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Characterization and Utilization of Carboxyl-Terminated Polybutadiene

by

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ABSTRACT

Investigations have been conducted to characterize and evaluate different commercially available carboxyl-terminated polybutadiene prepolymers and their corresponding gumstocks and propellants. Results show: (1) functionality differences exist among the commercial polymers, (2) polymer functionality has to be maintained to obtain improved physical properties through molecular weight increases, and (3) these polymers are best protected against oxidative crosslinking by the incorporation of amine-type antioxidants.

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FOREWORD

This is the final report on work conducted by the Naval Weapons Center, China Lake, California during the period January 1966 through June 1968 to investigate solid propellant binders for use in solid rocket motors for advanced air-launched missiles. This work was supported by the Naval Ordnance Systems Command under OrdTask RMMP-22-082/216-1/F009-06-01.

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NOMENCLATURE

ABCPA	Azo-bis-3-cyanopentanoic acid
A_n	Number average backbone length, Angstroms
AO	Antioxidant
ARP	As-received polymer
A_w	Weight average backbone length, Angstroms
-CN	Cyano group
CTPB	Carboxyl-terminated polybutadiene
DB&R	DeBell and Richardson
FeOct	Iron octoate
f	Functionalites
GAP	Glutaric acid peroxide
GPC	Gel permeation chromatography
Log a_T	Temperature shift factors
M_a	Acid eqivalent weight (also $\overline{M}_{\varepsilon}$)
MAPO	Tris-[1-(2-methyl) aziridine] phosphineoxide
M_n	Number average molecular weight (also $\overline{M}_n$)
M_w	Weight average molecular weight (also $\overline{M}_w$)
NWC	Naval Weapons Center
P	Polydispersity
PBAA	Polybutadiene-acrylic acid
PBNA	Phenyl-β-naphthylamine
Q	Molecular weight of the repeating polymer unit
T_β	Secondary transition temperature
T_g	Glass transition temperature

T_{gel}	Gel time
THF	Tetrahydrofuran
T_o	Common reference temperature
UTP	Uniaxial tensile property
VPO	Vapor pressure osmometry
$X-\rho$	Crosslink density
γ_m	Elongation at maximum tensile strength
σ_m	Maximum tensile strength
3M	Minnesota Mining and Manufacturing

INTRODUCTION

Prior to the advent of carboxyl-terminated polybutadiene (CTPB) prepolymers polybutadiene-acrylic acid (PBAA) copolymers were widely used as solid propellant binder systems. The main advantages of the PBAA system over that of its predecessors were a lower glass transition (T_g), and decreased moisture embrittlement and sensitivity of the cure reaction. However, some motor failures, caused by grain cracking, were due to stress build-ups that occurred during thermal cycling in cases where PBAA was used as the propellant binder. Stress build-ups and resulting cracking could be attributed to the nonhomogeneity of the carboxyl group distribution along the polybutadiene backbone, an effect which is related to the reactivity of the binder monomers. With the discovery of the "living" polymers by Swarc (Ref. 1), it became possible to synthesize CTPB polymers.

The first commercial CTPB polymer tested in a propellant system gave characteristics superior to the PBAA systems.

The Phillips Petroleum Company made this CTPB, CTL-II, commercially available, followed by General Tire and Rubber Company making Telagen CT available. During the same time interval, two additional CTPB prepolymers became available, HC-434 (Thiokol Chemical Corporation) and Hycar HC (B.F. Goodrich Company). HC-434 and Hycar HC were prepared by a free radical polymerization. HC-434 was manufactured using glutaric acid peroxide (GAP) as the initiator, azo-bis-3-cyanopentanoic acid (ABCPA) peroxide was used in the preparation of Hycar HC.

Extended use of CTPB in propellant systems soon uncovered at least two critical problem areas, nonreproducibility of propellant properties and grain cracking still occurred. These problems could not be solved within the scope of the existing manufacturing specifications. The specifications were either too broad or inadequate. Proprietary information had limited their usefulness.

The Naval Weapons Center (NWC), China Lake, California, began a study to determine which CTPB polymer parameters needed to be characterized and specified so reproducible physical properties of CTPB propellant could be obtained.

A contract was let to Minnesota Mining and Manufacturing Company (3M) to complement the work at NWC. The contract covered three phases: (1) determine the synthesis parameters for both anionic and free radical CTPB polymers, (2) prepare specified CTPB prepolymers for gumstock and propellant experiments at NWC, and (3) characterize CTPB polymers (including commercially available ones) in a meaningful manner.

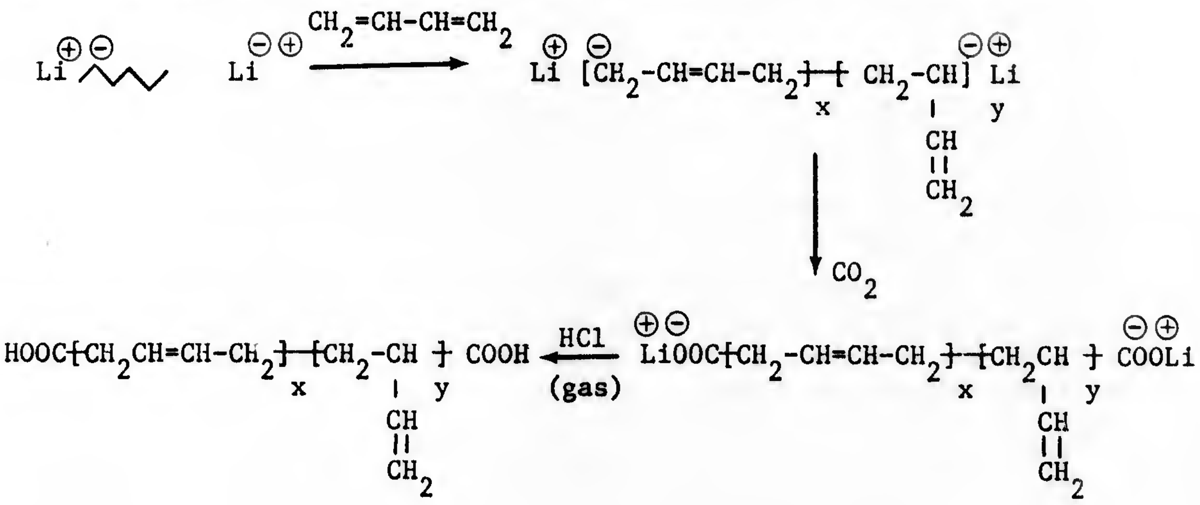
All four commercially available CTPB polymers were used in NWC studies on CTPB prepolymers, gumstocks, propellants, and curing systems.

CTPB prepolymers were studied and evaluated through the determination of number average molecular weights (M_n), gel times with a given curative, oxidative stability, weight average backbone length (A_w), number average backbone length (A_n), and polydispersity (P) from gel permeation chromatography (GPC).

The corresponding gumstocks were evaluated through the determination of their uniaxial tensile properties, crosslink densities, percent gel, glass transition temperatures, and oxidative stability. Propellants were evaluated from the standpoint of aging stability, uniaxial tensile properties, dynamic mechanical properties, and glass transition temperatures.

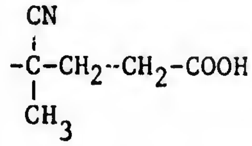
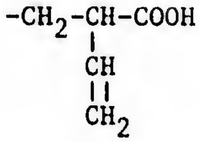
PROPERTIES AND MEASUREMENTS OF CTPB

The four primary manufacturers of CTPB prepolymers are Phillips Petroleum Company, General Tire and Rubber Company, Thiokol Chemical Company, and B.F. Goodrich Company. Phillips Petroleum and General Tire and Rubber prepare their CTPB prepolymers via an anionic mechanism (Ref. 2 and 3) that uses a dilithio anion initiator. The sequence of synthesis reactions is:



Representative microstructures are shown in the x and y brackets which are for x cis and trans 1,4 addition and for y vinyl 1,2 addition. Thiokol Chemical and B.F. Goodrich prepare their prepolymers via a free radical mechanism. Thiokol Chemical uses GAP as the initiator (Ref. 2 and 3) for placement of terminal functional groups; B.F. Goodrich uses ABCPA (Ref. 2 and 3). The terminal carboxyl structures of all four CTPB prepolymers are summarized in Table 1.

TABLE 1. Types of Terminal Carboxyl Groups on the Commercially Available CTPB Prepolymers.

Commercial CTPB	Type of initiation	Terminal carboxyl group
Hycar HC	Free radical	 $-\underset{CH_3}{\overset{CN}{C}}-CH_2-CH_2-COOH$
HC-434	Free radical	$-CH_2-CH_2-CH_2-COOH$
Telagen CT and CTL-II	Anionic	$-CH_2-CH=CH-CH_2-COOH$ and  $-CH_2-\underset{\substack{\mid\\ CH\\ \|\\ CH_2}}{CH}-COOH$

Because of the nature of free radical polymer additions, cis and trans 1,4 and vinyl 1,2 microstructure compositions cannot be varied as extensively as anionic polymerizations. Nevertheless, due to the solvent combinations used in the synthesis of CTPB prepolymers via the anionic mechanism, all four commercial CTPB prepolymers have roughly the same microstructure compositions (Ref. 2).

NUMBER AVERAGE MOLECULAR WEIGHT

CTPB prepolymers are cured by condensation reaction, therefore, prepolymer functionalities (f) directly affect gumstock properties and their lot-to-lot reproducibility. Here the functionality of the prepolymer is defined as $f = \overline{M}_n/\overline{M}_a$, where $\overline{M}_n$ is the number average molecular weight and M_a is the acid equivalent weight. It is very important that the functionalities of the prepolymers be known accurately. Previous experience has shown that M_a can be determined accurately; however, present experience has shown problems in determining $\overline{M}_n$ accurately.

Table 2 gives $\overline{M}_n$, $\overline{M}_a$, and f values of the different commercial CTPB prepolymers showing: (1) lot-to-lot variations, (2) manufacturer-to-manufacturer variations, (3) variations of $\overline{M}_n$ values obtained by two different laboratories, and (4) variations of f with $\overline{M}_n$ for a series of specially synthesized Telagen CT prepolymers (Lots AM-14, AM-214, and AM-253).

TABLE 2. Number Average Molecular Weights ($\overline{M}_n$), and Equivalent Weight ($\overline{M}_a$), and Average Functionalities (f) of Commercial CTPB Prepolymers.

Prepolymer	Lot	$\overline{M}_n$	$\overline{M}_a$	f
Telagen CT	AM-14	2,315[a]	1,290	1.79
	AM-14	2,150[b]	1,290	1.67
	AM-214	7,300[a]	3,817	1.91
	AM-214	7,700[b]	3,817	2.02
	AM-253	5,500[b]	2,882	1.91
	3-65	5,120[a]	3,190	1.60
	108	6,040[b]	3,077	2.08
	110	4,950[a]	2,950	1.68
	110	5,340[b]	2,950	1.81
CTL-II	2137	4,780[a]	2,610	1.83
	22D-7	4,850[a]	2,850	1.70
HC-434	98M	3,900[a]	1,800	2.17
	H731	4,280[a]	1,940	2.21
	H570-A	4,500[a]	1,850	2.43

[a] Determined by 3M Company from vapor pressure osmometry (VPO) measurements.

[b] Determined by manufacturer from VPO measurements.

There is a good reproducibility of $\overline{M}_a$ values and poorer reproducibility in $\overline{M}_n$ values in going from lot-to-lot of a given commercial prepolymer. The greater spread in $\overline{M}_n$ values is reflected in the functionality data. The $\overline{M}_n$ and f variations are most pronounced with the Telagen CT prepolymers where the functionalities of the commercial prepolymer lots vary from 1.68 to 2.08. It is of interest to note that the functionality of Telagen CT Lot AM-14 is lower than that of either Lot AM-214 or AM-253 (Lots AM-14, AM-214, and AM-253 were specially prepared).

All the CTPB prepolymers (Table 2) were supposedly treated to remove any volatile components (experience has shown that CTL-II prepolymers contain the highest percentage of volatiles). Also, all $\overline{M}_n$ measurements (VPO) were made in polar solvents such as chloroform or ethyl acetate and extrapolations were made to zero concentration. Therefore, carboxyl group association errors due to hydrogen bonding should have been minimized. Finally, $\overline{M}_n$ values were corrected for the presence of antioxidants.

Because of the $\overline{M}_n$ variations that are directly reflected in the functionality values, the meaningfulness of the resultant functionality values has to be questioned and confirmatory experiments have to be conducted.

Considering the low $\overline{M}_n$ values (2,000 to 8,000) of these CTPB prepolymers, either the kind of the impurities and their quantity must be known or their complete removal must be achieved to obtain meaningful data. The effectiveness and reproducibility of prepolymer pretreatments for the removal of volatiles for the determination of nonvolatile impurities and additives has to be demonstrated so that measurements made in various laboratories can agree.

GEL PERMEATION CHROMATOGRAPHY

With the advent of GPC as developed for polymers (Ref. 4), it has become possible to accurately and rapidly determine molecular weight distributions on the polydispersity (P) of polymers (P is defined as $\overline{M}_n/\overline{M}_w$, where $\overline{M}_w$ is the weight average molecular weight). Alternate determinations of $\overline{M}_w$ involve either the use of light scattering or ultra centrifugation. These alternate techniques are not useful with low molecular weight polymers.

Because of the rapidity and ease of the determinations, GPC was deemed an important analytical technique for investigating manufacturing reproducibility of CTPB prepolymers. Further, it was possible to check another problem area consisting of the comparison of the reproducibility of CTPB materials obtained from different sources. (This work was accomplished by the 3M Company under Navy Contract No. N123 (60530) 56386A and commercial laboratories, DeBell and Richardson (DB&R) and ArRo.) From GPC distribution curves and corresponding column calibrations, the number average backbone length (A_n) in angstroms, the weight average backbone length (A_w) in angstroms, the polydispersity of these polymers can be calculated readily. Values of A_n and A_w can be converted into $\overline{M}_n$ and $\overline{M}_w$ values by the use of the Q factors (Ref. 5) ($\overline{M}_n = A_n \times Q$ and $\overline{M}_w = A_w \times Q$), where Q is the molecular weight of the repeating polymer unit. However, there seems to be some discrepancy between the calculated and experimental values for nonfunctional group polymers (Ref. 6). This discrepancy appears to be even greater for CTPB prepolymers. The following example will illustrate the point. Since the Q factor of low molecular weight straight-chain polyethylene is 12, it is not unreasonable to assume that this number could be used to give "ballpark" $\bar{M}_n$ values for the CTPB prepolymers. However, if a representative A_n value of 236.6 for a CTL-II prepolymer is used together with this Q factor value of 12, an $\bar{M}_n$ of 2,839 is obtained. This value is meaningless because (1) the $\bar{M}_a$ of this prepolymer is 2,850, (2) the $\bar{M}_n$ as determined from VPO measurements is 4,850, and (3) the prepolymer will gel with trifunctional curatives. Therefore, no A_n and A_w values were converted to their corresponding $\bar{M}_n$ and $\bar{M}_w$ values. (No fractionated CTPB prepolymer was available for the experimental determination of Q from VPO $\bar{M}_n/A_n$ data.)

