A New Prepolymer: Lactone-Terminated Polybutadiene (LTPB) for High-Energy Solid Propellants

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The development of a new polybutadiene prepolymer with lactone terminals for use in solid propellants is reported. The data presented include those relating to the nature of reactions involved in synthesis, the spectroscopic and analytical studies to establish the nature of the functional terminals, and the mechanical and ballistic properties of the propellants based on the lactone-terminated polybutadiene (LTPB) prepolymer. Aging and low-temperature properties of the LTPB-based "Lactodiene" propellants are found to be comparable to the conventional carboxyl-terminated polybutadiene (CTPB)-based propellants. The studies on Lactodiene propellants bring out the experimental feasibility for a high-energy and high-density solid propellant system.

I. Introduction

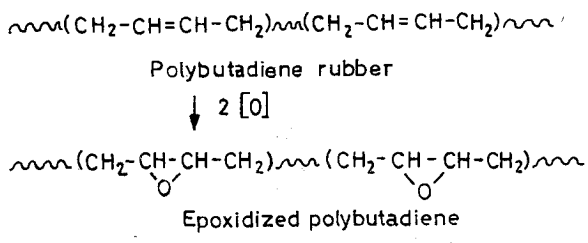
In composite propellants, polybutadiene prepolymers are considered as high-energy fuels. Poly(butadiene-acrylic acid) (PBAA) is the earliest prepolymer in this category wherein the functional COOH groups are randomly distributed along the chain. The uneven spacing of the carboxyl groups, which gives rise to poor mechanical properties of the PBAA-based propellant, is improved by the interjection of acrylonitrile groups between the polybutadiene and acrylic acid molecules. The resulting terpolymer, viz. poly(butadiene-acrylic acid-acrylo-nitrile) (PBAN), has more reproducible mechanical characteristics and is widely used as a fuel prepolymer in high-energy solid propellants. However, for better low-temperature properties and for improved performance, carboxyl-terminated polybutadiene (CTPB) prepolymer made by various methods[1-3] is preferred to PBAN. Hydroxyl-terminated polybutadiene (HTPB) is the most recent entrant; it permits solid loadings of up to 90% and still retains mechanical properties within acceptable limits. An extensive review of the work on polybutadiene-based solid propellants is given by Mastrolia and Klager.[4]

In the present paper we report the synthesis of a new prepolymer, lactone-terminated polybutadiene (LTPB), which has terminal functional groups different from those in any of the polybutadiene prepolymers reported so far. The characteristics of the propellant based on the LTPB prepolymer are also presented here. The prepolymer is designated as HEF-20, short for high-energy fuel of series 20.

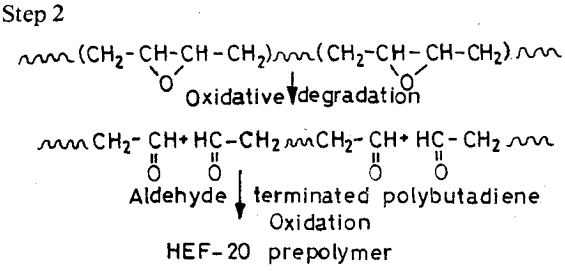
II. Synthesis

Polybutadiene rubber of high molecular weight ($0.2 - 0.3 \times 10^6$) is dissolved in a solvent such as benzene. The rubber solution is brought into contact with an oxidizing agent (perbenzoic acid solution in benzene) under controlled conditions (step 1). Calculated quantities of degradative oxident (periodic acid in glacial acetic acid) are added and refluxed (step 2). During the reflux, the terminal carbon atoms get oxidized to functional groups. At the end of the reaction, the prepolymer in benzene solution is successively washed to remove the acetic acid, and the solvent is recovered by distillation. The pure prepolymer HEF-20 thus obtained has the properties mentioned in Table 1. The reactions are as follows:

Step 1



Step 2



III. Results and Discussion

The final product, when analyzed for carboxyl content by potassium hydroxide titre method,[5] gave very low carboxyl equivalents (0.003 – 0.004 equivalent per 100 g), and the experimental values are given in Table 2. The molecular weight of HEF-20 from different batches was determined using a vapor pressure osmometer (Hewlett Packard model 302), and the results are given in Table 2, along with those from HC-434 (CTPB resin from Thiokol) for comparison.

