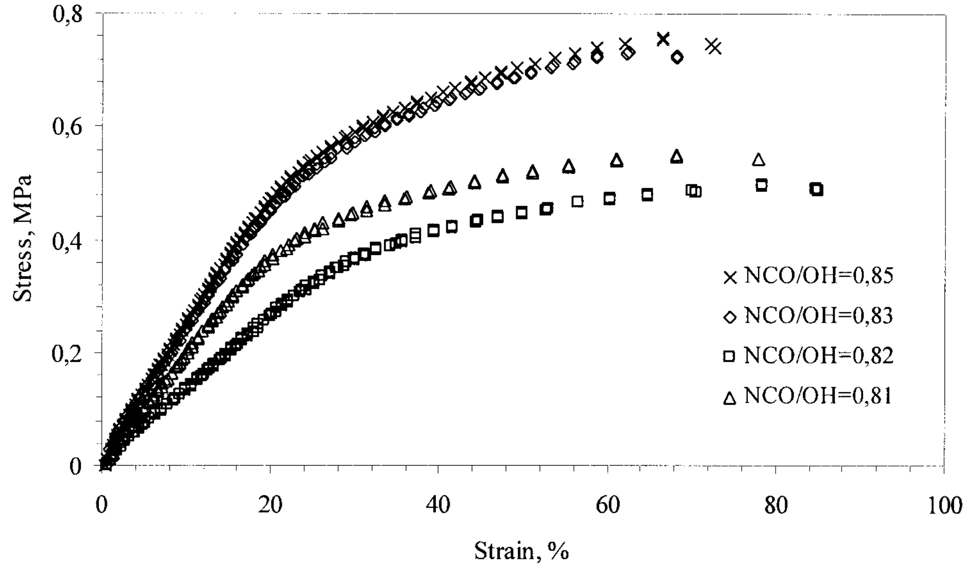

Figure 2 Stress–strain diagrams for the propellants with a triol/diol ratio of 0.09.

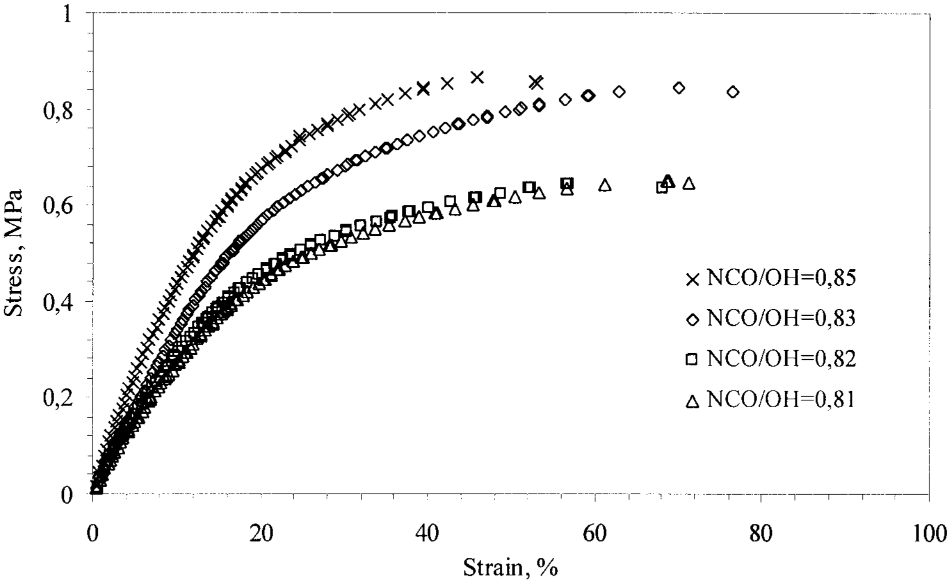

Figure 3 Stress–strain diagrams for the propellants with a triol/diol ratio of 0.11.

The hardness and modulus values follow almost the same trend with respect to the NCO/OH ratio. This observation can be attributed to the fact that the former measures the stiffness of the surface and the latter measures that of the bulk of the propellant. The increase in stress, modulus, and hardness and the decrease in strain with the NCO/OH ratio are expected because an increase in the NCO/OH ratio obviously leads to an increase in the crosslink density of the matrix.[11] The excess NCO functional groups give additional reactions with OH functional groups of the crosslinking agent TEA.