Numerous CTPB prepolymer samples were sent to DB&R for GPC analysis. Resultant calculations are shown in Table 3. The high P values obtained for the Telagen CT and CTL-II prepolymers appeared suspect because these materials were prepared via an anionic mechanism that is supposed to give narrow molecular weight distributions. The 3M Company has reported this unusual behavior and has attributed it to absorption properties of the columns used (Ref. 7). It was concluded that columns used by DB&R had absorption properties. This was confirmed by injecting stearic acid onto the columns and comparing theoretical and experimental A_n values. Also, one of the prepolymer samples was rerun on a different column set. The resultant data are included in Table 3.

TABLE 3. Effect of Columns with Sorption Properties on GPC Calculations (DeBell and Richardson).

Prepolymer	Lot	A_n	A_w	P
Sorption column set: $1.5\text{x}10^5$ Å, $3\text{x}10^4$ Å, $8\text{x}10^3$ Å, and $3\text{x}10^3$ Å				
Telagen	108	113.9	357.9	3.14
	110	117.7	353.8	3.01
CTL-II	2285	120.7	339.2	2.81
	22D-7	128.0	325.2	2.54
HC-434	98M	145.0	287.1	1.98
	H570A	140.2	297.0	2.12
Column set: 10^6 Å, $3\text{x}10^5$ Å, 10^4 Å, and 700 Å				
CTL-II	22D-7	236.6	317.2	1.34

Prepolymer samples were also sent to ArRo Laboratories for GPC analysis (ArRo used the same experimental procedures and conditions as DB&R). Data from the first set of prepolymer samples submitted are listed in Table 4. A second set of samples was also submitted for analysis using the preceding column set. However, examination of the data showed that the columns had acquired absorption properties. These data are very important because disagreement has been reported (Ref. 8) with 3M Company's adsorption observations. Data in Table 4 show unequivocally that it is possible for Styragel columns to acquire adsorption properties. An information exchange with ArRo Laboratories showed that highly polar polymer samples in a solvent other than Tetrahydrofuran (THF) had been run through the column set in question prior to the analysis of the second set of samples. Figure 1 shows the effect of the development of column adsorption properties on the GPC distribution curves where the low molecular weight species play a rather disproportionate role.

TABLE 4. Effect of Columns with Sorption Properties on GPC Calculations (ArRo).

Prepolymer	Lot	A_n	A_w	P
Column set (before sorption): 1.5×10^5 Å, 1.5×10^4 Å, 8×10^3 Å, and 800 Å				
Telagen	108	242.8	444.1	1.83
	110	228.1	405.7	1.78
CTL-II	22D-7	249.1	488.2	1.96
	2137	248.7	554.9	2.23
HC-434	98M	167.7	352.0	2.10
	H731	187.8	377.4	2.01
Column set (after sorption): 1.5×10^5 Å, 1.5×10^4 Å, 8×10^3 Å, and 800 Å				
Telagen	AM253	123.1	236.0	1.92
CTL-II	2285	126.1	284.3	2.25
	2BG-6	114.9	277.0	2.41
HC-434	87M	119.4	243.3	2.04
	H570A	116.9	235.7	2.02
Column set: 3×10^6 Å, 10^5 Å, 10^4 Å, and 10^3 Å				
Telagen	AM253	206.6	369.2	1.79
CTL-II	2285	232.5	452.6	1.95
	2BG-6	224.8	442.4	1.97
HC-434	87M	204.9	411.3	2.01
	H570A	165.0	345.0	2.09

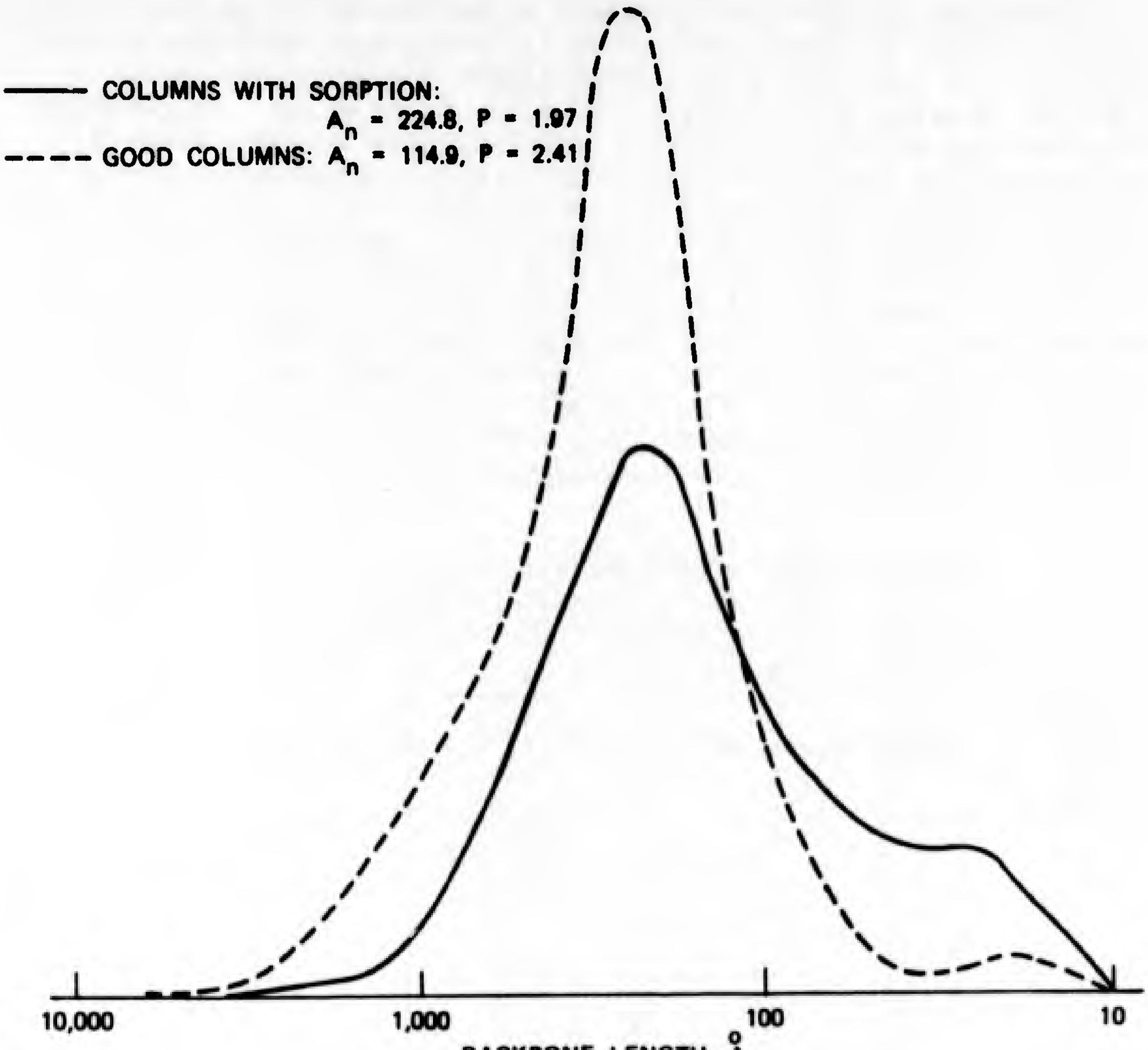


FIG. 1. The Effect of Columns With Sorption Properties on the GPC Chromatograms of CTL-II Lot 2BG-6.

An experiment was also conducted to determine what effect, if any, column set gel sizes had on the GPC analysis of the CTPB prepolymers. Data from Table 5 show an effect that is manifested in the P values. The GPC chromatograms are shown in Fig. 2. In addition to the differences in the peak heights for the two column sets, there is a shift in the peak due to the prepolymer and to the antioxidant (AO) present.

TABLE 5. Effect of a High Column Set and a Low Column Set on the GPC Chromatograph of a Particular CTPB Prepolymer.

A_n	A_w	P
High column set: 10^6 Å, 3×10^5 Å, 10^4 Å, and 700 Å		
236.6	317.2	1.34
Low column set: 8×10^3 Å, 3×10^3 Å, 250 Å, and 60 Å		
268.9	457.2	1.70

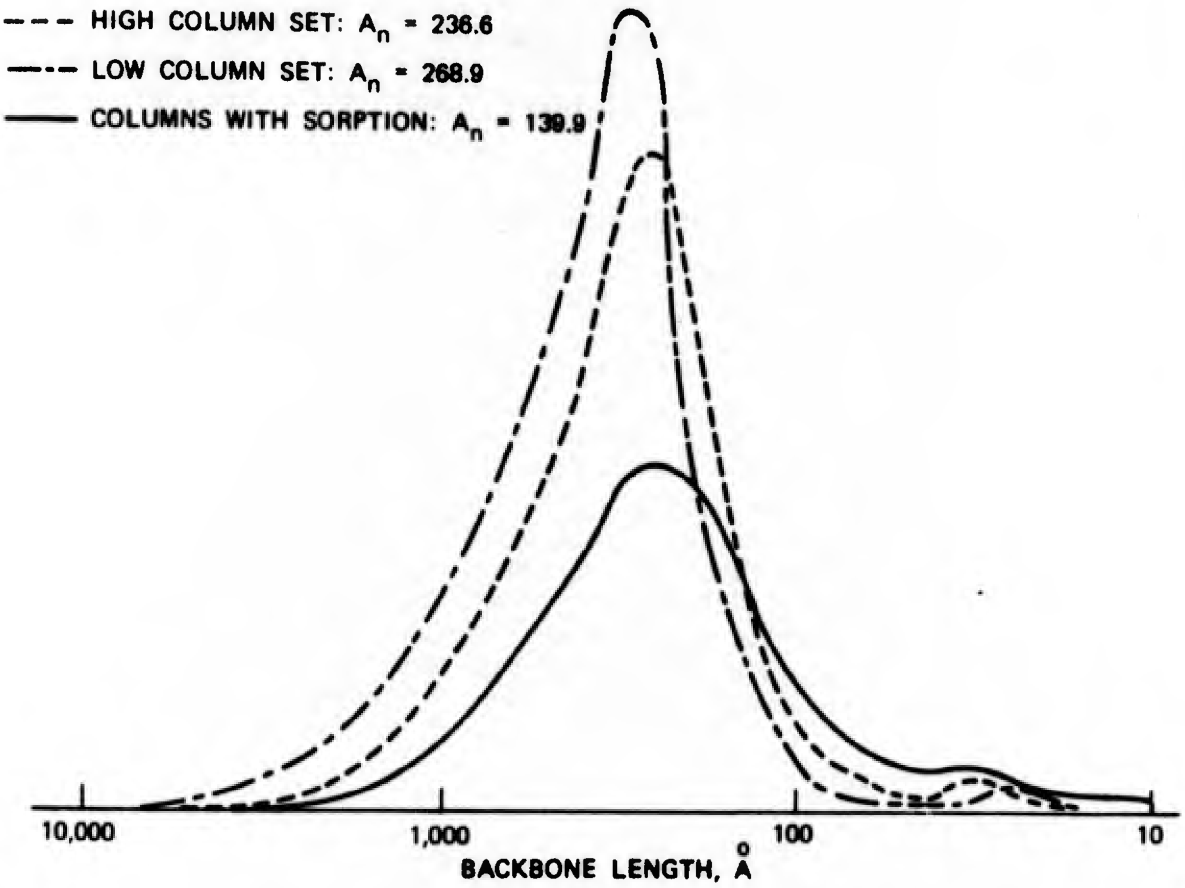


FIG. 2. The Effect of a High Column Set, a Low Column Set, and a Column Set with Sorption Properties on the GPC Chromatograms of CTL-II Lot 22D-7.

Comparative GPC data on both commercial and specially prepared CTPB prepolymers are shown in Table 6. In place of the polystyrene standards used to calibrate their columns by both ArRo and DB&R, 3M Company used CTPB fractions. Examination of the data shows that reproducibility of GPC data from the three laboratories is fair-to-good. However, the spread in the data (A_n, A_w, and P values) is too great to detect most commercial polymer lot-to-lot variations except where the variation is great as in CTL-II Lot T-193.

In concluding this discussion of GPC as an analytical technique for characterizing CTPB prepolymers, the following recommendations are being made for its use as a quantitative analytical tool: (1) check Styragel column sets for adsorption properties with a long-chain aliphatic acid and compare experimental and theoretical A_n values; (2) determine the best combination of column set gel sizes; (3) calibrate columns with fractionated CTPB, and relate this calibration to that obtained with polystyrene standards; (4) set aside an acceptable column set solely for the analysis of CTPB prepolymers; (5) experimentally determine Q so that A_n and A_w values can be converted into $\bar{M}_n$ and $\bar{M}_w$ values; and (6) correct GPC chromatograms for peak broadening (Ref. 9 and 10).

GELATION TIMES (REACTIVITY DETERMINATIONS)

Functionality variations in functional groups containing polymers can also be obtained by determining the gel time of the polymer (T_{gel}) with a standard curative. The experimental technique described in Ref. 11 is very suitable for use with CTPB polymers. Consequently, the T_{gel} was determined for the different CTPB prepolymers using equivalent amounts of tris-[1-(2-methyl) aziridine] phosphine oxide (MAPO) as the curative. Data listed in Table 7 show a significant lot variation in the CTL-II prepolymers. The unusually short T_{gel} of CTL-II Lot T-193 has not changed over a 2-year period. Recalling the unusually high P value of this particular lot of CTL-II in respect to other lots of CTL-II (Table 6) suggests that this particular lot of CTL-II has an abnormally high functionality that is related to the prepolymer molecular weight distribution. Nevertheless, it should be remembered that this lot of CTL-II was an early production run, and is not representative of present day production.

TABLE 6. Comparative Gel Permeation Chromatography Data on Commercial CTPB Prepolymers.