The infrared spectrum (taken from Perkin Elmer model 700) of the HEF-20 prepolymer sample is given in Fig. 1. The carbonyl group absorption band appears at 1730 cm^{-1}, and a

Table 1 Properties of HEF-20

1) Viscosity (Brookfield)	= 200 to 300 P
2) Molecular weight (by vapor pressure osmometry)	= 3000 to 4000
3) COOH equivalent/100 g	= 0.0032 to 0.0038
4) Total functionality equivalent/100 g	= 0.045 to 0.055
5) Density (g/ml) at 25° C	= 0.98 ± 0.02

Presented as Paper 75-1335 at the AIAA/SAE 11th Propulsion Conference, Anaheim, Calif., Sept. 29-Oct. 1, 1975; submitted Feb. 24, 1977; revision received May 2, 1978.

Index categories: LV/M Propulsion and Propellant Systems; Fuels and Propellants, Properties of.

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Table 2 Carboxyl equivalents and molecular weights of different batches of HEF-20

Expt. no.	PBD/220	PBD/226	PBD/233	PBD/249	HC-434
COOH eqv./100 g	0.0035	0.0036	0.0039	0.0035	0.045
$\bar{M}_\eta$	3300	3900	3350	3500	4100
Expected $\bar{M}_\eta$	3500	3500	3500	3500	...

small shoulder is observed at 1710 cm^{-1}, showing the presence of a small quantity of carbonyl of the carboxyl group; on the other hand, HC-434 shows a strong absorption band at 1710 cm^{-1} (Fig. 2), and the carboxyl content was found to be 0.045 equivalent per 100 g of HC-434 (Table 2).

The NMR spectrum (taken from 100-MHz Jeol spectrometer) of the HEF-20 prepolymer is given in Fig. 3. The spectrum is indicated by an additional signal at 3.2 ppm when compared to the HC-434 NMR spectrum (Fig. 4). The signal at 3.2 ppm in the NMR spectrum (Fig. 3) indicates the presence of a proton of an ester type.

The infrared absorption at 1730 cm^{-1} did not change even after drastic oxidation (to the extent of affecting the double bonds) of the HEF-20 prepolymer with permanganate or dichromate, indicating the absence of oxidizable carbonyl groups in the prepolymer. The absence of aldehyde groups is confirmed by spectroscopic and chemical analyses. The prepolymer was hydrolyzed with sodium hydroxide in methanol, and the sodium salt recovered and dried was analyzed spectroscopically. The infrared spectrum of the sodium salt gave a strong absorption band at 1590 cm^{-1} corresponding to carbonyl absorption of the sodium carboxylate group (Fig. 5). The spectrum of the sodium salt also showed an absorption in the region of 3200 – 3700 cm^{-1}, indicating the presence of an OH group.

From the foregoing, it can be concluded that the functional groups of HEF-20 prepolymer are of the ester type. However, if the ester is formed from different molecules, the molecular weight of the prepolymer would not be in accordance with the equivalents of the oxidants used, as was found in the present case. Also, when HEF-20 was reacted with epoxy resin (based

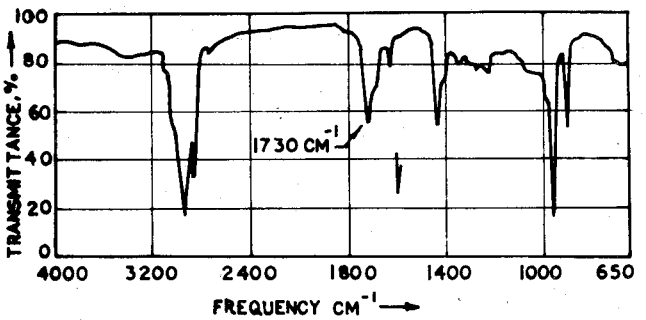


Fig. 1 Infrared spectrum of HEF-20 prepolymer.