Mechanical Properties Depending on the Triol/Diol Ratio

One of the parameters influencing the structures of elastomers and their mechanical properties is the degree of crosslinking induced by the triol.[12]

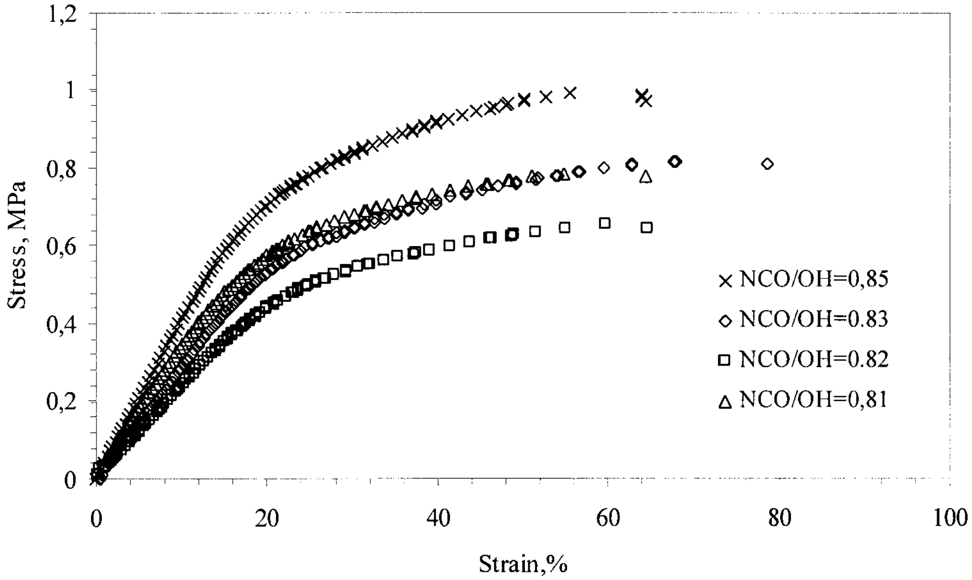

Figure 4 Stress–strain diagrams for the propellants with a triol/diol ratio of 0.13.

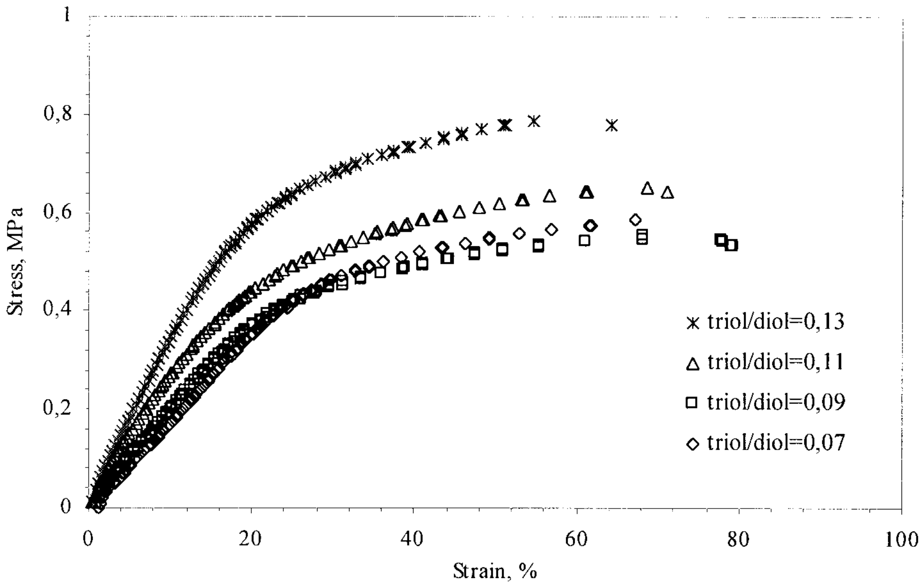

Figure 5 Stress–strain diagrams for the propellants with an NCO/OH ratio of 0.81.