Prepolymer	Lot	Lab	A_n[a]	A_w[b]	P[c]	$\bar{M}_a$[d]
Telagen	3-65	3M[e]	218.7	320.8	1.47	...
	3-65	A[f]	213.3	365.4	1.71	...
	108	3M	238.4	366.6	1.54	3,077
	108	A	242.8	444.1	1.83	3,077
	110	A	214.7	339.7	1.58	3,030
	110	3M	228.1	405.7	1.78	3,030
	110	DBR[g]	237.1	378.4	1.60	3,030
	AM253	3M	213.8	333.6	1.56	2,882
	AM253	A	206.6	369.2	1.79	2,882
	AM14	3M	114.9	159.1	1.38	1,289
	AM14	A	98.8	182.0	1.84	1,289
	AM214	A	277.8	704.1	2.53	3,817
	AM214	3M	286.5	645.0	2.25	3,817
CTL-II	22D-7	3M	230.9	381.2	1.65	2,882
	22D-7	A	249.1	488.2	1.96	2,882
	22D-7	DBR	236.6	317.2	1.34	2,882
	2137	3M	233.8	434.8	1.86	2,967
	2137	A	248.7	554.9	2.23	2,967
	2285	3M	242.0	424.9	1.76	2,950
	2285	A	232.5	452.6	1.95	2,950
	2BG-6	A	224.8	442.4	1.97	2,755
	T-193	A	231.4	652.1	2.82	3,030
HC-434	98M	3M	177.7	297.3	1.67	1,825
	98M	A	167.7	352.0	2.10	1,825
	H570A	3M	195.1	325.4	1.67	1,923
	H570A	A	165.0	345.6	2.09	1,923
	H731	A	187.8	377.4	2.01	1,946

[a] Number average backbone length, Å.

[b] Weight average backbone length, Å.

[c] Polydispersity.

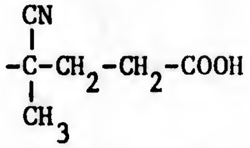
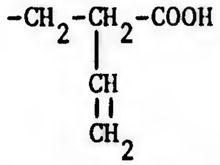
[d] Acid equivalent weight.

[e] Minnesota Mining and Manufacturing Company.

[f] ArRo Laboratories.

[g] DeBell and Richardson Laboratories.

TABLE 7. Gel Times of Different CTPB Prepolymers Cured with MAPO at Equivalency at 135°F Under Nitrogen.

Prepolymer	Terminal carboxyl group	T_{gel}
HC-434 Lot 69M	$-CH_2-CH_2-CH_2-COOH$	37 hr 30 min
HC-434 Lot 98M		33 hr 20 min
Hycar CT Lot 12	 $-\overset{CN}{\underset{CH_3}{C}}-CH_2-CH_2-COOH$	6 hr 26 min
CTL-II Lot T-193	$-CH_2-CH=CH-CH_2-COOH$ +  $-CH_2-\underset{\underset{\underset{CH_2}{\parallel}}{CH}}{CH_2}-COOH$	14 hr
CTL-II Lot 2285		23 hr 45 min
CTL-II Lot 2AP6		22 hr 40 min
Telagen CT Lot 3-65	Same as CTL-II	28 hr 50 min

The data in Table 7 also show prepolymer reactivity differences. The order of reactivities of the prepolymers (Hycar >> CTL-II ≈ Telagen CT > HC-434) is not unexpected considering the different terminal carboxyl groups (Ref. 2 and 3), but the very fast reactivity of Hycar is surprising. Similar fast T_{gel} data have been obtained on Hycar type prepolymers prepared by the 3M Company under contract for NWC.

To gain more information about the functionality of the different CTPB prepolymers, they were reacted with an epoxy chain extender at two different equivalency levels (epoxy/carboxyl = 0.70 and 1.00). The data in Table 8 show that only CTL-II Lot T-193 has an abnormal functionality. This functionality difference is further shown in Table 9.

TABLE 8. Reactivity of Different Commercial CTPB Prepolymers with a Chain Extender[a] at Epoxy/Carboxyl (E/C) = 0.70 and 1.00.

Prepolymer	E/C = 0.70	E/C = 1.00
CTL-II Lot T-193	X[b]	X
CTL-II Lot 2285	S[c]	X
HC-434 Lot 69M	S	X
HC-434 Lot 98M	S	X
Hycar Lot 12	S	X
Telagen Lot 3-65	S	X

[a] N,N-Dipropane oxide-butylamine.

[b] Crosslinked after 5 days at 135°F.

[c] Soluble after 5 days at 135°F.

TABLE 9. Intrinsic Viscosities of CTPB Prepolymers Reacted with the Chain Extender, Phenyl-MAPO at Equivalency at 135°F.

Prepolymer	Unreacted carboxyl, %	N, poise[a]
CTL-II Lot T-193	35.0	0.724
Telagen Lot 3-65	36.5	0.281

[a] Viscosity after 2 days.

EVALUATION OF THE LOT-TO-LOT REPRODUCIBILITY OF COMMERCIAL CTPB PREPOLYMERS THROUGH CURED GUMSTOCKS

MAPO CURE

In the preceding section, the importance of knowing accurately the f of the CTPB prepolymers and the variation of the f of these prepolymers in a given manufacturer's lot was stated. Measurement errors indicated the necessity for performing confirmatory experiments to gain the necessary reliable information on prepolymer f and lot-to-lot variations.

Since the $\overline{M}_a$ values of these CTPB prepolymers are readily and accurately known, as well as the equivalent weights of available curatives, the prepolymers were evaluated from the standpoint of their cured gumstocks by accurate and easily reproducible crosslink density (X-ρ), % gel, and uniaxial tensile property (UTP) measurements. The X-ρ measurements were made on cast cylindrical samples using the procedure in Ref. 12. UTP measurements were made on cast end-bonded specimens. Finally, it should be stated that all three prepolymers contained approximately 1% by weight of the antioxidant, Calco 2246 [2,2'-methylene-bis-(4-methyl-6-tertiary-butylphenol)]. Normally, HC-434 contains phenyl-β-naphthyl amine (PBNA) as the antioxidant, however, Thiokol was requested to substitute Calco 2246 so that all prepolymers would contain the same antioxidant and could be evaluated satisfactorily.

Crosslink-Density and % Gel

The X-ρ and % gel data on various lots of the different commercial MAPO cured CTPB gumstocks are summarized in Table 10. CTL-II and HC-434 gumstocks show good prepolymer reproducibility, whereas Telagen CT gumstocks (Lots 3-65, 108, and 110) show fair-to-poor reproducibility. At this point, reference is again made to Table 2, which dealt with $\overline{M}_n$, $\overline{M}_a$, and f values of the various prepolymers. From that data it was indicated that the commercial lots of Telagen CT prepolymer had a greater spread in f than either CTL-II or HC-434 prepolymers. The present data (Table 10) confirm this. The present data also indicate the following order of prepolymer f: HC-434 > CTL-II > Telagen CT.

The data from Table 10 show a definite f difference among the specially prepared Telagen CT prepolymers that only differed in their $\overline{M}_n$ (from ~2,000 to ~8,000). This is primarily evidenced by the % gel data. On the basis of these data, the following f order would be indicated: AM-14 > AM-253 > AM-214. This does not support the data from Table 2 that indicate the following f order: AM-253 = AM-214 > AM-14. Because of the previously discussed problem associated with the $\overline{M}_n$ measurements, the f order based on % gel data appears more meaningful and accurate. It is of interest to compare Telagen CT Lot AM-14 with HC-434 Lot 98M in Table 10, since both samples have equal X-ρ values even though they are approximately 6% different in % gel and have $\overline{M}_n$ values of 2,200 and 3,900, respectively.

TABLE 10. Crosslink Density (X-ρ) and % Gel Data Obtained on Various Lots of Commercial CTPB Cured with Equivalent Amount of MAPO.[a]

Sample prepolymer	Lot	X-ρ x 10^4	% gel
X-11 Telagen CT	3-65	0.57	83.5
X-12	108	0.77	88.6
X-13	110	0.65	86.5
X-23	AM-214	0.42	82.0
X-24	AM-14	1.38	89.1
X-25	AM-253	0.66	86.0
X-3 CTL-II	2285	0.99	91.3
X-20	22D-7	0.85	90.8
X-21	2137	0.89	91.5
X-8 HC-434	H-570A	1.49	95.4
X-18	98M	1.36	94.8
X-22	H-731	1.33	94.9

[a] Cured 2 weeks at 135°F.

Uniaxial Tensile Properties

The UTP of the preceding gumstocks are summarized in Table 11. General reproducibility of prepolymer lots observed in Table 10 is confirmed here, especially in respect to maximum tensile strengths, σ_m. The σ_m data again reflect the preceding f observations (HC-434 > CTL-II > Telagen CT). Considering that CTL-II and Telagen CT have similar $\overline{M}_n$ values and the gel fractions of the CTL-II gumstocks are greater than those of the Telagen CT gumstocks, it is surprising that the elongations (γ_m) for the latter are not greater than that of the former. Also, for tightness of cure, the HC-434 gumstocks exhibit excellent γ_m values. These last two observations tend to show that for a given molecular weight range the best combination of properties is obtained if f values are maximized.

It is difficult to relate the UTP of the gumstocks made from the specially prepared Telagen prepolymers with their corresponding X-ρ and % gel values with any certainty (Table 11). It can only be stated that the UTP tend to reflect the $\overline{M}_n$ changes of the starting prepolymers.

TABLE 11. Uniaxial Tensile Properties of Various Lots of Commercial CTPB Cured with MAPO at Equivalency.

Sample prepolymer	Lot	E, psi	σ_m, psi	γ_m, %
X-11 Telagen CT	3-65	64	35	94
X-12	108	94	48	96
X-13	110	83	43	99
X-23	AM-214	41	29	123
X-24	AM-14	126	48	50
X-25	AM-253	67	38	94
X-3 CTL-II	2285	109	55	95
X-20	22D-7	109	59	107
X-21	2137	104	55	100
X-8 HC-434	H507-A	174	81	82
X-18	98M	155	75	89
X-22	H-731	166	73	79

Again, comparison of the UTP of Telagen CT Lot AM-14 and HC-434 Lot 98M gumstocks which have equal X-ρ values shows more the effect of f than the effect of prepolymer molecular weight. This can be illustrated by observing that the Telagen CT sample has a lower % gel and a lower σ_m value than HC-434. This again illustrates the need for maintaining prepolymer f for the best combination of gumstock physical properties.

MAPO/EPON 812 CURE

The various commercial CTPB prepolymers were also evaluated with the MAPO/Epon 812 curative system (0.77 equivalents MAPO, 0.23 equivalents Epon 812). This particular system was chosen (based on earlier work) for corresponding propellant evaluation. Techniques and procedures that were used to evaluate the MAPO cured gumstocks were also used with these MAPO/Epon 812 cured gumstocks.

Crosslink-Density and % Gel

Data on the X-ρ and % gel values of the different polymers are presented in Table 12. Examination and comparison of the data with the data on the corresponding MAPO cured gumstocks show that the X-ρ values are decreased by approximately 55 to 60%. A decrease was expected because the reported f of Epon 812 is 2.30; therefore, it should function, in part, as a chain extender. However, using average values of the % gel, decreases of 6.5 to 8% are observed between the differently cured samples; this was unexpected.

TABLE 12. Crosslink Density (X-ρ) and % Gel Data Obtained on Various Lots of Commercial CTPB Cured with MAPO/Epon 812 at Equivalency[a] (0.77 MAPO/0.23 Epon 812).

Sample	Prepolymer	Lot	X-σ x 10^4	% gel
X-26	Telagen CT	110	0.30	78.1
X-20		108	0.35	80.9
X-27	CTL-II	2137	0.35	84.4
X-31		22D-7	0.35	84.4
X-28	HC-434	H-731	0.63	89.1
X-32		98M	0.54	87.9
X-33		H-570A	0.59	88.3

[a] Cured 2 weeks at 135°F.

Uniaxial Tensile Properties

Data on the UTP values of the different polymers are presented in Table 13. Taking average lot-to-lot values of σ_m with a given polymer, decreases on the order of 16 to 27% are observed in respect to MAPO cured gumstocks. This tends to show that some chain extension is taking place and is reflective of decreases in X-ρ values; nevertheless, some of this effect is influenced by the % gel values (compared to MAPO cured system). Elongations have increased by a factor of ~1.7 for the CTL-II and Telagen CT polymers and by a factor of ~1.9 for HC-434 polymers.

TABLE 13. Uniaxial Tensile Properties of Various Lots of Commercial CTPB Cured with MAPO/Epon 812 at Equivalency (0.77 MAPO/0.23 Epon 812).

Sample	Prepolymer	Lot	E, psi	σ_m, psi	γ_m, %
X-26	Telagen CT	110	28	26	157
X-30		108	38	33	177
X-27	CTL-II	2137	48	37	160
X-31		22D-7	49	40	196
X-28	HC-434	H-731	85	50	141
X-32		98M	72	51	168
X-33		H-570A	71	49	159

Even though the MAPO/Epon 812 curative system does impart some interesting changes in gumstock properties when compared to a MAPO cure, the changes do not conflict with the conclusions regarding polymer functionalities from the data obtained with a MAPO cure.

ROLE AND EFFECTIVENESS OF DIFFERENT ANTIOXIDANTS IN CTPB PREPOLYMERS AND GUMSTOCKS

The unsaturated nature of these CTPB prepolymers makes them very susceptible to attack by atmospheric oxygen, forming hydroperoxides. Therefore, these prepolymers have to be protected by antioxidants because under certain environmental conditions and in the presence of some metal impurities, decomposition of the hydroperoxide results, causing oxidative crosslinking. To aid reproducibility of gumstock and propellant physical properties after receipt of a given prepolymer lot and to ensure against undesirable side reactions, the presence of a sufficient quantity of an efficient antioxidant is needed.

Previously, a study was conducted on the effectiveness of certain additional antioxidants (different chemical structures and functionalities) in propellant formulations that were aged at 180°F. The most promising candidate antioxidant was Flexzone 5L, N-alkyl, N'-phenyl-P-phenylenediamine (F-5L). Since CTL-II and Telagen CT contain Calco 2246 as the antioxidant, and HC-434 contains PBNA as the antioxidant, these antioxidants as well as F-5L were reevaluated singly as well as in combination in the following work.

METAL IMPURITIES

To gain more information about the oxidative stability of the CTPB prepolymers, several experiments were conducted. The first experiment dealt with determining whether or not any trace metals capable of entering into redox reactions with hydroperoxides to generate free radicals were present. Table 14 shows the metal impurities and their concentrations that were found.

TABLE 14. Trace Metal Impurities in Commercial CTPB Prepolymers.

Prepolymer	Lot	Iron, ppm	Copper, ppm
Hycar	12	1.9	1.0
Telagen CT	3-65	1.2	0.87
HC-434	69M	6.5	1.1
CTL-II	T-193	6.5	1.2

Since these metals are present, care must be exercised to reduce exposure of the prepolymer to atmospheric oxygen to minimize hydroperoxide formation.

HYDROPEROXIDE PRESENCE

Another experiment was devised to determine the presence of hydroperoxides in the CTPB prepolymers and to further check the efficacy of the antioxidants PBNA, F-5L, and Calco 2246. Thus, a single lot of HC-434 prepolymer, which had been previously divided into three sublots by the manufacturer, contained 1% by weight of F-5L, PBNA, or Calco 2246 antioxidants. For the experiment, one set of samples of each sublot contained the prepolymers with approximately 0.15% by weight of iron octoate (FeOct) under nitrogen.

