Structure–Property Relationship of HTPB-Based Propellants. I. Effect of Hydroxyl Value of HTPB Resin

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SYNOPSIS

Composite propellants based on hydroxyl-terminated polybutadiene (HTPB) resin are the most common contemporary solid propellants for launch vehicle and missile applications. A series of HTPB resins, manufactured by free-radical polymerisation using a peroxide initiator, with varying molecular weights and hydroxyl values, was used in propellant formulation experiments with a view to studying the resin production variables and their influence on the resultant propellant properties. It is seen that HTPB resins with a wide range of hydroxyl values could be effectively utilized in propellant formulations. Also, propellants with higher strain capability and chain flexibility could be produced from lower hydroxyl value resins. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Composite propellants based on hydroxyl-terminated polybutadiene (HTPB) resin are the current state-of-the-art propellants for solid rocket motor applications.[1,2] These propellants are projected to have excellent long-term storage capability based upon chemical structural aging studies. Formulation tailoring has been attempted on polyurethane propellants as early as 1960.[3,4] In composite solid propellants, polyurethane elastomer is present as a four-component system consisting of a long-chain diol such as hydroxyl-terminated polybutadiene, a curing agent such as toluene diisocyanate, a low molecular weight chain-extender such as butanediol, and a crosslinker such as trimethylolpropane, together with other ingredients like inorganic oxidizer, metallic fuel, burn-rate modifier, cure catalyst, etc. Drastic changes in properties of the elastomer can be induced by varying the molecular weight of the prepolymer and the crosslink density. Average molecular weight between crosslinks can be varied by adusting the ratio of crosslink component to the chain-extender component.[5]

At the Vikram Sarabhai Space Centre in India, a wide range of rocket motors, covering propellant grains of 25 tonnes each down to a few hundred grams needed for the Polar Satellite Launch Vehicle (PSLV), are made using HTPB resin developed in-house.[6] The manufacture of HTPB prepolymer is carried out by free radical polymerization using a peroxide initiator. The resin specifications have been standardized based on the desired mechanical properties of the finished propellant. The baseline specifications of similar HTPB prepolymer used elsewhere were taken as a guideline. It was felt necessary to have a better understanding of the effect of variations in prepolymer structure on the propellant processing and the resultant mechanical properties. Toward this end, HTPB resins of varying structure were synthesized for the study. The structure was varied in terms of molecular weight, functionality, hydroxyl value, etc.

HTPB prepolymer prepared under several polymerization conditions were used in propellant formulation trials by earlier investigators over a limited range of molecular weights.[7] The functionality distribution of HTPB prepolymer had been studied, and the results correlated with mechanical properties.[8,9] It is possible that HTPB resins different from the standard HTPB resin can give rise to propellants of different capabilities under identical cure condition. It is also likely that, with judicious modifications of the propellant compositions, a new generation of propellants can be obtained for a variety of applications. In the present paper, properties of

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various grades of HTPB prepolymer produced and its influence on the resultant propellant properties are reported.

EXPERIMENTAL

Production of HTPB Prepolymer

HTPB prepolymer is produced by free radical polymerization of 1,3-butadiene using hydrogen peroxide as initiator.[10] The polymerization reactions can be summarized as follows.

Initiator Decomposition

H_2O_2 is thermally cleaved to produce free radicals as shown below.

$$H_2O_2 \rightarrow 2OH$$

Initiation

The free radicals formed initiate the polymerization reaction with butadiene:

$$OH^{\bullet} + CH_2{=}CH{-}CH + CH_2 \rightarrow HO{-}CH_2{-}CH{=}CH{-}C^{\bullet}H_2$$

Propagation

Further propagation of polymerization proceeds as follows:

$$HO{-}CH_2{-}CH{=}CH{-}C^{\bullet}H_2 + nCH_2{=}CH{-}CH{=}CH_2 \rightarrow HO\{CH_2{-}CH{=}CH{-}CH_2\}_nCH_2{-}CH{=}CH{-}C^{\bullet}H_2$$

Termination

Polymer chain termination takes place by combination of two growing chains having free radicals.

$$HO\{CH_2{-}CH{=}CH\}_nCH_2CH{=}CH{-}C^{\bullet}H_2 + HO\{CH_2{-}CH{=}CH\}_mCH_2CH{=}CH{-}C^{\bullet}H_2 \downarrow HO\{CH_2{-}CH{=}CH{-}CH_2\}_{n+m+2}OH$$