HTPB resins with lower hydroxyl values or higher molecular weights, that is, lower functionality, require high triol contents to achieve higher tensile strength and modulus and moderately high elongation. At higher HTPB functionality, the effect of the triol content on the tensile strength is diminished.[1] Because the HTPB resin used in this study had a functionality of 1.93, it could not lead to the formation of an elastomeric matrix by reacting with diisocyanate alone. Therefore, a certain amount of TEA had to be used as a crosslinking agent to achieve enhanced gelation and formation of the three-dimensional network, which provided the improved mechanical properties. In this respect, the triol/diol ratio is another useful tool for controlling the physical and mechanical properties of HTPB-based propellants in addition to the NCO/OH ratio.

The stress–strain diagrams for the propellants with various triol/diol ratios at different constant NCO/OH ratios are given in Figures 5–8. The numerical values obtained from the stress–strain

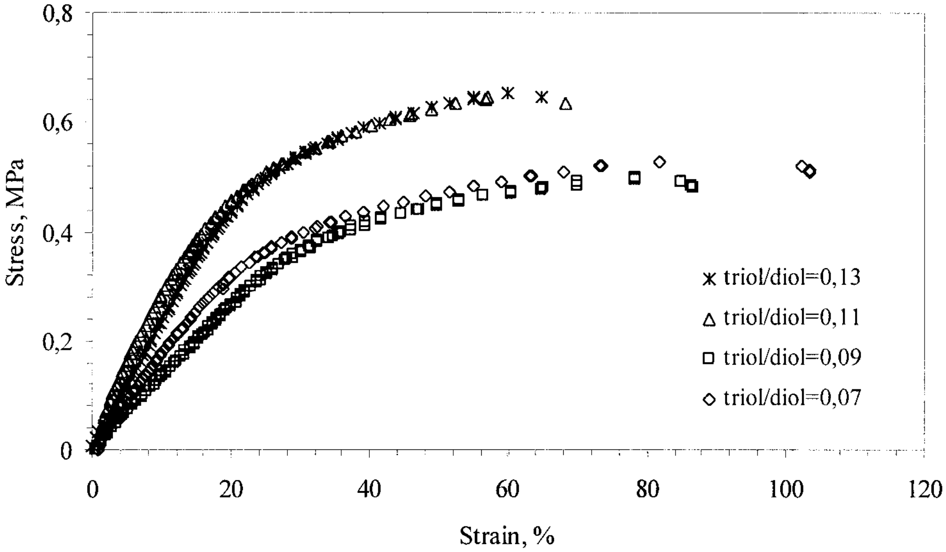

Figure 6 Stress–strain diagrams for the propellants with an NCO/OH ratio of 0.82.

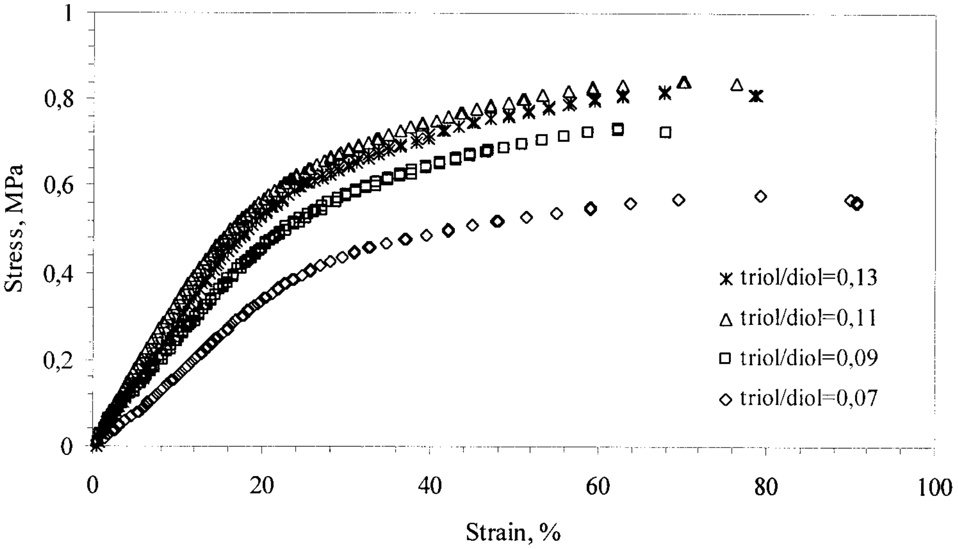

Figure 7 Stress–strain diagrams for the propellants with an NCO/OH ratio of 0.83.

diagrams for the stress, elongation, and modulus are listed in Table I.