The sealed prepolymer samples were aged up to 30 weeks at 135°F. The progression of aging was periodically followed with intrinsic viscosity measurements. All prepolymers aged only slightly except the Calco 2246 and FeOct sample which gelled between 21 and 30 weeks. The "as received" prepolymer with Calco 2246 alone did not gel. This prepolymer gelled because of the redox reaction between the hydroperoxides and the FeOct which generated free radicals. Nevertheless, no gelation could occur until the antioxidant was used. This confirms that F-5L as well as PBNA are better antioxidants than Calco 2246 because they did not allow gelation in the presence of FeOct under the experimental conditions and time. In conclusion, it has been shown that the CTPB prepolymers contain both hydroperoxide and trace metal impurities that can function as "drier catalysts". Very careful handling and storage of these prepolymers is necessary. It is suggested that an efficient antioxidant should be added to the prepolymers in addition to the one present in the "as received" samples.

ANTIOXIDANTS AND PHYSICAL PROPERTIES

Since it has been shown that the CTPB prepolymers contain both metal impurities and hydroperoxides and that some antioxidants offer better protection to the prepolymers than others, an experiment was designed to quantitatively determine, if possible, what effect, if any, this would have on the corresponding MAPO cured gumstocks. A MAPO cure was chosen because of its (1) inertness towards phenolic and amine compounds (the antioxidants) under the conditions employed and (2) use as a propellant curative. Preceding procedures for preparing and evaluating specimens were employed here.

Table 15 illustrates the effectiveness of the different antioxidants and added antioxidants on the X-ρ and % gel values of the three commercial gumstocks. Neither PBNA nor Calco 2246 has any effect on these properties, either as the only antioxidant or as added antioxidant. However, F-5L has a definite effect. The greatest changes are observed with the CTL-II gumstocks. Decreasing changes are noted with the Telagen CT and HC-434 gumstocks. The preceding observations have been confirmed by the UTP listed in Table 16. The protective action against oxidation of the F-5L antioxidant and to a lesser extent the PBNA antioxidant does have some physical meaning.

TABLE 15. Effect of Different Antioxidants and Added Antioxidants on Crosslink-Density (X-ρ) and % Gel Data Obtained on Commercial CTPB Prepolymers Cured with MAPO at Equivalency.[a]

Sample	Prepolymer	Lot	Antioxidant	Added antioxidant[b]	X-ρ x 10^4	% gel
X-13	Telagen CT	110	Calco 2246[c]	....	0.65	86.5
X-14		110	Calco 2246	F-5L[d]	0.45	83.4
X-3	CTL-II	2285	Calco 2246	....	0.99	91.3
X-4		2285	Calco 2246	F-5L	0.52	86.2
X-6		2285	Calco 2246	PBNA[e]	0.97	90.8
X-8	HC-434	H-570A[f]	Calco 2246	....	1.49	95.4
X-15		H-570A	Calco 2246	F-5L	1.09	93.7
X-9		H-570B[f]	F-5L	....	1.10	94.5
X-16		H-570B	F-5L	Calco 2246	1.09	93.7
X-10		H-570C[f]	PBNA	....	1.34	95.0

[a] Cured 2 weeks at 135°F.

[b] Present as 1% of gumstock weight.

[c] 2,2'-methylene-bis-(4-methyl-6-tertiary-butylphenol).

[d] N-alkyl, N'-phenyl-p-phenylenediamine.

[e] Phenyl-β-naphthylamine.

[f] Same lot of prepolymer but differs only in the antioxidant present (1% by weight).

TABLE 16. Uniaxial Tensile Properties of CTPB Prepolymers Containing Antioxidant or Additional Antioxidant Cured with MAPO at Equivalency.

Sample	Prepolymer	Lot	Added antioxidant[a]	E, psi	σ_m, psi	γ_m, %
X-13	Telagen CT	110	....	83	43	99
X-14		110	F-5L[b]	48	36	156
X-3	CTL-II	2285	....	109	55	90
X-4		2285	F-5L	52	46	210
X-6		2285	PBNA[c]	117	60	97
X-8	HC-434	H-570A[d]	....	174	81	82
X-15		H-570A	F-5L	152	76	111
X-9		H-570B[d]	....	132	70	105
X-16		H-570B	Calco 2246[e]	157	77	98
X-10		H-570C[e]	....	164	77	88

[a] Present as 1% of gumstock weight.

[b] N-alkyl, N'-phenyl-p-phenylenediamine.

[c] Phenyl-β-naphthylamine.

[d] Same lot of prepolymer but differs only in the antioxidant added (1% by weight).

[e] 2,2'-methylene-bis-(4-methyl-6-tertiary-butylphenol).

EVALUATION OF CTPB PREPOLYMERS IN PROPELLANTS

The real test of any differences in these CTPB prepolymers is with their usage as propellant binders. Even though differences can be detected in the prepolymers or gumstocks, some of these can be masked by the cured propellant properties. This masking could be due in part to either cure interference from the oxidizer and/or some oxidative crosslinking.

MOLECULAR WEIGHT AND FUNCTIONALITY

Table 17 presents the pertinent data that illustrate the effect of different $\overline{M}_n$ prepolymers on propellant UTP. The prepolymers and gumstocks were evaluated earlier (Tables 2, 10, and 11), wherein, differences were attributed to f differences (f HC-434 > Telagen Lot AM-14 > Telagen Lot AM-253 > Telagen Lot AM-214). Propellant UTP reinforce this earlier conclusion but surprisingly, BDE-211 did have a greater σ_m than that of BDE-210. Nevertheless, BDE-212 has the best combination of σ_m and γ_m values which illustrates the importance of f. Also, the data show that to improve γ_m by increasing $\overline{M}_n$, f must be maintained.

TABLE 17. Effect of CTPB Polymer Molecular Weight on Propellant Uniaxial Tensile Properties.

Propellant[a]	Prepolymer	Lot	$\overline{M}_n$	X-ρ x 10^4[b]	% gel[c]	E, psi	σ_m, psi	γ_m, %
BDE-209	Telagen CT	AM-14	2,150	1.38	89.1	3,817	233	13
BDE-210	Telagen CT	AM-253	5,500	0.66	86.0	2,132	166	27
BDE-211	Telagen CT	AM-214	7,700	0.42	82.0	2,391	180	25
BDE-212	HC-434	733	4,280	1.33	94.9	3,012	221	30

[a] Cured with MAPO/Epon 812 (0.77 MAPO/0.23 Epon 812) at equivalency for 2 weeks at 135°F with 86% solids loading.

[b] Prepolymer cured with MAPO at equivalency for 2 weeks at 135°F.

[c] Percent gel of MAPO cured gumstocks.

ANTIOXIDANTS

The effects of different and added antioxidants were determined. The data (Table 18) show that Calco 2246 has no effect on the propellant UTP when it is an added antioxidant. The same observation holds for PBNA, but when F-5L is present either as the only antioxidant or as an added antioxidant, large differences in UTP are noted. The effect is greater in CTL-II propellants than in HC-434 propellants. This confirms previous gumstock data and conclusions. Comparison of the properties of BDE-183 with BDE-187 again shows that Epon 812 functions in part as a chain extender in the MAPO/Epon 812 curative system.

COMPARATIVE AGING

Aging data (140°F under nitrogen) obtained from HC-434, CTL-II, and Telagen CT propellants are shown in Fig. 3 and 4. Comparison of the values indicates that propellant properties stabilize after the first month. The higher f of the HC-434 is illustrated by its higher σ_m values in comparison to CTL-II and Telagen CT.

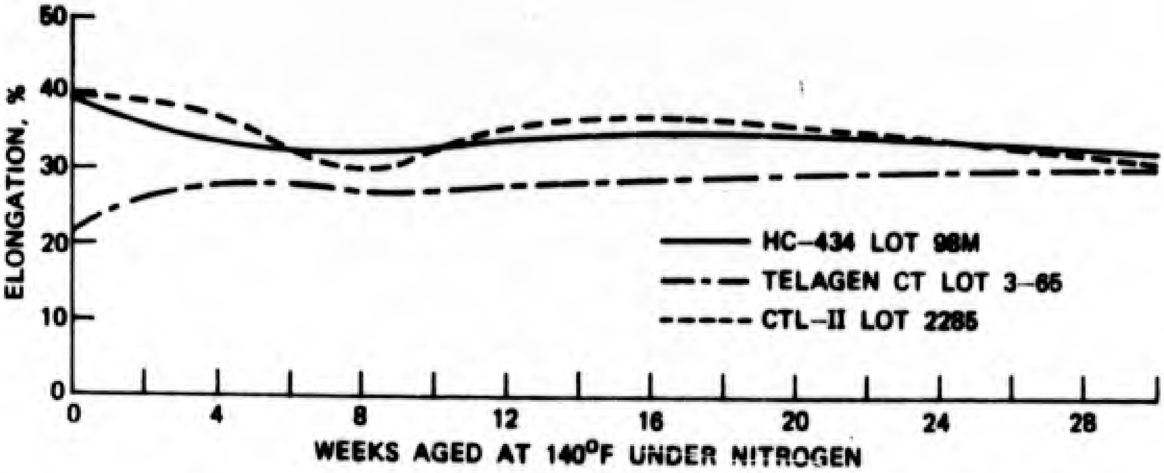


FIG. 3. Evaluation of Commercial CTPB Prepolymers that all Contain the Same Antioxidant in 86% Solids Loaded Propellants Cured with MAPO/Epon 812 (0.77 MAPO/0.23 Epon 812) at 1.02 Equivalency for 2 Weeks at 135°F.

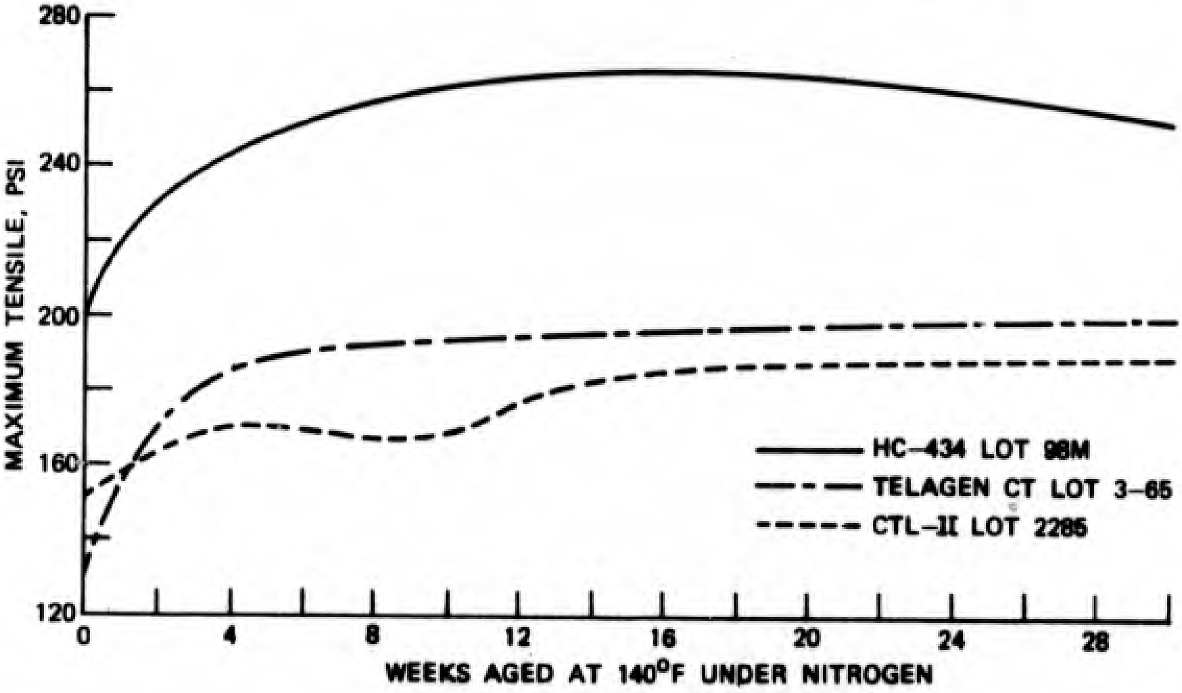


FIG. 4. Evaluation of Commercial CTPB Prepolymers That All Contain the Same Antioxidant in 86% Solids Loaded Propellants Cured with MAPO/Epon 812 (0.77 MAPO/0.23 Epon 812) at 1.02 Equivalency for 2 Weeks at 135°F.

TABLE 18. The Effect of Antioxidants and Added Antioxidants on Propellant Uniaxial Tensile Properties.

Propellant[a]	Prepolymer	Lot	Antioxidant[b]	Added antioxidant[c]	E, psi	σ_m, psi	γ_m, %
BDE-183[d]	CTL-II	2285	Calco 2246	...	2,235	158	31
BDE-184[d]	CTL-II	2285	Calco 2246	Calco 2246	1,901	156	33
BDE-185[d]	CTL-II	2285	Calco 2246	F-5L	670	114	64
BDE-187[e]	CTL-II	2285	Calco 2246	...	2,540	153	18
BDE-198[f]	HC-434	H-570A[g]	Calco 2246	...	3,742	211	29
BDE-199[f]	HC-434	H-570B[g]	F-5L	...	2,401	182	43
BDE-200[f]	HC-434	H-570C[g]	PBNA	...	3,841	208	33

[a] All propellants contained 86% solids by weight.

[b] Antioxidant added by manufacturer.

[c] One percent antioxidant (based on binder weight) added at the start of propellant mixing.

[d] Cured with MAPO/Epon 812 (0.77 MAPO/0.23 Epon 812) at 1.02 equivalency ratio for 1 week at 135°F.

[e] Contained the same quantity of MAPO present in BDE-183, -184, and -185, and cured for 1 week at 135°F.

[f] Cured with MAPO/Epon 812 (0.77 MAPO/0.23 Epon 812) at 1.02 equivalency ratio for 3 weeks at 135°F.

[g] Same lot of prepolymer (prepolymer sublotted by manufacturer and a different antioxidant added to each sublot at 1% by weight level).

DYNAMIC MECHANICAL BEHAVIOR

The preceding three propellants (HC-434, CTL-II, and Telagen CT) were also characterized by means of dynamic mechanical measurements. The apparatus used was designed by Lepie and Adicoff. It is a modification of a previously described device (Ref. 13). Mechanical loss measurements (Fig. 5, 6, and 7) show a spread of 5°C in the glass transition temperatures (T_g) which is probably reflective of microstructure. Effects of $\overline{M}_n$, if present, are minimal. The $\overline{M}_n$ of the HC-434 polymer is approximately 1,000 less than either CTL-II or Telagen CT which would tend to support $\overline{M}_n$ effects. However, f also plays an important role.