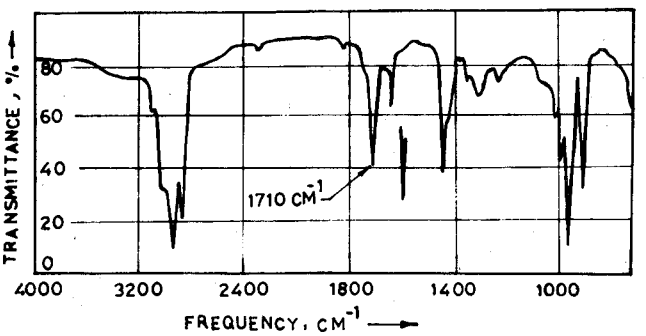


Fig. 2 Infrared spectrum of HC-434 prepolymer.

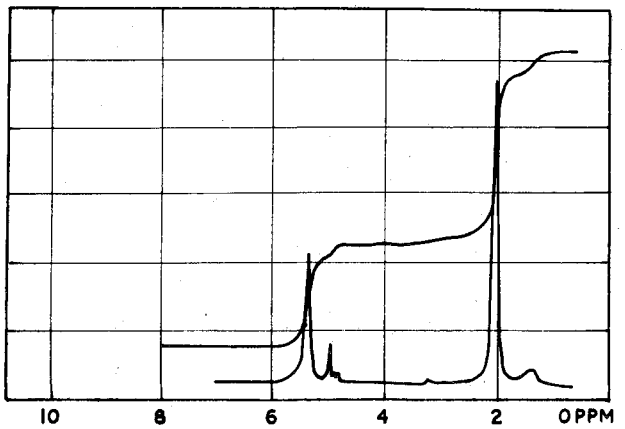


Fig. 3 NMR spectrum of HEF-20 prepolymer.

Table 3 Variation of mechanical properties with variation of functional group to curing agent ratio in equivalents

Experiment no.	Functional group to curing agent ratio in equivalents	Tensile strength, kg/cm^2	Elongation, %	Shore A hardness
02D – 414	1:0.3	2.5	945	5 – 7
02D-561A	1:0.5	3.4	900	7 – 8
02D-561B	1:1.0	4.3	850	15
02J-127	1:1.5	7.1	487	20

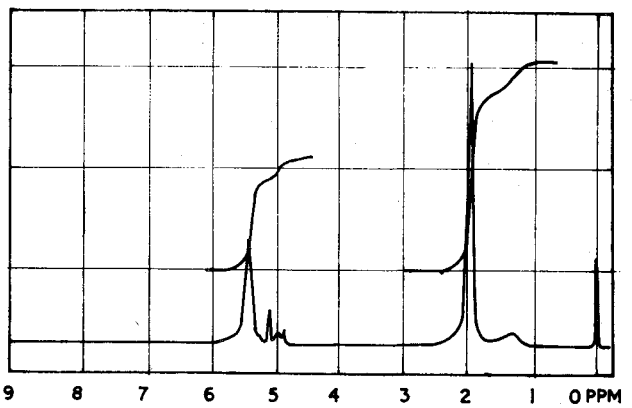


Fig. 4 NMR spectrum of HC-434 prepolymer.