As can be seen from Table I, the ultimate stress first decreases with the triol/diol ratio, reaching a minimum at a triol/diol ratio of 0.09 for the propellants with NCO/OH ratios of 0.81 and 0.82, and then starts to increase, whereas for the propellants with *R* values of 0.83 and 0.85, a regular increase is observed with the increasing triol/diol ratio. Although the initial modulus increases with the increasing triol/diol ratio for the propellants with an *R* value of 0.81, it shows irregular changes for the other propellants with NCO/OH ratios of 0.82, 0.83, and 0.85. Generally, the surface of the propellant is observed to be more brittle at higher triol/diol ratios. The strain values obtained at maximum stress show variation with the increasing triol/diol ratio parallel to that in the modulus values, indicating that strain decreases as the propellant gets harder with the increasing triol/diol ratio. The increasing triol/diol ratio causes the crosslink density and, therefore, the stiffness of the propellant to increase, whereas the strain capability is noticeably reduced at higher levels of triol.

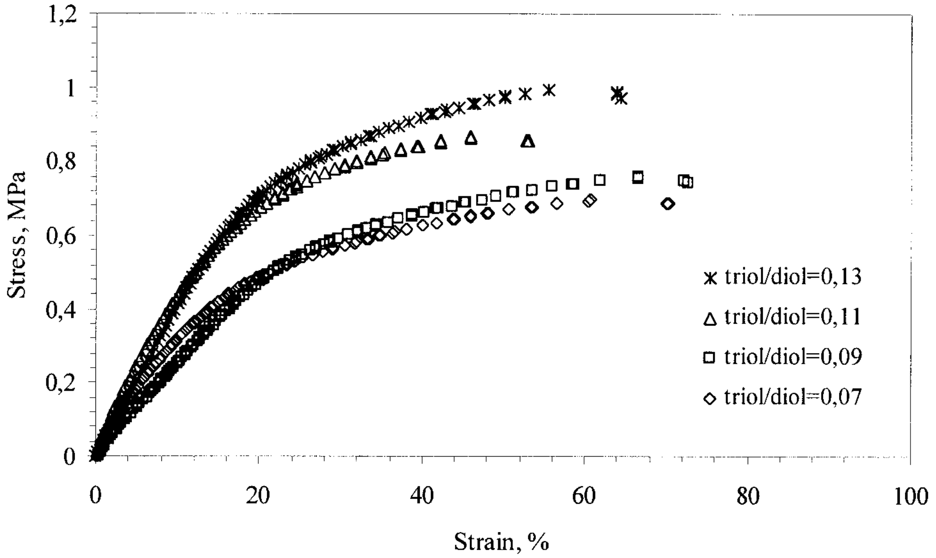

Figure 8 Stress–strain diagrams for the propellants with an NCO/OH ratio of 0.85.

CONCLUSIONS

The following points have emerged from this investigation of the effects of NCO/OH and triol/diol ratios varied within a quite narrow range on the mechanical properties of HTPB/AP-based propellants:

- The propellants with an NCO/OH ratio of 0.82 have minimum stress, modulus, and hardness with maximum strain capability, whereas the propellants with an NCO/OH ratio of 0.85 show just the opposite behavior.
- For the propellants with a triol/diol ratio of 0.11, as the NCO/OH ratio is elevated, the stress, hardness, and modulus values also increase, whereas the strain value decreases.
- Variation in the isocyanate level has a greater effect on the mechanical properties at higher triol/diol ratios.
- The change in the triol/diol ratio is most effective at an NCO/OH ratio of 0.81 and least effective at an R value of 0.83.
- The propellant with a triol/diol ratio of 0.11 and an NCO/OH ratio of 0.85 is hardest; that is, it has the highest modulus and hardness and the lowest strain.
- The highest stress value is obtained for the propellant with an R value of 0.85 and a triol/diol value of 0.13.
- The propellants with triol/diol–NCO/OH ratio combinations of 0.11–0.83, 0.11–0.85, 0.13–0.81, 0.13–0.83, and 0.13–0.85 are not acceptable for upper stage case-bonded rocket applications because of either high tensile strength or high modulus.

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