As the f increases (X-ρ increases) for a given molecular weight, the T_g is raised. It has been shown that the f of HC-434 > CTL-II > Telagen CT. If a comparison of the mechanical loss measurements of the CTL-II propellant with its corresponding gumstock (Fig. 7 and 8) is made, it can be observed that the propellant solids cause the T_g to be raised by 5°C. The secondary transition (T_β) noted in these measurements is rather unusual because it occurs above T_g. Thus, it cannot be attributed to the molecular movements of any pendant groups along the backbone of the polymer. Nevertheless, it is important because of its magnitude even though it occurs between -30 to -36°C. Finally, it should be noted that the transition is not as pronounced in the gumstock as it is in the propellant. This is reasonable since in the propellant the binder is essentially a thin film and hence more sensitive.

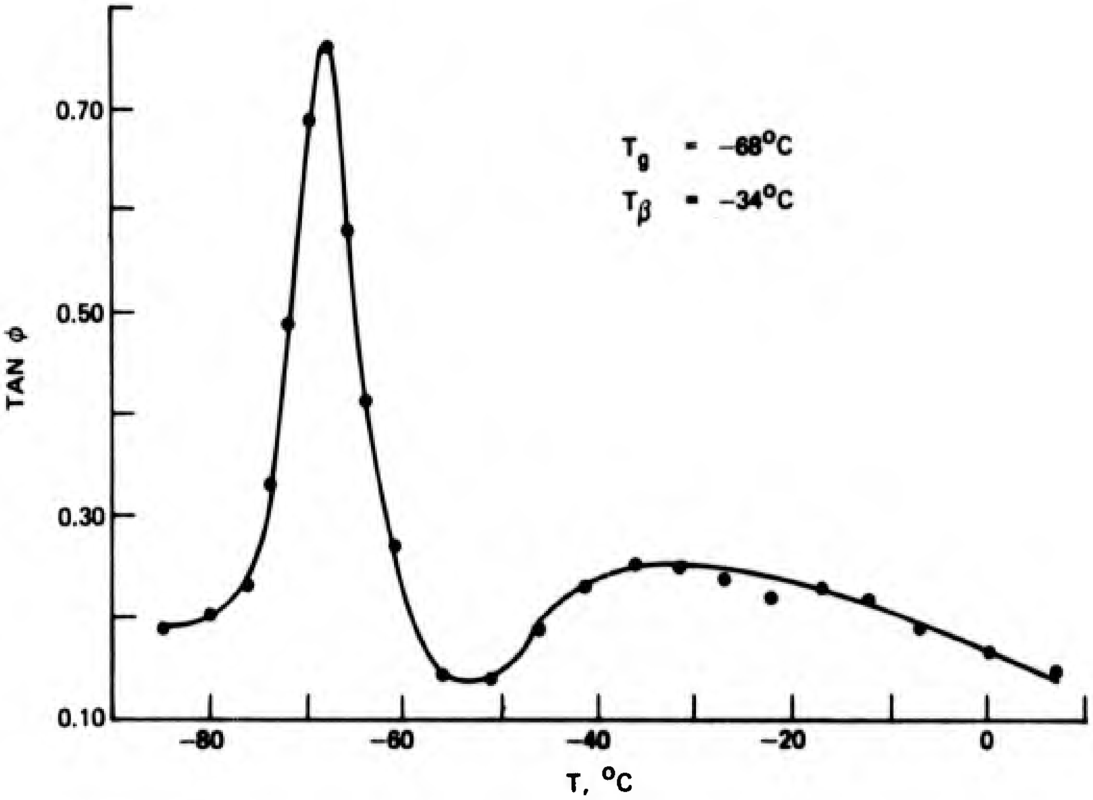


FIG. 5. Dynamic Loss Measurements at 0.10 Hz of an HC-434 Propellant Showing the Glass Transition Temperature (T_g) and a Secondary Transition Temperature (T_β).

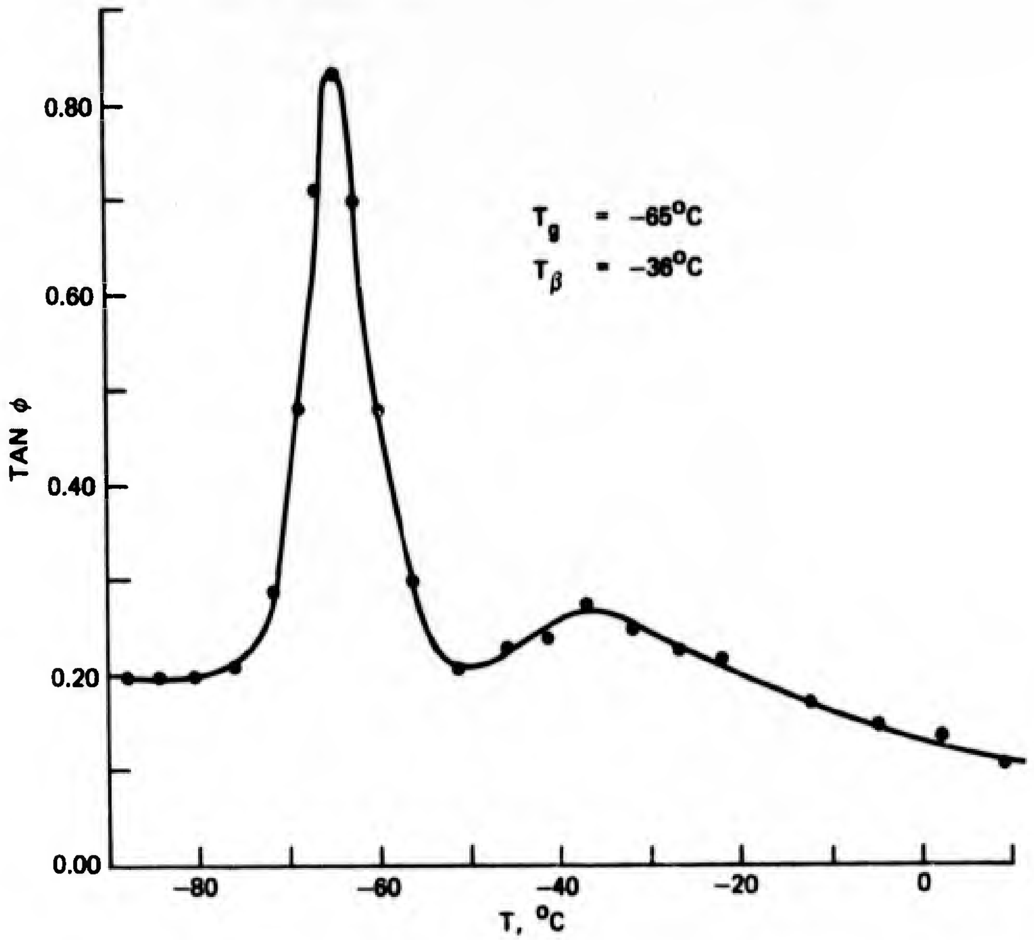


FIG. 6. Dynamic Loss Measurements at 0.10 Hz of a Telagen CT Propellant Showing the Glass Transition Temperature (T_g) and a Secondary Transition Temperature (T_β).

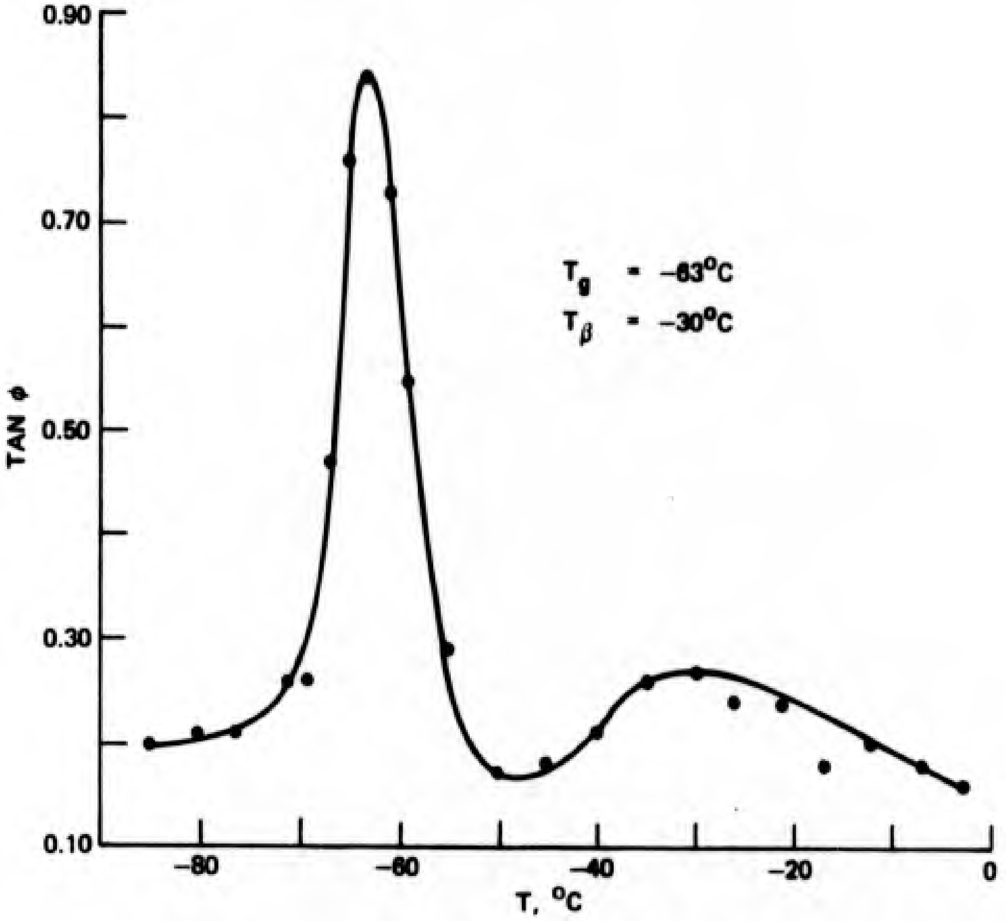


FIG. 7. Dynamic Loss Measurements at 0.10 Hz of a CTL-II Propellant Showing the Glass Transition Temperature (T_g) and a Secondary Transition Temperature (T_β).

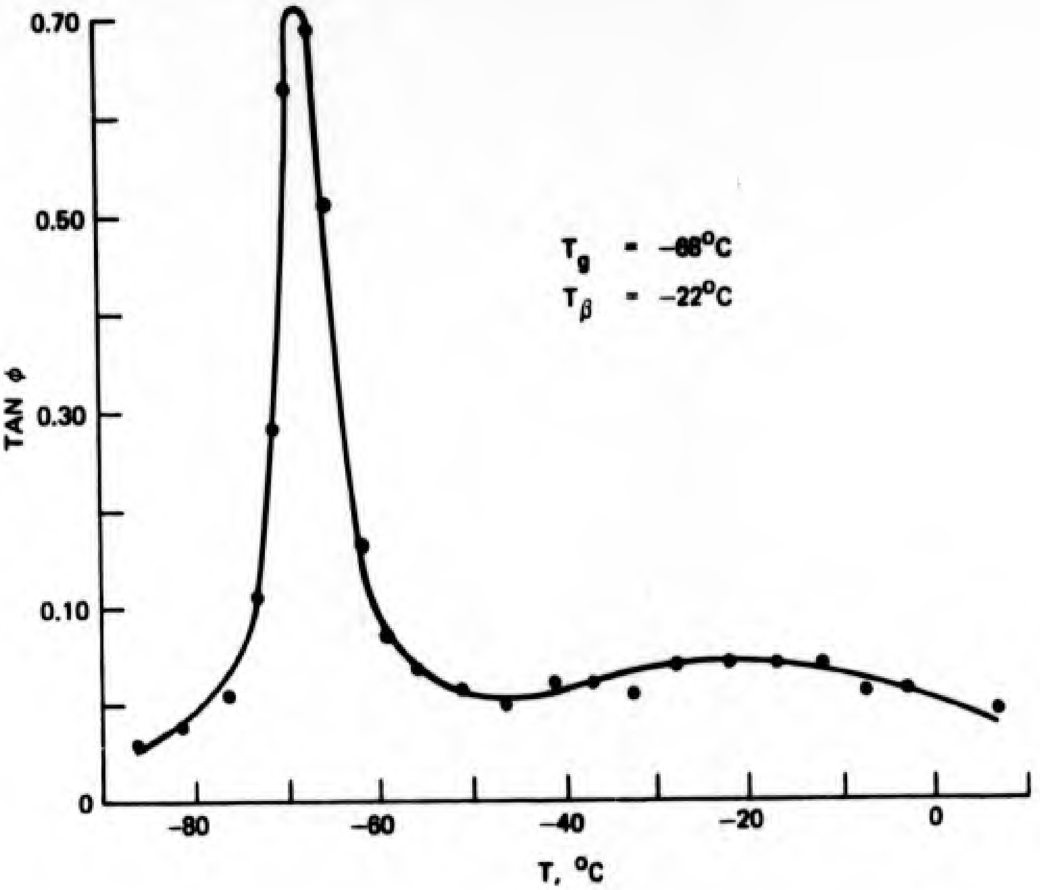


FIG. 8. Dynamic Loss Measurements at 0.10 Hz of a CTL-II Gumstock Showing the Glass Transition Temperature (T_g) and a Secondary Transition Temperature (T_β).

To directly compare the dynamic mechanical behavior of these propellants a common reference temperature (T_o) was chosen, where $T_o = T_g + 50°C$, even though the T_g values had a spread of 5°C. Considering this, and the fact that data were not available for the calculated T_o values, a T_o value of −23°C was used. Temperature shift factors (Log a_T) show good to excellent agreement (Fig. 9, 10, and 11) between experimental and theoretical values (Ref. 14).

$$\text{Log } a_T \text{ (universal average)} = \frac{-8.86 + (T-T_o)}{101.6 + (T-T_o)}$$

The divergence of the HC-434 propellant might be explained on the basis that it had the lowest T_g value. Finally, it is seen that there is excellent agreement between the experimental and theoretical log a_T values of the CTL-II gumstock (Fig. 12). In this case, T_o was taken to be T_g +50°C or −17°C.