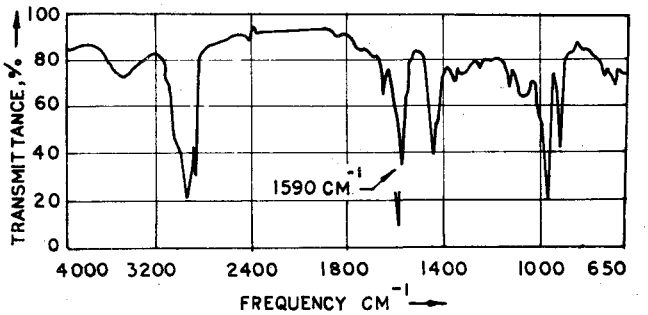
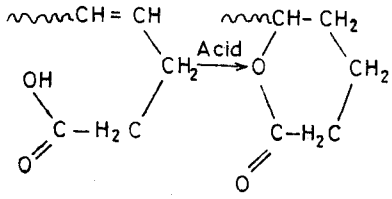


Fig. 5 Infrared spectrum of NaOH hydrolyzed HEF-20 prepolymer.

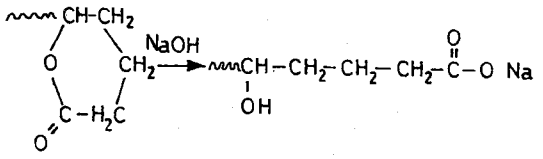
on bisphenol-A and epichlorohydrin) and aziridine at 80° C for 72 h, the prepolymer cured well. The mechanical properties of the cured prepolymer with different prepolymer to curing agent ratios are given in Table 3. It is clear that, by changing the curing agent to prepolymer ratio, the mechanical properties change, thus indicating the participation of the functional groups in the cure reaction.

Thus the terminal groups of HEF-20 prepolymer are identified to be intramolecular esters or lactones. Since the reflux reaction in the synthesis (step 2) was carried out at pH 1 to 3, the terminal COOH group can get converted into a lactone by proton transfer to the adjacent C = C group as



(1)

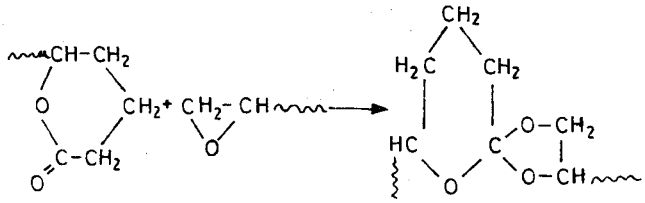
The sodium carboxylate formation of the prepolymer on hydrolysis with NaOH could be as



(2)

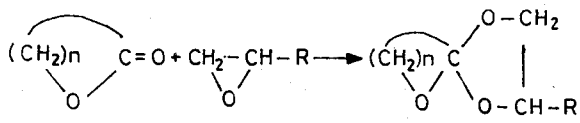
The appearance of OH group absorption in the infrared spectrum of the sodium salt (Fig. 5) could also be explained by reaction (2). The signal at 3.2 ppm in the NMR spectrum of the HEF-20 prepolymer (Fig. 3) could be from the proton attached to the carbon atom that is participating in the lactonization reaction.

The reaction of HEF-20 with epoxy system could be of the following type:



(3)

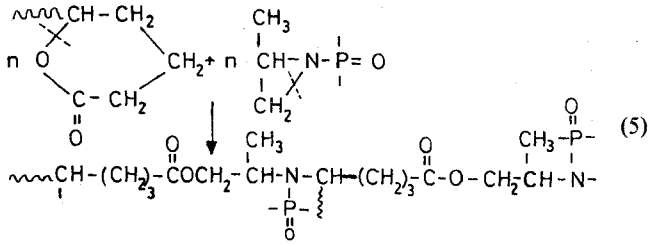
As an analogy, we can consider the reaction between a lactone ring and epoxides, as stated by Boden Benner[6]:



(4)

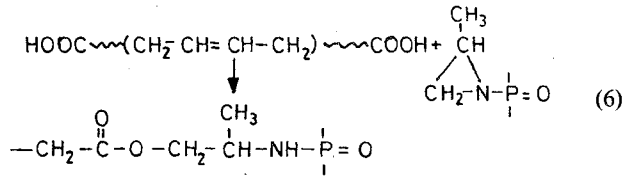
The reaction of the HEF-20 prepolymer with the aziridine system was further analyzed spectroscopically. It is found that the lactone ring opens while reacting with aziridine.