In free radical polymerization, process parameters like reaction temperature, initiator–monomer ratio, and solvent ratio are the critical process parameters that affect the product quality. The quantity of initiator required in the reaction recipe is determined by the half-life period of the initiator. Keeping all other process parameters constant, H_2O_2 content in the reaction recipe was increased gradually, and the resulting HTPB resins were used in the present study. With increase in H_2O_2 content, due to the availability of more free radicals, the chance of collision increases, and this results in increased hydroxyl value and decreased molecular weight for the product. Average functionality, which is the ratio of molecular weight to equivalent weight, decreases with decreasing H_2O_2 content.

Characterization of Resin

Four experimental batches of HTPB resin together with the standard resin, were characterised to evaluate the relevant properties, and the results are given in Table I. The HTPB resins showed OH values in the range of 43–20 and molecular weights 2600–4500, with a corresponding increase in viscosity. The average functionality, which is the ratio of molecular weight to equivalent weight, is found to be less than 2 in batches 3 and 4 indicating that the percentages of monofunctionals are more in these cases or there is a possibility of nonfunctionals present.

Propellant Formulation Experiment

The experimental batches of HTPB resin have been used in propellent trials with a standard formulation as baseline.

Baseline Propellant Formulation

HTPB + TDI	=	10.78
Ambilink (diol + triol)	=	0.12
Plasticizer, antioxidant, Burn-rate modifier	=	3.50
Aluminum	=	18.00
Ammonium perchlorate	=	67.60
		100.00

Ambilink is a diol/triol combination with 67/33 of 1,4-butanediol and trimethylolpropane. No cure catalyst was employed.

The experiments were carried out with varying ratios of curative to resin, i.e., NCO/OH ratios

Table I Properties of Experimental Batches of Resin

	Experimental Batch Number				
Properties	Standard	E-01	E-02	E-03	E-04
1. Viscosity (30°C, CPS)	6300	6000	9070	13,600	41,300
2. OH value (mg KOH/g)	43	40	35	28	20
3. Acid value (mg KOH/g)	0.3	0.3	0.2	0.1	0.2
4. Mol wt (M_n by VPO)	2600	2900	3300	3500	4500
5. Mol wt (M_n by GPC)	3600	4400	5400	6500	8200
6. Polydispersity (M_w/M_n by GPC)	1.96	1.82	1.75	1.66	1.62
7. Equiv wt	1300	1370	1600	2000	2800
8. Average functionality (M_n/equiv wt)	2	2.1	2	1.75	1.6

ranging from 0.7 to 1.05. Propellant processing was done in a small sigma blade mixer at 800 g level. The end-of-mix viscosity was measured with a Brookfield viscometer. The propellant slurry was vacuum-cast into cartons and cured at 60°C for 5 days. Mechanical properties of the cured samples were evaluated.

RESULTS

Effect of NCO/OH Ratio

Tensile properties of a composite propellant depend mainly on the tensile properties of the matrix, particle size, shape, distribution and the concentration of the solid ingredients, and the binder–filler interaction. Because of the presence of interacting filler like ammonium perchlorate, one has to operate at substoichiometric levels of curatives so as to achieve the desired mechanical properties. Hence composite propellant is often formulated with NCO/OH ratios in the range of 0.7–0.9.

Variation of tensile strength and elongation are plotted as a function of NCO/OH ratios in Figures 1 and 2. Generally, in all cases as NCO/OH ratio increases, tensile strength increases and elongation decreases. This is expected because increased NCO/OH leads to increased crosslinking of the matrix in