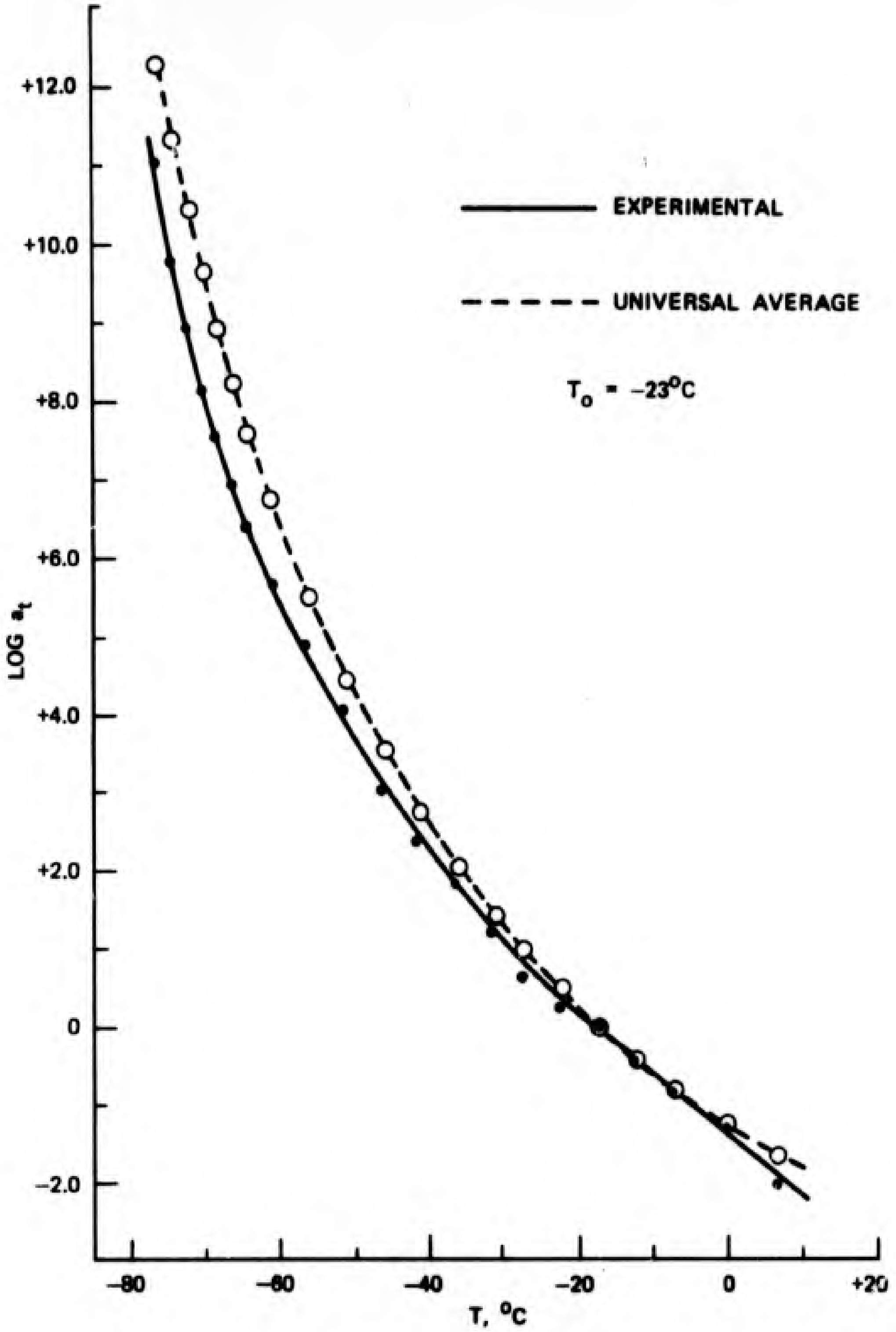


FIG. 9. Temperature Shift Factors of an HC-434 Propellant.

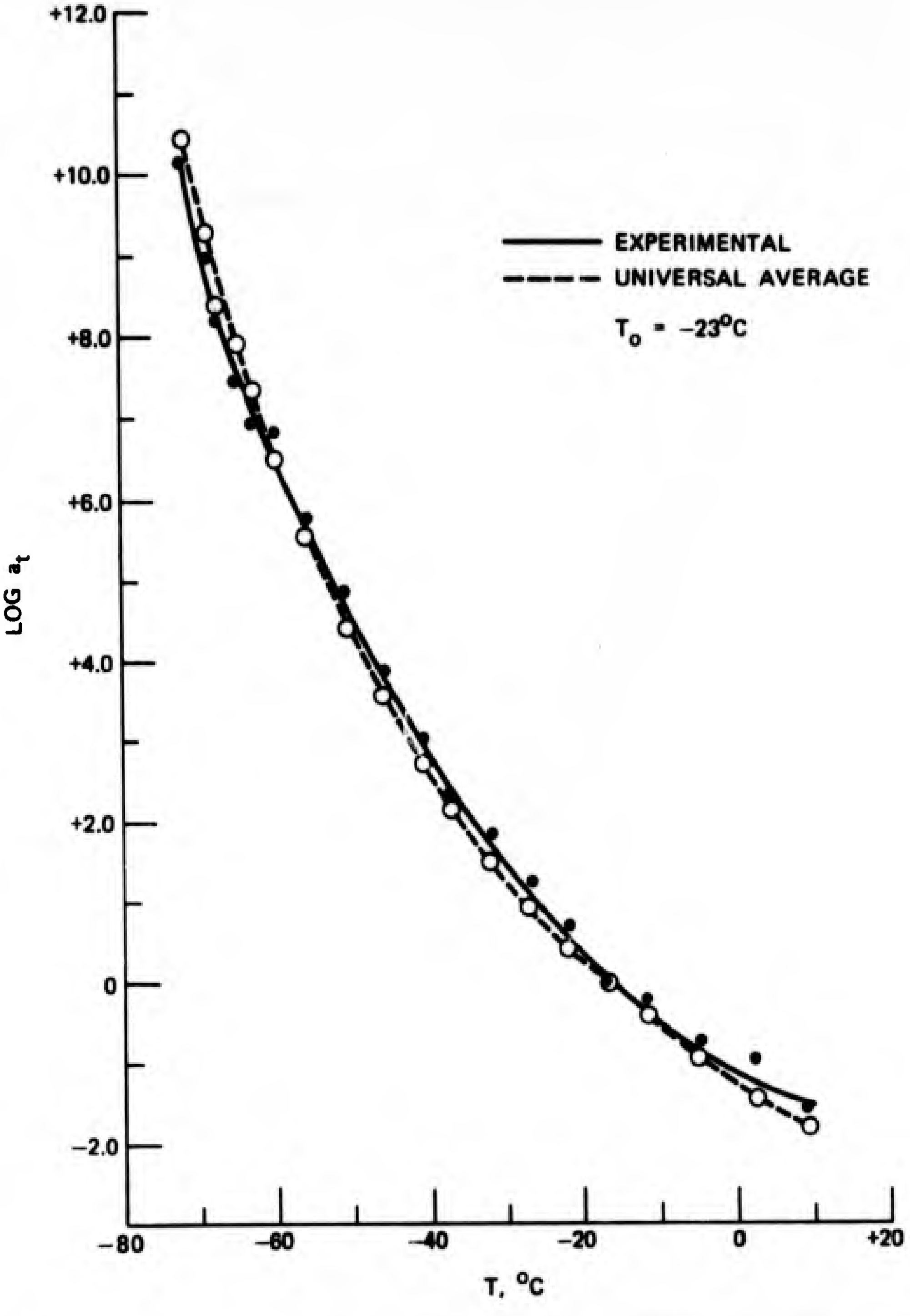


FIG. 10. Temperature Shift Factors of a Telagen CT Propellant.

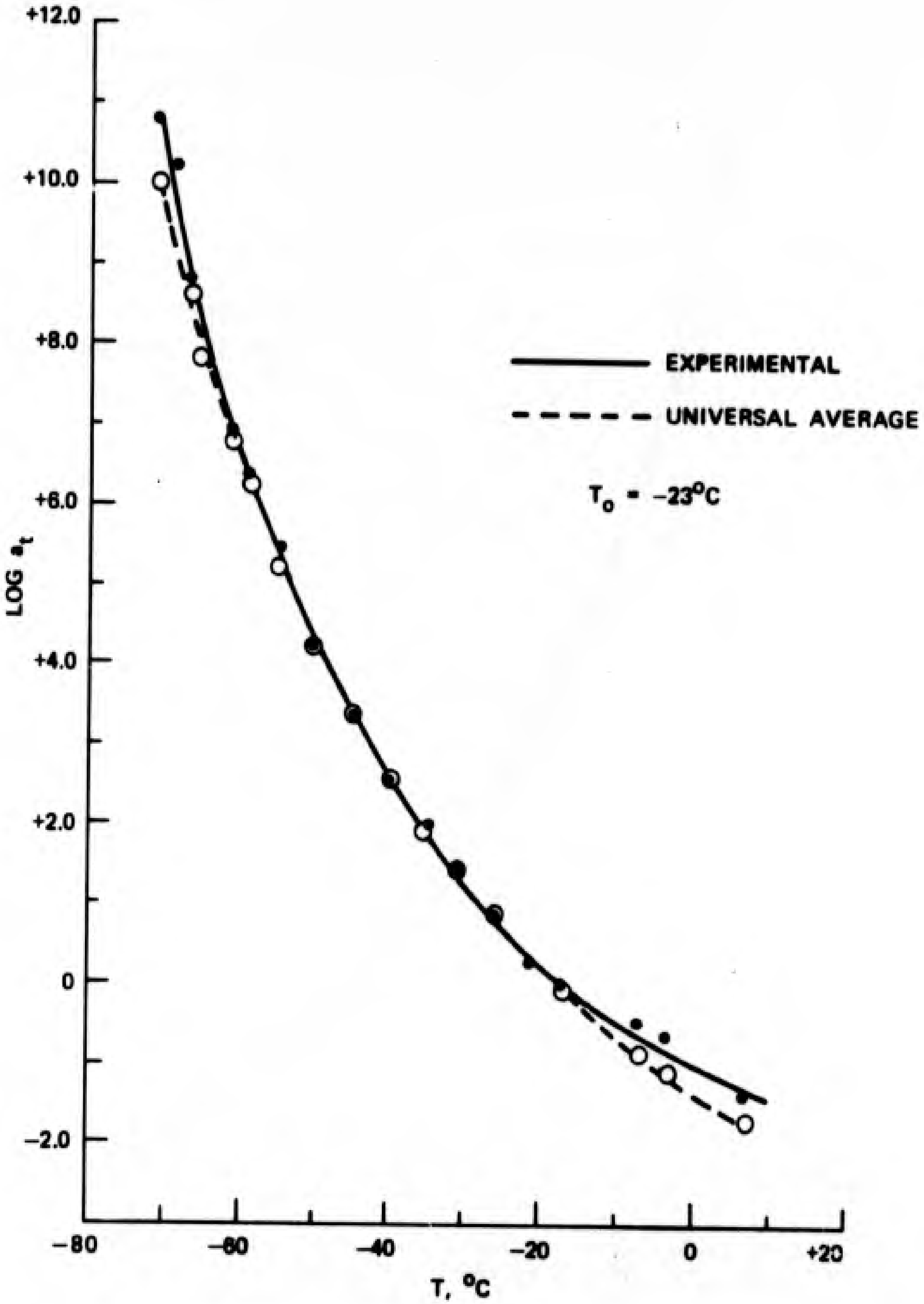


FIG. 11. Temperature Shift Factors of a CTL-II Propellant.

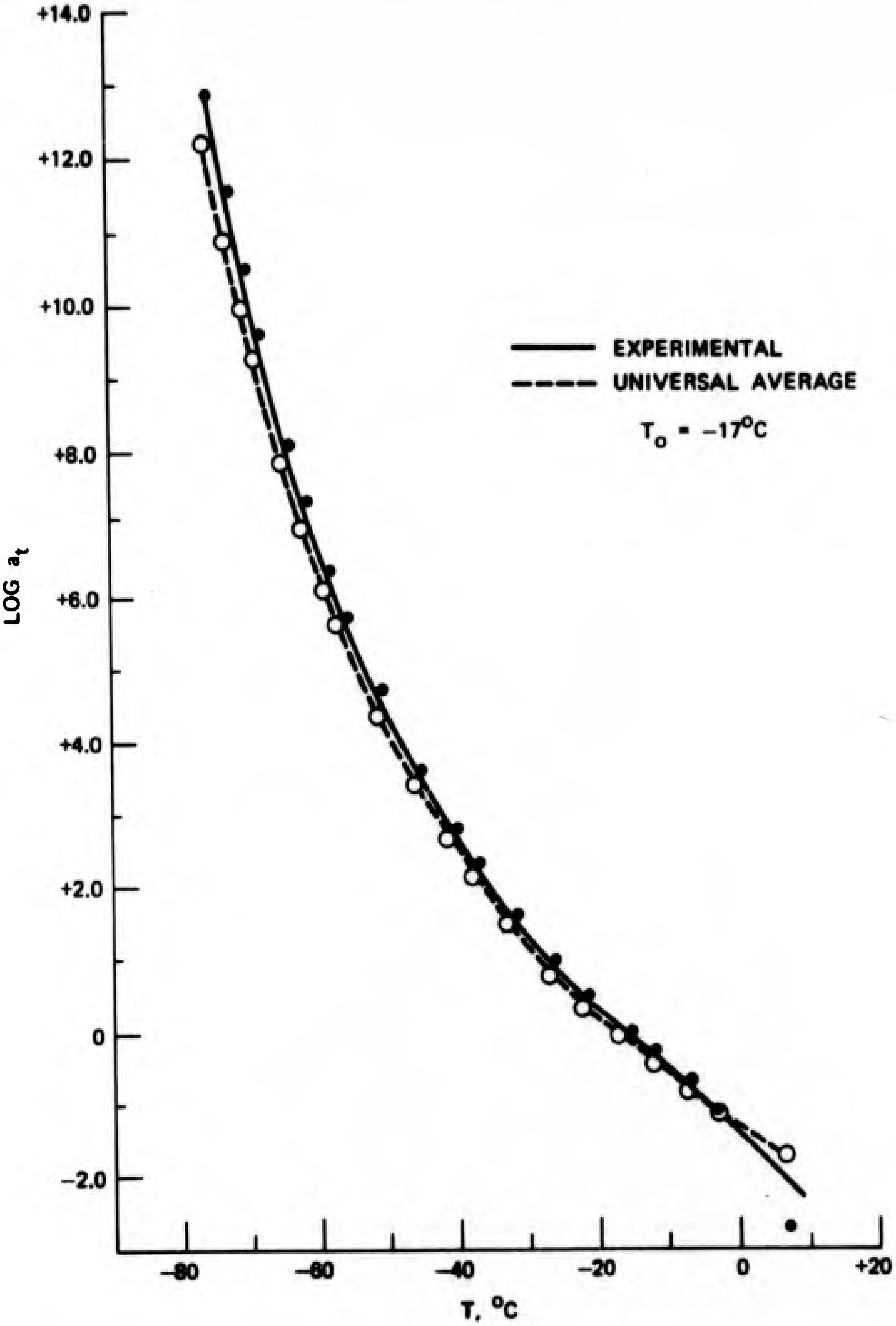


FIG. 12. Temperature Shift Factors of a CTL-II Gumstock.