The infrared spectrum of the HEF-20 aziridine cured system (Fig. 6) shows the presence of the >C=O absorption band at 1745 cm^{-1}. This indicates that the >C=O group of the HEF-20 prepolymer, even after complete cure with aziridine, is unaffected. The absence of any shift of the >C=O group absorption toward lower frequencies indicates the absence of substituted amide resulting from the acyl-oxygen cleavage of the lactone ring with the aziridine. The reaction seems to proceed through the ring opening of the lactone by the alkyl-oxygen bond cleavage. The evidence for the aziridine ring opening is derived from the absence of the absorption band at 1214 cm^{-1} (Fig. 6) which is the characteristic of the ring $\left(\begin{matrix}H\\N\\\Delta\end{matrix}\right)$.[7] Thus the reaction between HEF-20 and aziridine could be of the following type:



(5)

It is also observed that the HEF-20 aziridine cure reaction differs from the well-known CTPB-aziridine cure reaction[8]:



(6)

The infrared spectrum of the CTPB-aziridine cure system (Fig. 7) shows the presence of 1) −NH− stretching absorption at 3350 cm^{-1}, 2) N−H deformation frequency[9] at 1550 cm^{-1}, and 3) −P=O absorption band of −NH−P=O group at 1190 cm^{-1}.[9] These specific absorption frequencies are absent in the infrared spectrum of the HEF-20-aziridine cured system (Fig. 6), supporting the proposed reaction (5).

IV. Propellant Formulation Studies

The viscosity buildup data of the HEF-20 prepolymer with epoxy (bisphenol-A type) and aziridine (MAPO) curing agents at 80°C are given in Fig. 8. The data indicate that the rate of buildup is rather slow for epoxy as compared to MAPO.

In order to study the suitability of the prepolymer in propellant technology, propellant formulation studies with solids loading varying from 84 to 88% using ammonium

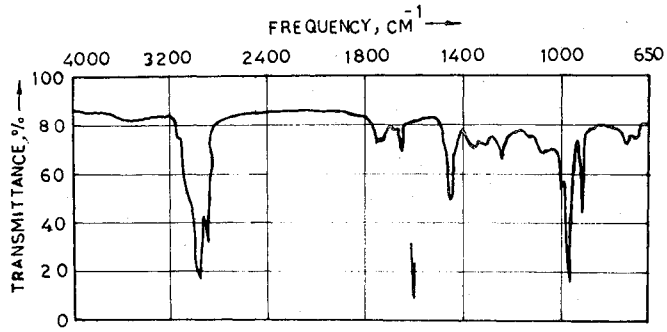


Fig. 6 Infrared spectrum of HEF-20 aziridine cured system.

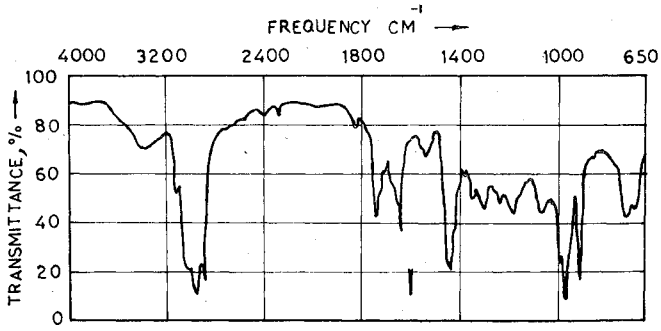


Fig. 7 Infrared spectrum of HC-434 aziridine cured system.

perchlorate and aluminum were conducted, and the prepolymer is found to take solids loading up to 88% with good propellant processing characteristics. The formulations, designated as Lactodiene-8205 and CTPB-8205 (based on HC-434), are given in Table 4. The slurry viscosity buildup data at 60°C are given in Fig. 9. The curing cycle optimization was arrived at by studying the mechanical properties of the samples drawn from 2-kg cartons at different time intervals kept at 60° and 80°C. From the tensile and elongation values as shown in Fig. 10, the optimum curing time for the Lactodiene propellants is found to be 8 days at 80°C.