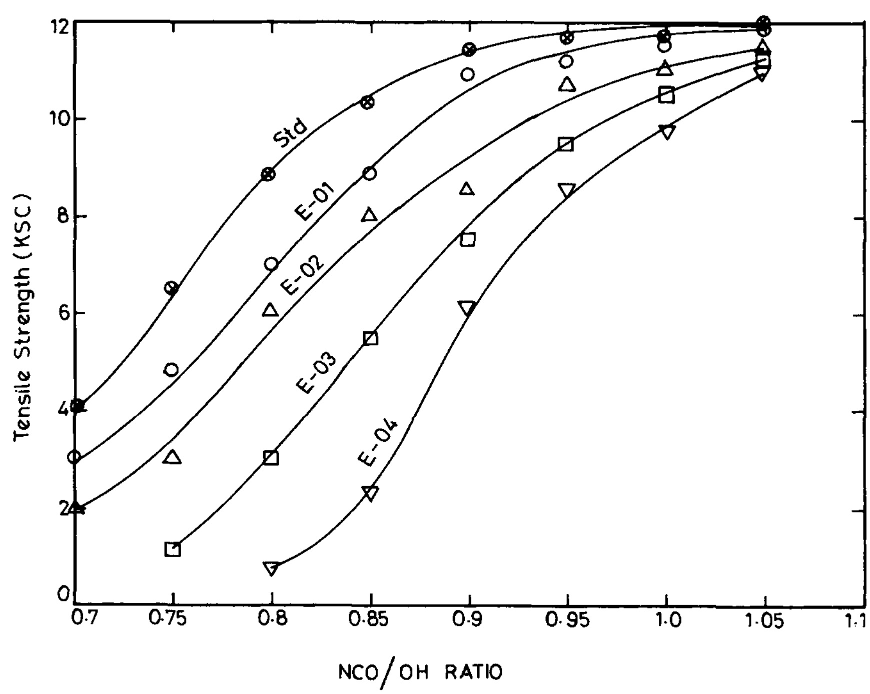

Figure 1 Variation of tensile strength with NCO/OH ratio.

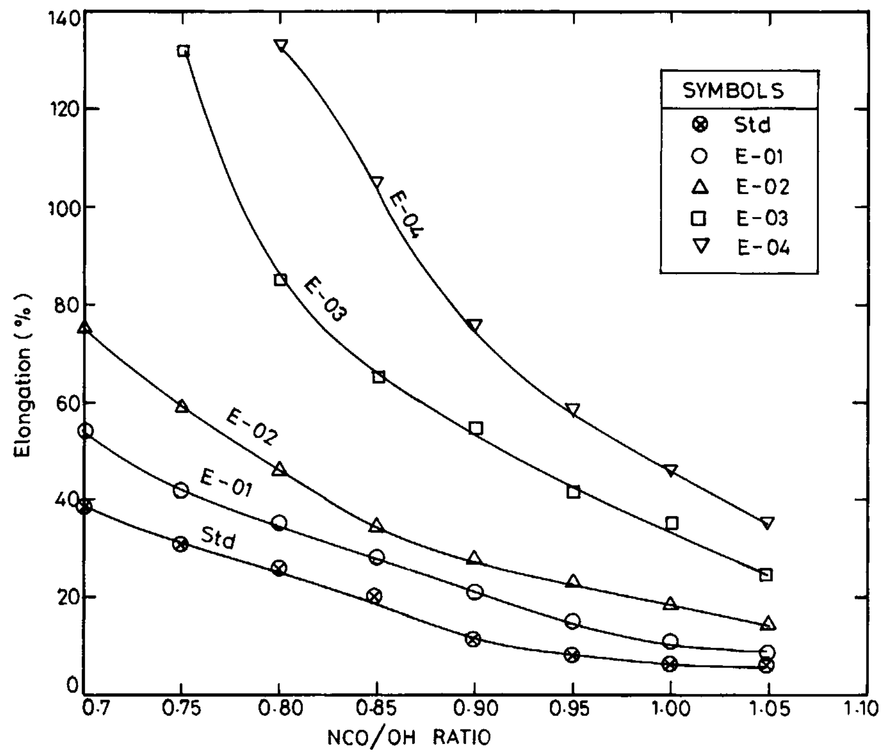

Figure 2 Variation of elongation with NCO/OH ratio.