The time and temperature dependence of the shear moduli of the propellants (Fig. 13, 14, and 15) definitely shows the existence of a second transition occurring between log t/a_T values of approximately -5.00 to -2.00. This is, in all probability, reflective of the T_β observed in the mechanical loss measurements (Fig. 5, 6, and 7). Finally, since the CTL-II gumstock also shows this second transition (Fig. 16), this means it is independent of the propellant solids loading and is a fundamental property of the polymer system.

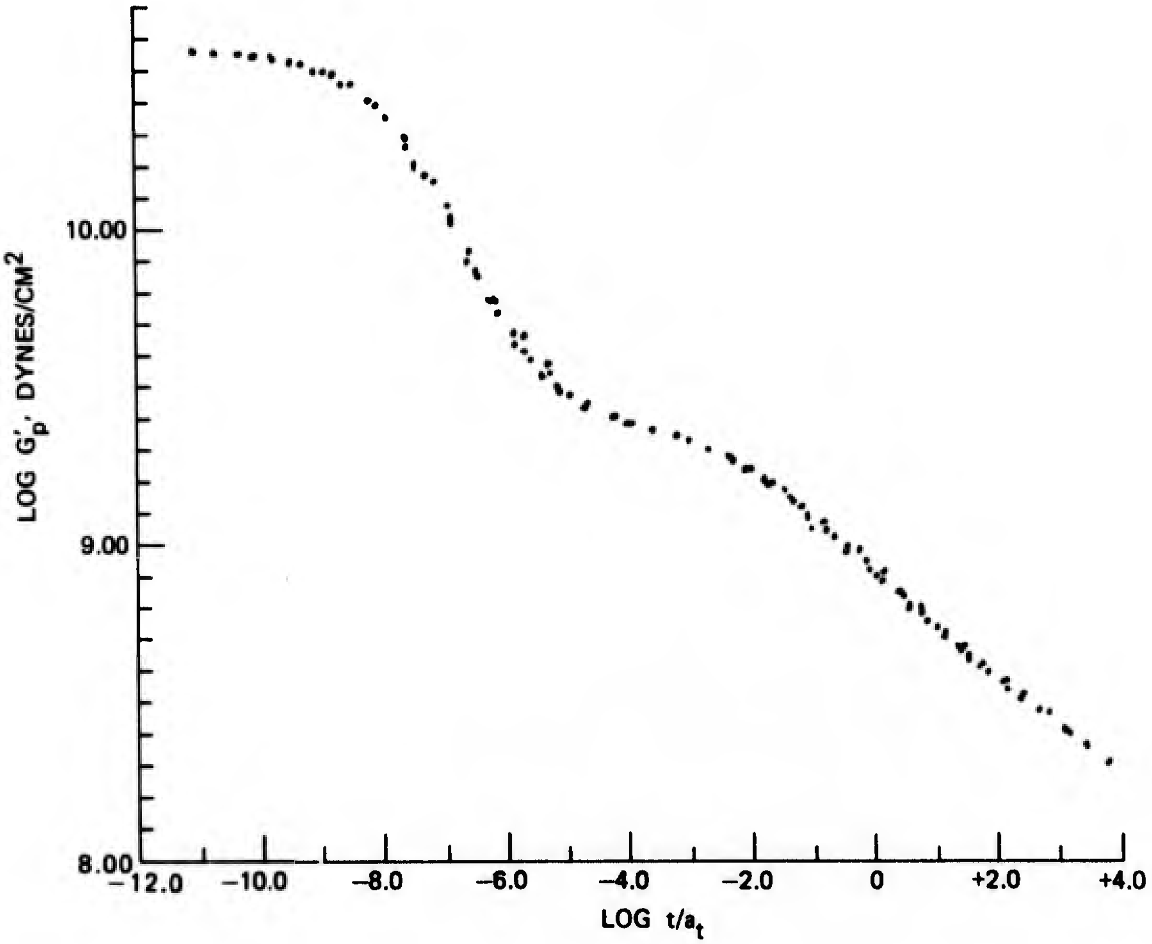


FIG. 13. Time and Temperature Dependence of the Dynamic Shear Modulus of an HC-434 Propellant.

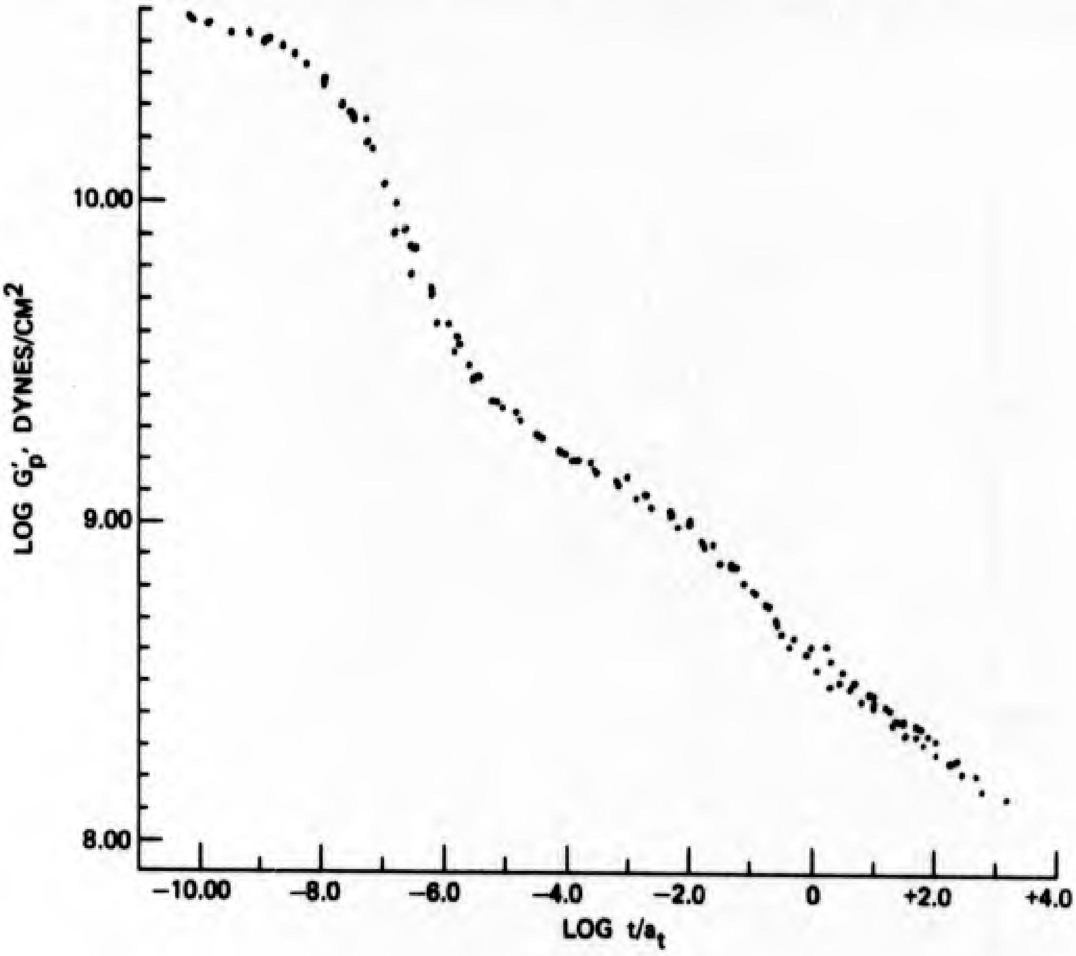


FIG. 14. Time and Temperature Dependence of the Dynamic Shear Modulus of a Telagen CT Propellant.

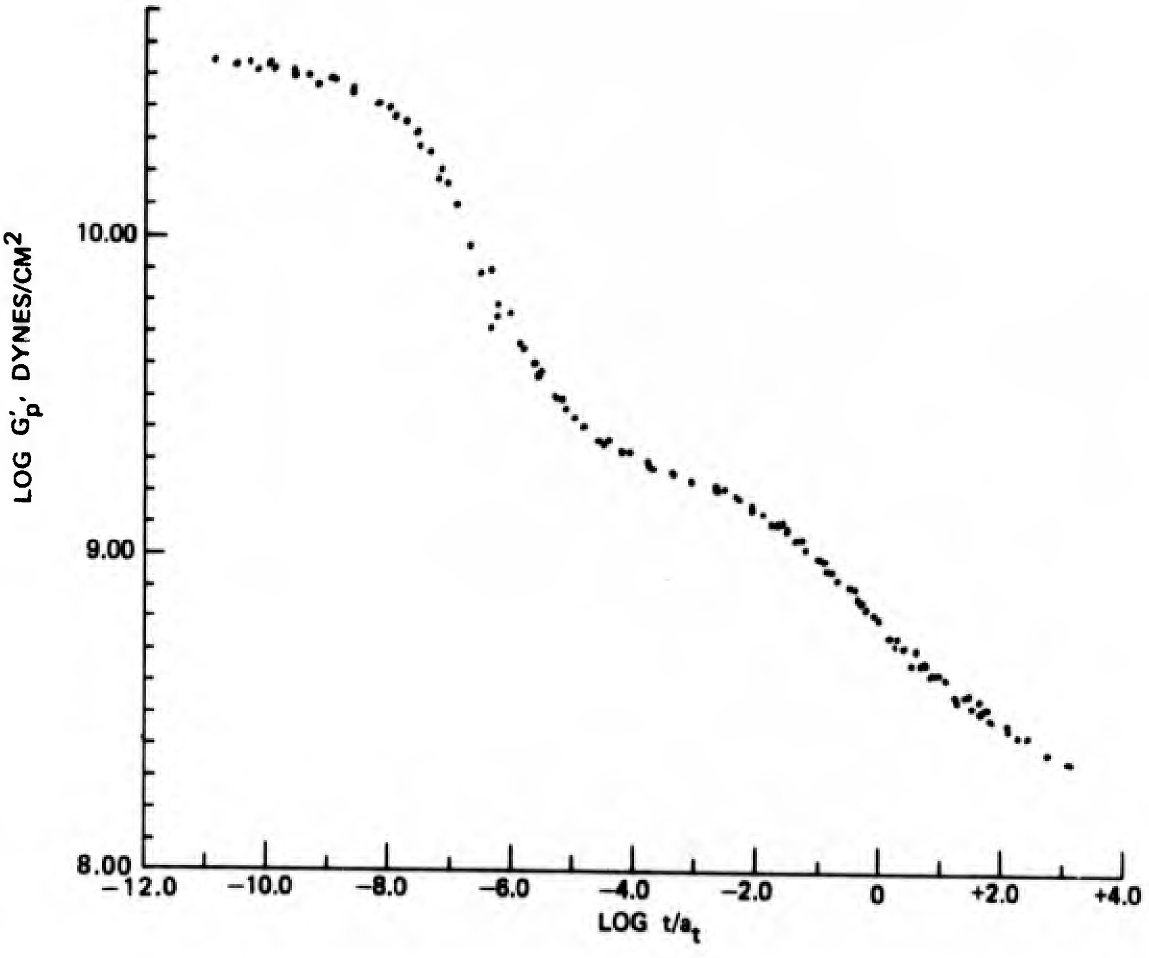


FIG. 15. Time and Temperature Dependence of the Dynamic Shear Modulus of a CTL-II Propellant.

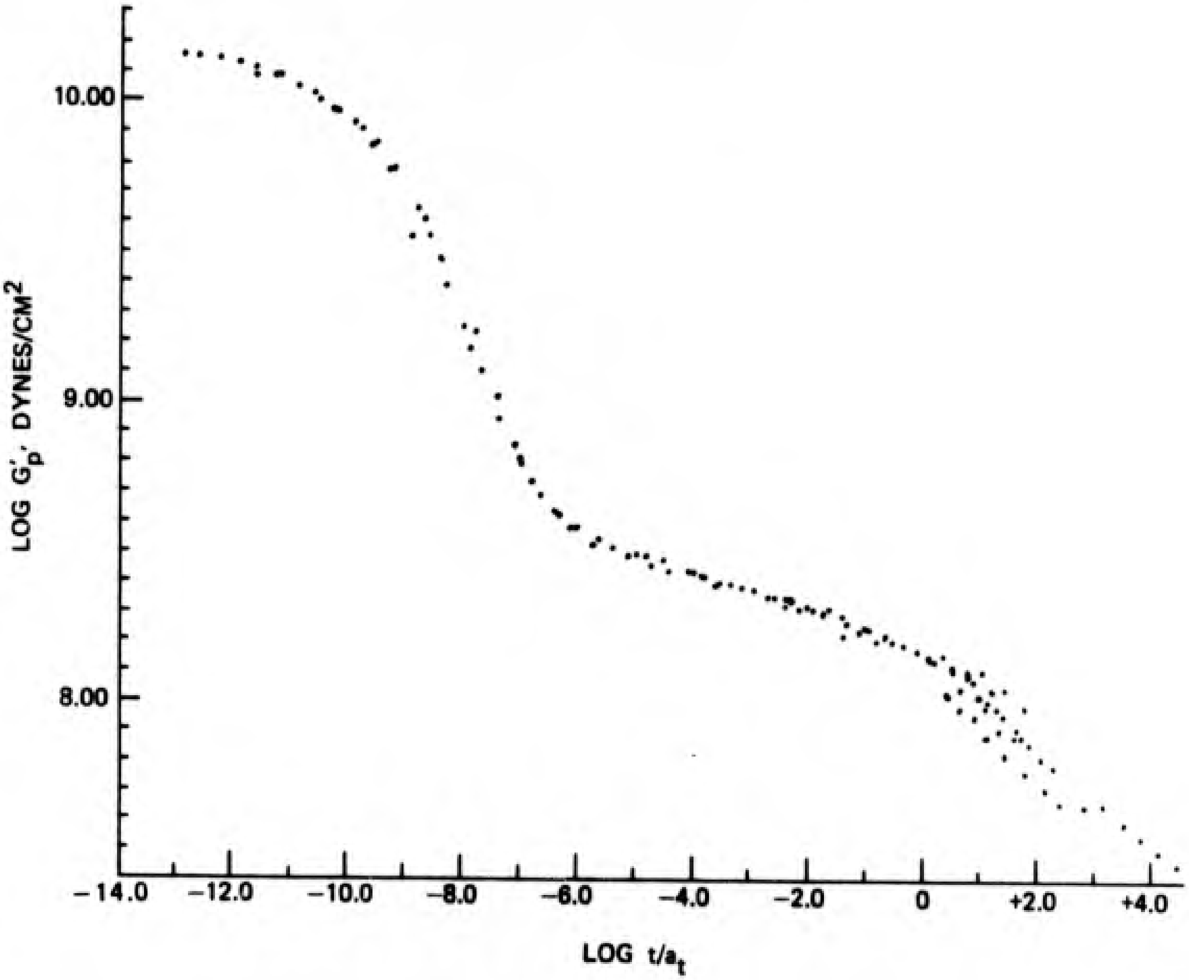


FIG. 16. Time and Temperature Dependence of the Dynamic Shear Modulus of a CTL-II Gumstock.