The physical, mechanical, and ballistic properties of Lactodiene-8205 and CTPB-8205 obtained from 2-kg developmental motors are given in Table 5. The mechanical properties of the Lactodiene-8205 propellant appear to be better than those of the CTPB-8205 propellant, whereas the specific impulse values of the two formulations are comparable. The Smith's failure envelope (Fig. 11) and master stress-strain curve (Fig. 12) for the two formulations are generated based on the uniaxile tensile data at different temperatures and strain rates. The shift to the right in the failure envelope of Lactodiene-8205 compared to CTPB-8205 indicates that the former has better mechanical properties. The data of the Lactodiene-8208 (88% solids loading) included in Table 5 indicate the ability of the prepolymer HEF-

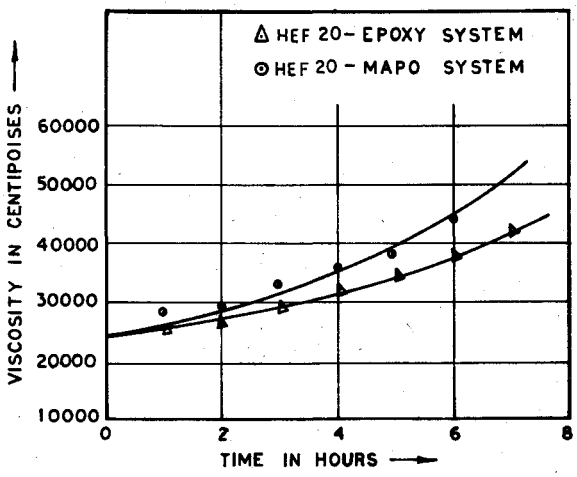


Fig. 8 Viscosity buildup of HEF-20 prepolymer with epoxy and aziridine systems.

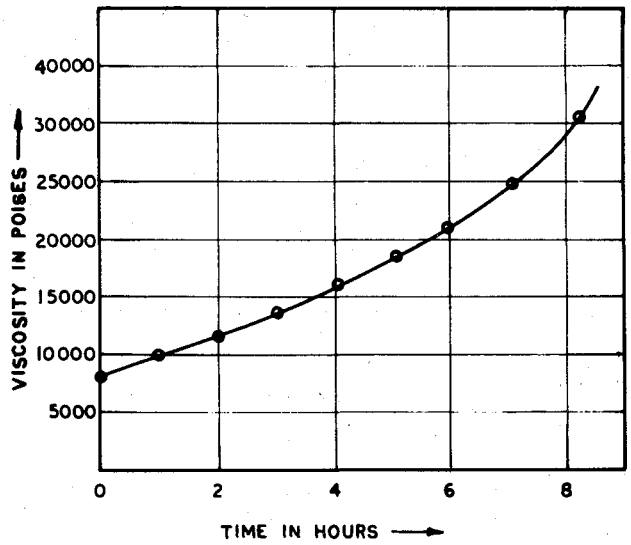


Fig. 9 Slurry viscosity buildup at 60°C of Lactodiene-8205 propellant.

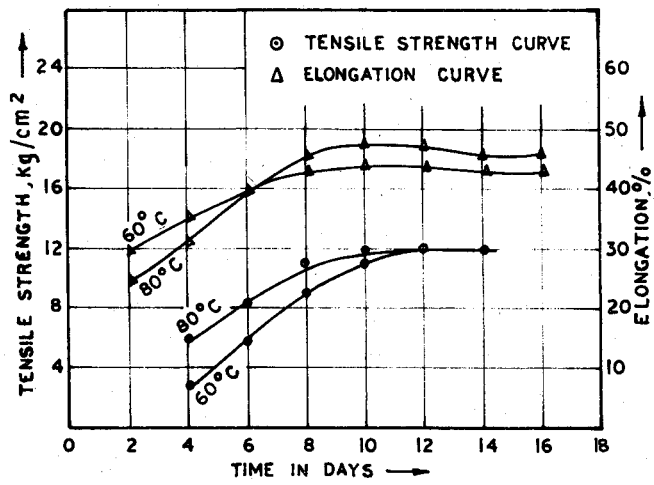


Fig. 10 Effect of cure time on the mechanical properties of Lactodiene-8205 propellant.