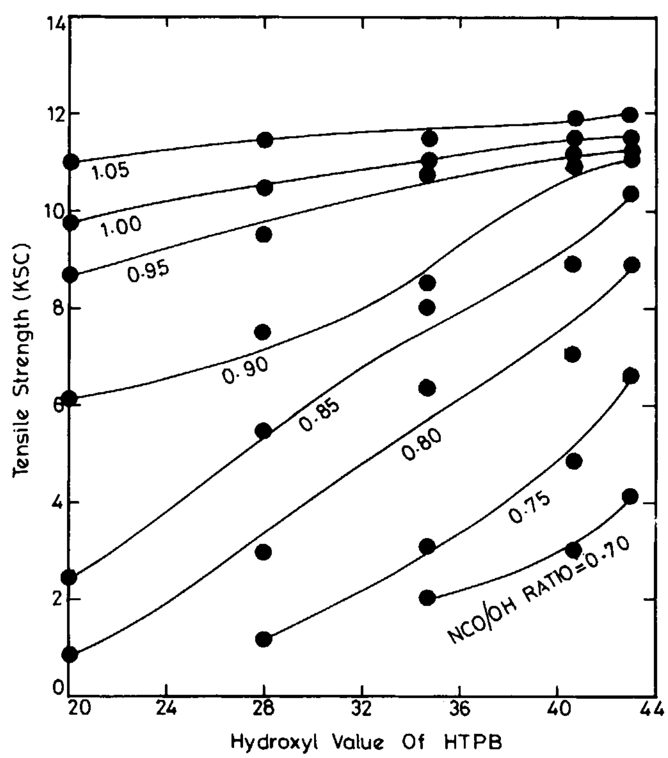

Figure 3 Tensile strength vs. hydroxyl value of HTPB resin.

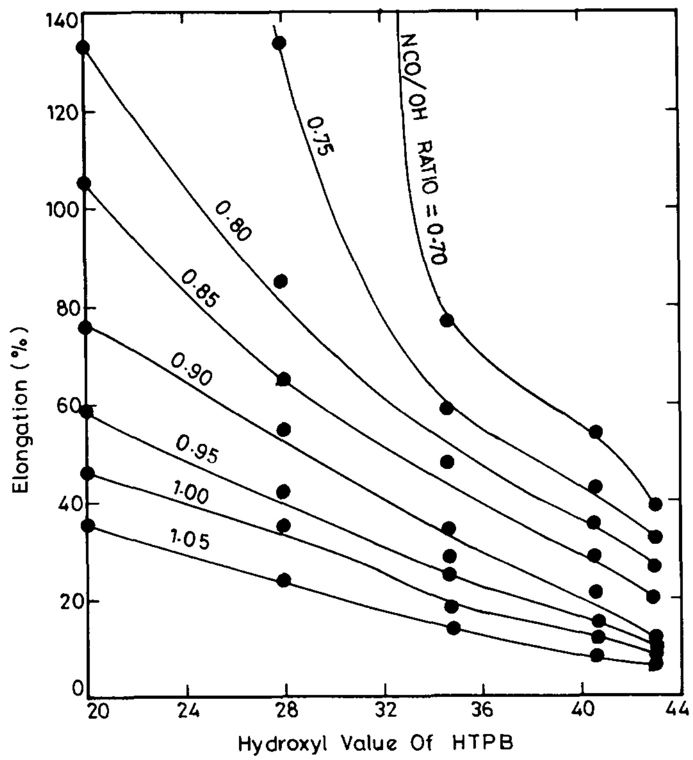

Figure 4 Elongation vs. hydroxyl value of HTPB resin.

all the cases. Standard HTPB cures even at as low an NCO/OH ratio as 0.7, whereas HTPB grades with lower hydroxyl values (grades E-03 and E-04) do not cure at NCO/OH ratio of 0.7. This is because the functionality of these two grades are below 2 (1.75 and 1.60, respectively), and they do not form good 3-dimensional matrix at ratios far below stoichiometry. In the case of E-04, curing does not take place even at NCO—OH ratio of 0.75, indicating the presence of monofunctional and nonfunctional polymer chain ends. Above the NCO/OH ratio of 1, the OH value is found to have very little influence on the tensile strength, but substantial variations are seen in elongation of the finished product.

Effect of Hydroxyl Value

Mechanical properties have been plotted against hydroxyl values, with NCO/OH ratios as a parameter, in Figures 3 and 4 in order to get an idea of the overall influence of OH value and NCO/OH ratio. It is seen that, at hydroxyl values in the range of 40–50, the sensitivity of elongation to NCO/OH ratio is less than that in lower OH-value ranges. This is indicative of the fact that the resin with OH value in this range is the most suitable for the production of large propellant grains, where mix-to-mix variability could be minimized and a large scatter in mechanical properties avoided. It is observed that at an NCO/OH ratio of 0.95, the E-04 grade of resin gives propellant with a tensile strength of 8.7 kg/cm^2 and an elongation of 59% whereas E-03 give similar properties at NCO/OH ratio of 0.9 or even less.