CHARACTERIZATION OF SPECIALLY SYNTHESIZED OR MODIFIED CTPB PREPOLYMERS

Two contracts were negotiated with the 3M Company to aid in attempts at complete characterization of these CTPB prepolymers. The first contract dealt primarily with the reproducible synthesis of the CTPB prepolymers via a free radical and an anionic mechanism (Ref. 3). The second contract dealt with the characterization of the commercially available CTPB prepolymers. This latter contract included development of new analytical techniques, if necessary (Ref. 15).

The polymer synthesis contract was considered important because parameters necessary for reproducibility of these prepolymers must be known. Generally, this type information is considered to be of a proprietary nature. Also, once the necessary parameters for reproducibility are known, the problem of reproducibility from a cost effectiveness standpoint can be studied.

The 3M Company was requested to reproducibly prepare CTPB prepolymers via both mechanisms (free radical and anionic). They were readily able to do this for the free radically initiated prepolymers (Table 19) which are representative of HC-434 and Hycar CT. Here again, the prepolymers containing the cyano group are much more reactive (see Table 7). All polymers had a high gel content.

Surprisingly, the GAP-initiated polymers with an $\overline{M}_a$ of ~2,700 had a T_{gel} about twice as great as that experienced with an $\overline{M}_a$ of ~1,150. The ABCPA initiated polymers all gave essentially the same T_{gel} regardless of $\overline{M}_a$. The only explanation for the differences noted with the GAP-initiated polymers is that the polymers with the higher $\overline{M}_a$ had a lower functionality than those with the lower $\overline{M}_a$. Considering the small molecular weight range under investigation, differences in T_{gel} cannot be accounted for on the basis of diffusion factors.

The properties of propellants prepared from these prepolymers are listed in Table 20. Comparison of the σ_m values shows good lot-to-lot reproducibility. There is some divergence in the elongation values; however, earlier it was shown that the presence of the antioxidant F-5L can effect changes in physical properties. The higher σ_m values of the propellants prepared from the ABCPA-initiated prepolymers are probably due to functionality differences. Nevertheless, the reactivity of the terminal carboxyl group may contribute to the differences. Since the oxidizer interferes with the MAPO cure, the greater reactivity of the ABCPA-initiated prepolymer may offset some of the interference.

TABLE 19. Characterization Data on 3M Synthesized CTPB Prepolymers (Free Radically Initiated).

Prepolymer	Initiator	$\overline{M}_a$[a]	Antioxidant, %	T_{gel}[b], min	% gel[c]
37-26W	GAP[d]	2,732	1.7 Calco 2246	3,690	94.1
51-37	GAP	1,190	2.0 Calco 2246[e]	1,740	95.1
51-38	GAP	1,149	0.3 F-5L[f]	1,790	96.4
51-39	GAP	2,702	1.1 Calco 2246	3,970	92.6
31-8E	ABCPA[g]	2,304	0.75 F-5L, 0.75 DPQ[h]	204	95.2
31-10E	ABCPA	2,188	1.8 Calco 2246	....	....
31-11E	ABCPA	2,217	1.1 F-5L	212	....
37-15	ABCPA	1,176	1.5 Calco 2246	195	96.3
37-16	ABCPA	1,176	0.8 F-5L	205	97.0

[a] Acid equivalent weight.

[b] Time to gelation at 135°F with MAPO as the curative.

[c] Polymers cured with MAPO at equivalency for 1 week at 135°F.

[d] Glutaric acid peroxide.

[e] 2,2'-methylene-bis-(4-methyl-6-tertiary-butylphenol).

[f] N-alkyl, N'-phenyl-p-phenylenediamine.

[g] Azo-bis-cyanopentanoic acid.

[h] 2,6-diphenyl quinone.

TABLE 20. Uniaxial Tensile Properties of Propellants Using 3M Synthesized CTPB Prepolymers.

Propellant[a]	Prepolymer	E, psi	σ_m, psi	γ_m, %
BDE-124	31-8E	4,190	196	14
BDE-125	31-10E	4,540	200	10
BDE-126	31-11E	3,680	182	17
BDE-160	37-15	6,187	248	7
BDE-161	37-16	6,085	239	8
BDE-171	51-37	4,700	174	8
BDE-172	51-38	4,710	186	13
BDE-181	37-26W	2,512	112	13
BDE-182	51-39	2,309	103	14

[a] Cured with MAPO at equivalency for 1 week at 135°F with 80% solids loading.

Because of time considerations, the 3M Company was unable to reproducibly prepare the CTPB prepolymers via the anionic mechanism. However, they were able to determine that reproducibility was directly related to the rate and efficiency of the carbonation step in the polymer synthesis. They also found that if the carbonation step is slow and inefficient, not only is the final prepolymer functionality decreased, but the molecular weight distribution of the final prepolymer is increased. Because 3M was unable to prepare these prepolymers by the anionic method, it was impossible to determine the effects of (1) known amounts of monofunctional polymer and (2) different backbone microstructures on propellant physical properties.

Under the second contract (Ref. 15), the 3M Company was requested to modify a commercial lot of HC-434 and CTL-II prepolymers. The modifications consisted of either adding or subtracting materials that are representative of possible synthesis impurities so that their effects on propellant properties could be determined.

Tables 21 and 22 show the prepolymers and their modifications. For example, HC-434 prepolymer has to be washed to remove the initiator coupling product, suberic acid. During this washing process, low molecular CTPB is also removed. Thus varying amounts of low molecular weight CTPB (obtained by fractionation and methanol extraction) and sebacic acid were added. Sebacic acid was substituted for suberic acid because of its solubility. Nevertheless, sebacic acid was not completely soluble in the polymer (especially at the higher concentrations). Most of these modifications would make the polymers unacceptable according to specifications, but only gross effects were being studied. With the CTL-II polymer, the main synthesis impurity was the methylnaphthylenes (initiator by-product). A small quantity of low molecular weight CTPB, obtained via a methanol extraction, gave molecular weights which were about three times those obtained from HC-434.

TABLE 21. 3M-Modified HC-434, Lot 98M, CTPB Prepolymer.

Prepolymer	Modification	$\overline{M}_a$[a]
I-1	ARP[b]	1,830
I-2A	ARP + 1% SA[c]	1,660
I-2B	ARP + 3.9% SA[c]	1,570
I-3	ARP + 3% CTPB ($\overline{M}_a$ = 640)	1,780
I-4A	ARP + 2% MeOH extractables	1,760
I-4B	ARP + 10% MeOH extractables	1,490

[a] Acid equivalent weight.

[b] As received polymer.

[c] Sebacic acid.

TABLE 22. 3M-Modified CTL-II, Lot 2AP6, CTPB Prepolymer.

Prepolymer	Modification	$\overline{M}_a$[a]
II-1	ARP[b]	3,000
II-2	ARP + 3% MN[c]	2,890
II-3	ARP + 3.2% CTPB ($\overline{M}_a$ = 640)	2,670
II-5A	ARP + 2% MeOH extractables	2,990
II-5B	ARP + 10% MeOH extractables	3,070
II-6	PWOE[d]	3,330

[a] Acid equivalent weight.

[b] As-received polymer.

[c] Methylnaphthylenes.

[d] Polymer without extractables.

For the HC-434 propellants (Table 23) small amounts of sebacic acid appear to catalyze the reaction, whereas, large amounts appear to cause a reduction in X-ρ through possible homopolymerization of the curative (through larger scale catalysis). The low molecular weight CTPB materials (including methanol extractables) tend to have the same effect as sebacic acid at the 1% level.

TABLE 23. Uniaxial Tensile Properties of Modified HC-434, Lot 98M, CTPB Propellants[a].

Prepolymer	E, psi	σ_m, psi	γ_m, %
I-1	2,550	288	31
I-2A	3,920	292	25
I-2B	1,230	211	34
I-3	2,350	275	28
I-4A	2,850	278	23
I-4B	2,810	298	24

[a] Cured with MAPO/Epon 812 (0.77 MAPO/0.23 Epon 812) at 1.02 equivalence level at 86% solids loading for 3 weeks at 135°F.

In the case of the CTL-II propellants (Table 24), the presence of either methylnaphthylenes or low molecular CTPB has little effect on physical properties. However when these materials are removed from the polymer, propellant elongations show improved properties.

This experiment tends to show that polymeric impurities do not play as important a role on physical property effects as does prepolymer functionality.

TABLE 24. Uniaxial Tensile Properties of Modified CTL-II, Lot 2AP6, CTPB Propellant[a].

Prepolymer	E, psi	σ_m, psi	γ_m, %
II-1	2,760	152	18
II-2	3,210	165	16
II-3	2,860	165	18
II-5A	2,630	154	22
II-5B	2,520	138	20
II-6	2,240	152	26

[a] Cured with MAPO/Epon 812 (0.77 MAPO/0.23 Epon 812) at 1.02 equivalence level at 86% solids loading for 3 weeks at 135°F.

SUMMARY

Comparative $\overline{M}_n$ data on CTPB prepolymers, as determined by vapor pressure osmometry, show problems of accuracy and reproducibility due to polymer additives and impurities. These additives and impurities must be removed or corrected before meaningful data can be obtained. Because of the problems, the available $\overline{M}_n$ data could not be used to determine accurately prepolymer f variations.

The GPC has been investigated as an analytical technique. A number of problem areas were uncovered. Circumstances did not permit meaningful conversion of number average backbone lengths into $\overline{M}_n$ values for use in determining prepolymer f. Experience has also shown that (1) the styraget columns can acquire absorption properties towards the polymers and (2) the column permeability combinations affect GPC data. Suggestions have been made for use of GPC as a quantitative analytical tool.

Gel times (T_{gel}) have been used effectively to determine the relative lot-to-lot reproducibility of a given CTPB polymer. The method also permits the determination of their relative reactivities. Current prepolymer reproducibility was good; however, an earlier lot of CTL-II was found to have an unusually high f. The reactivities of the polymers are: Hycar CT >> CTL-II ≈ Telagen CT > HC-434.

The commercial CTPB prepolymers were also characterized as gumstocks through the use of crosslink-density, % gel, and uniaxial tensile property measurements. Assessment of data shows some f differences in the polymers. The f order is as follows: HC-434 > CTL-II > Telagen. Reproducibility appeared good for most of the polymers. It has also been shown that f must be maintained to improve gumstock elongations at a constant curative level through increases in $\overline{M}_n$. Finally, in the MAPO/Epon 812 curative system data analysis has shown that the Epon 812 functions in part as a chain extender.

Investigations were conducted to determine the role and effectiveness of antioxidants in the CTPB polymers. Trace metals, which are capable of acting as "drier catalysts" and hydroperoxide catalyts, have been found in the polymers. The antioxidants Calco 2246, PBNA, and F-5L were looked at in detail either as single antioxidants or as added antioxidants in CTPB gumstock. MAPO was used as the curative because of its inertness towards the antioxidants under the conditions that were employed. Assessment of data showed that neither Calco 2246 nor PBNA have any appreciable effect on gumstock properties, whereas F-5L does have an effect. The order of the effects in the different polymers is as follows: CTL-II > Telagen CT > HC-434. Changes in properties caused by the presence of F-5L were attributed to its protective action against oxidative crosslinking.

The different CTPB polymers were also evaluated in propellants to determine (1) the effect of different $\overline{M}_n$ polymers on uniaxial tensile properties, (2) the effectiveness of different "as received" or added antioxidants for protection against oxidation, and (3) the role of Epon 812 epoxide in the MAPO/Epon 812 curative system. Preceding conclusions concerning these factors in gumstocks held when propellant data were analyzed.

An aging study (32 weeks at 140°F under nitrogen) on HC-434, CTL-II, and Telagen CT propellants cured with the MAPO/Epon 812 system at 80% solids loading was conducted. Propellant properties stabilized between 2 to 4 weeks. The higher f of the HC-434 polymer manifested itself through the tensile properties of its propellant. Elongations of the three propellants were remarkably similar even though their corresponding gumstocks showed differences. Finally, it was shown that the MAPO/Epon 812 curative system yields a stable propellant.

Propellants made from HC-434, CTL-II, and Telagen CT polymers were characterized via dynamic mechanical measurements. Mechanical loss measurements showed a spread of 5°C in the T_g of the propellants. This was attributed to small differences in backbone microstructure composition.

A second transition was noted above the T_g. Temperature-time reduced propellant master curve data of the shear moduli show the definite existence of this second transition. Dynamic mechanical analysis of a CTPB gumstock also showed the second transition. Therefore, the transition is independent of propellant solids loading and appears to be a fundamental property of the polymer system.

A characterization was completed on CTPB prepolymers synthesized by the 3M Company under Navy Contract No. N123(60530)50116A. The polymers were synthesized via free radical mechanisms. Data showed that syntheses were reproducible.

Under Navy Contract No. N123(60530)5638A the 3M Company modified some HC-434 and CTL-II prepolymers with additives which were reflective of synthesis variables and impurities. Modifications were analyzed via propellant properties.

CONCLUSIONS

To obtain meaningful $\overline{M}_n$ measurements on CTPB prepolymers, it is necessary to make corrections for the presence of low molecular weight species.

Suggestions have been made (based upon experimental experience) for use of gel permeation chromatography as a quantitative analytical tool.

The following f order has been found for the commercially available CTPB prepolymers: HC-434 > CTL-II > Telagen CT. Also, to improve gumstock and propellant elongations at a constant curative level through increases in $\overline{M}_n$, polymer f has to be maintained.

Two trace metals which are capable of acting as "drier catalysts" and hydroperoxides have been found in the CTPB polymers. The polymers can be adequately protected by the addition of amine-type antioxidants.

Evaluation of the different CTPB polymers in 86% solids loaded propellants showed tensile strengths reflective of polymer f. However, propellant elongations were remarkably similar.

Dynamic mechanical measurements on CTPB propellants and gumstocks have shown the presence of a transition in addition to the glass transition which appears to be a fundamental property of the binder system.

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13. ABSTRACT

Investigations have been conducted to characterize and evaluate different commercially available carboxyl-terminated polybutadiene prepolymers and their corresponding gumstocks and propellants. Results show: (1) functionality differences exist among the commercial polymers, (2) polymer functionality has to be maintained to obtain improved physical properties through molecular weight increases, and (3) these polymers are best protected against oxidative crosslinking by the incorporation of amine-type antioxidants.

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