Table 4 Composition of Lactodiene-8205 and CTPB-8205 propellants

Sl no.	Ingredients, wt %	Lactodiene-8205	CTPB-8205
1)	Resin	11.7 (HEF-20)	10.2 (HC-434)
2)	Ammonium perchlorate (250 μ average size)	65.0	65.0
3)	Aluminum (18 μ average size)	20.0	20.0
4)	Diepoxy and aziridine curators	1.6	1.4
5)	Additives	1.7	3.4
	Total	100.0	100.0

Table 5 Properties of Lactodiene-8205, -8208, and CTPB-8205 propellants

Serial no.	Propellant characteristics	Lactodiene-8205	CTPB-8205	Lactodiene-8208
1)	Specific impulse at 1000 psi at sea level, s	237	236	...
2)	Burning rate at 1000 psi, mm/s	6.5	6.3	...
3)	Tensile strength, kg/cm² (uniaxial), at break	12 – 14	8 – 12	12 – 15
4)	Elongation at break, %	40 – 50	25 – 35	28 – 30
5)	Initial modulus, kg/cm²	60 – 75	70 – 80	90 – 100
6)	Hardness at cut surface (shore A)	80 – 85	75 – 80	85 – 90
7)	Density, g/cm³	1.78	1.75	1.84
8)	Calorific value, cal/g	1610	1600	1750
9)	Slurry viscosity, P, at 60° C	7000	5000	12,000

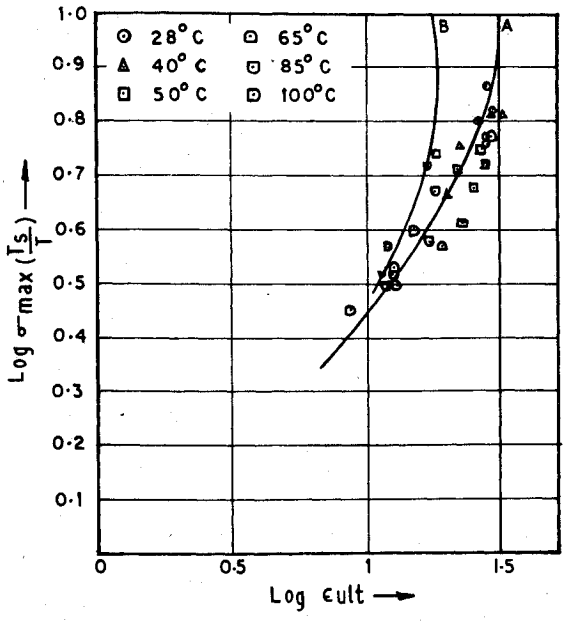


Fig. 11 Failure boundary: curve A, Lactodiene-8205 propellant; curve B, CTPB-8205 propellant.