Variation of initial modulus against hydroxyl value has been plotted in Figure 5 with NCO/OH ratio as a parameter. It is observed that formulations with higher molecular weight resins result in propellant with optimum initial modulus of less than 100 kg/cm^2, which is desirable in making case-bonded propellant grains. This is partly due to the fact that higher molecular weight chains impart higher chain flexibility and better elongation even at higher NCO/OH ratios. Lower functionality of the high molecular weight resin also contribute to this effect to some extent.

Effect of Molecular Weight between Crosslinks

Molecular weight between crosslinks is more useful than simple functionality in evaluating the effects of prepolymer modifications on elastomer properties.

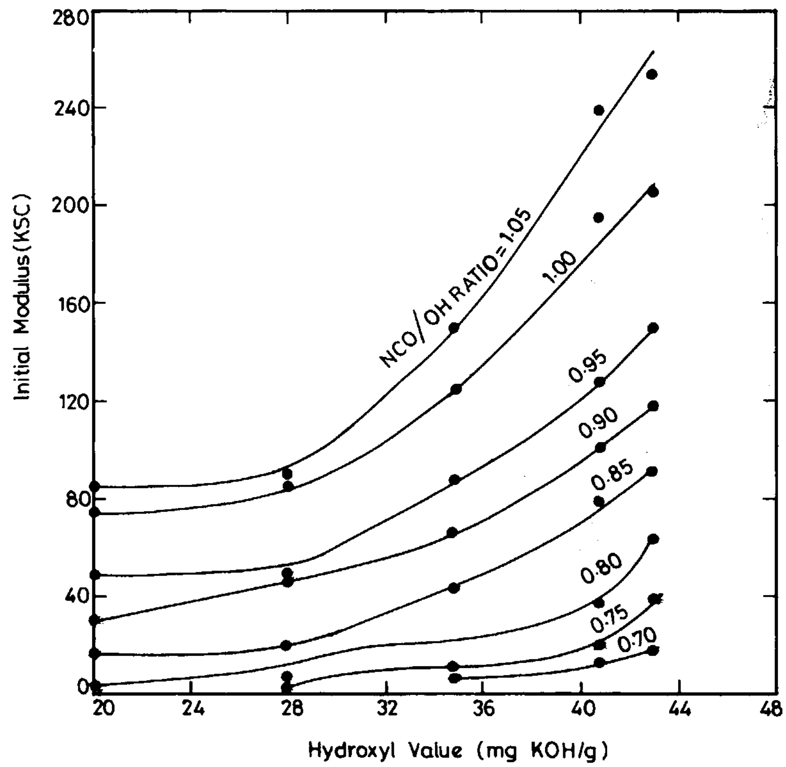

Figure 5 Initial modulus vs. hydroxyl value of HTPB resin.

Here molecular weight per branch point, M_c, has been calculated using the equation

$$M_c = \frac{A + B + C + D}{\text{molar amount of curators} \times \text{NCO/OH ratio}}$$

where A = weight (g) of HTPB per mole of HTPB, B = weight (g) of isocyanate per mole of HTPB, C = weight (g) of butanediol per mole of HTPB, and D = weight (g) of TMP per mole of HTPB. Table II gives values of M_c calculated for the four experimental batches of resin at different NCO/OH ratios. Figure 6 gives the variation of mechanical properties with molecular weight between crosslinks (M_c). The tensile strength data for all the five batches are found to superpose to a master curve. This shows that even low molecular weight resins can be tailored to give the desired M_c and the associated tensile strength, which is independent of the resin molecular weight, whereas, in the case of elongation, two different elongation values may be achieved for the same M_c, as indicated by the two different curves—one for E-03, E-04 and another for E-01, E-02 and standard resins. The achievement of the same tensile strength data for all the batches of the resin irrespective of the molecular weight may be due to the same filler content, filler size, and particle size distribution maintained throughout the study. It is possible to make propellant with the desired strain capability by varying the resin parameters provided that such changes do not impede processability.

Throughout these experiments, the ratio of crosslinker to chain-extender has been kept constant deliberately, with a view to understanding how OH variations of prepolymer influence the mechanical properties of a particular system. But the presence of a chain extender may be appropriate in the case of low molecular weight HTPB resins like E-01 or

Table II Molecular Weight between Crosslinks

NCO/OH ratio	Standard	E-01	E-02	E-03	E-04
0.70	3310	3390	3700	4120	4750
0.75	2930	3310	3480	3660	4240
0.80	2630	2700	2940	3270	3820
0.85	2340	2420	2640	2950	3420
0.90	2140	2190	2390	2660	3100
0.95	1940	1980	2170	2430	2830
1.00	1770	1820	1980	2220	2590
1.05	1620	1670	1820	2040	2380

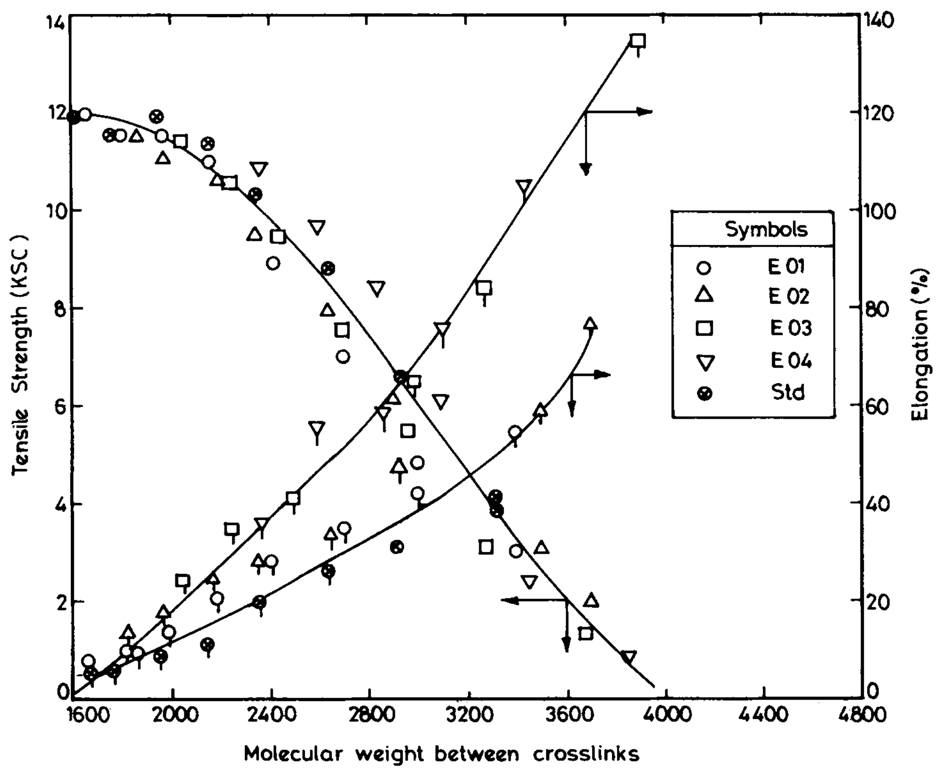

Figure 6 Variation of mechanical properties with M_c.

standard HTPB, but grades like E-03 and E-04, whose functionality is less than 2, may not require chain extenders at all to increase the molecular weight between crosslinks, because the molecular weight of the HTPB backbone itself is higher. Hence they may require more crosslinkers to obtain a 3-dimensional matrix. Thus a different combination of diol and triol may be appropriate for grades E-03 and E-04. This aspect was investigated separately and is reported in Part II.[11]

CONCLUSIONS

It is observed that HTPB resin with wide range of hydroxyl values can be tailored to give the desired tensile strength for the end product by suitable variation in the NCO/OH ratio. However, the strain capability of the end product does depend on the hydroxyl value of the resin. HTPB resin with OH values above 30 are not amenable to tailoring so as to yield strain capability beyond a certain limit, whereas resins with OH value below 30 give end products with higher strain capability for the same M_c. Even though resins with OH values above 30 result in a lower strain capability product, the advantages of this grade of resins are better processability and reduced sensitivity to NCO/OH ratio. The implication of this observation is that if we operate in this range, minor variations occuring in the large scale production may not show up as a large scatter in properties of the finished product and the sensitivity to formulation variabilities is minimum. Also, the sensitivity of mechanical properties to OH values is found to be minimum at an NCO/OH ratio of ~ 1.

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