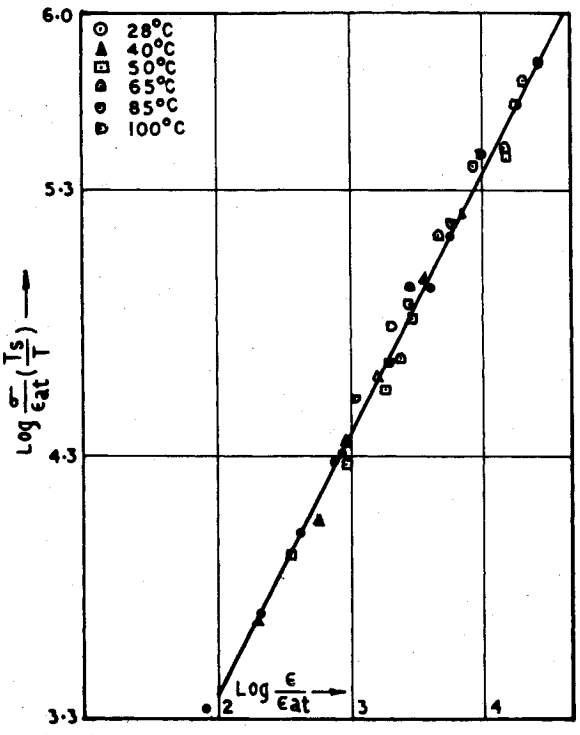


Fig. 12 Master stress-strain curve for Lactodiene-8205 propellant.

20 to give good physical and mechanical properties at higher solids loading.

The glass transition temperature of HEF-20 prepolymer was found to be −78°C, which is comparable to that of CTPB prepolymer. The low-temperature properties of Lactodiene-8205 determined at 0° and −20°C are given in Table 6. The data indicate that Lactodiene propellants exhibit excellent low-temperature properties, and the trend is in good agreement with the reported values for polybutadiene-based propellants.[4]

The useful life of the Lactodiene propellants is arrived at by conducting accelerated aging studies at 60°, 80°, and 100°C. The tensile strength increases first and remains steady throughout the observation. But the elongation decreases

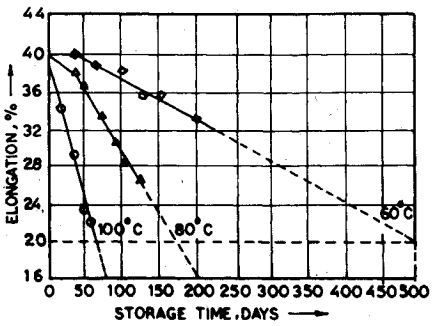


Fig. 13 Effect of storage on elongation of Lactodiene-8205 propellant.

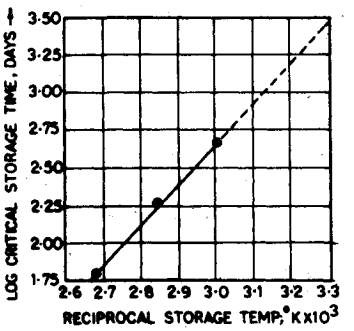


Fig. 14 Storage life of Lactodiene-8205 propellant.

Table 6 Low-temperature properties of Lactodiene-8205 propellant

Serial no.	Temperature, °C	Tensile strength at break, kg/cm²	Elongation at break, %	Initial modulus, kg/cm²
1	25	12.3	40	65
2	0	15.5	50	85
3	−20	19.3	65	100

steadily with time. The log of the time taken for the elongation to reach its half-value at 60°, 80°, and 100°C from Fig. 13 is plotted against the reciprocal of temperature in absolute units. From this linear graph (Fig. 14), the time taken for the propellant to reach its elongation to 50% to that of the observed value at room temperature is found by extrapolation. The approximate useful life of the Lactodiene-8205 propellant is thus found to be about 7 years. All of the mechanical properties were evaluated using INSTRON Table model 1111 using die of American Society for Testing Materials specification D-412-68 (type C) at a cross-head speed of 50 mm/min at 25° C.

V. Conclusion

A new prepolymer, HEF-20, with the terminal functionality of lactones has been synthesized by subjecting high-molecular-weight polybutadiene rubber to controlled oxidative degradation. The lactone rings react with general curing agents used for carboxyl-terminated polybutadiene prepolymer. The thermophysicochemical and ballistic studies of the LTPB based "Lactodiene" propellant bring out the feasibility of a high-energy, high-density propellant system.

Acknowledgment

The authors gratefully acknowledge the many useful discussions with G. C. Joshi, N. V. Viswanathan, M. Janardhanan, Sreenivasa Setty, K. S. Sastri, G. K. Kuruvila, V. N. Krishnamurthy, V. G. Kumar, P. K. Trama, and R. Sivaramakrishnan.

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