Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

Saturated Hydrocarbon Polymers for Solid Rocket Propellants

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To cite this Article Milo, A. J. Di and Johnson, D. E.(1969) 'Saturated Hydrocarbon Polymers for Solid Rocket Propellants', Journal of Macromolecular Science, Part A, 3: 7, 1419 — 1442

To link to this Article: DOI: 10.1080/10601326908051835

URL: http://dx.doi.org/10.1080/10601326908051835

J. MACROMOL. SCI.–CHEM., A3(7), pp. 1419-1442, November, 1969

Saturated Hydrocarbon Polymers for Solid Rocket Propellants

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SUMMARY

Saturated carboxy- and hydroxy-terminated hydrocarbon prepolymers and selected aziridine, epoxide, and isocyanate curing agents were evaluated with the purpose of preparing an elastomeric binder for solid propellants. Viscosities at a given molecular weight were higher for polyisoprenes than for polybutadienes and higher for carboxy terminated than for hydroxy terminated. Isocyanates showed much less side reactions in the presence of ammonium perchlorate than did the aziridines or the epoxides. The polymers had glass transition temperatures between -40° and -82°C when measured by density change. Differential thermal analysis indicated two second-order transitions at about -64° and -38° for the saturated prepolymers and single transitions at about -75° and -90°C, respectively, for unsaturated prepolymers and polymers made from them. The polymers showed no tendency to crystallize. All of the polymers and propellants showed poor low-temperature behavior. The poor low-temperature properties have impeded acceptance of these materials by the industry. Partially saturated prepolymers show considerably improved low-temperature properties, indicating that saturated hydrocarbon chains are less flexible than the corresponding unsaturated one.

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Table 1. Structure and Properties of Some Prepolymers Studied

Prepolymer no.	Nominal structure	Weight		Weight ratio, molecular/equiv
		Molecular	Equivalent	
19.3	$[CH_2CH_2CH_2CH_2]_{15}$ $[CH_2CH(CH_2CH_3)]_9$ $[CH_2CH(CH_3)OH]_2$	1478	1015	1.45
19.4	$[CH_2CH_2CH_2CH_2]_{19}$ $[CH_2CH(CH_2CH_3)]_{10}$ $[CH_2CH_2OH]_2$	1737	1080	1.61
21.7	$[CH_2CH_2CH_2CH_2]_{12}$ $[CH_2CH(CH_2CH_3)]_{17}$ $[COOH]_2$	1708	966	1.77
23.3	$[CH_2CH_2CH_2CH_2]_{24}$ $[CH_2CH(CH_2CH_3)]_{10}$ $[COOH]_2$	2006	1003	2.00
25.7	$[CH_2CH_2CH_2CH_2]_{10}$ $[CH_2CH(CH_2CH_3)]_{19}$ $[CH_2CH_2OH]_2$	1693	990	1.71
41.2	$[CH_2CH(CH_3)CH_2CH_2]_8$ $[CH(iC_3H_7)CH_2]_{12}$ $[COOH]_2$	1511	797	1.90
43.2	$[CH_2CH(CH_3)CH_2CH_2]_7$ $[CH(iC_3H_7)CH_2]_6$ $[CH_2CH_2OH]_2$	1034	588	1.76

Under Air Force sponsorship, Aerojet-General undertook the task of evaluating saturated, terminally functional prepolymers and selected aziridine, epoxide, and isocyanate curing agents with the purpose of preparing an elastomeric binder for solid propellants. The solid propellant was to be superior to conventional ones in several important respects, such as having good low-temperature properties, being thermally stable, and being applicable to incorporation of advanced fuels and oxidizers. This paper is concerned mainly with some polymer aspects of the study.

A priori considerations eliminated use of unsaturated prepolymers based upon polybutadienes because of their instability to air oxidation and advanced oxidizers. Hydrogenated, anionically polymerized butadiene [1] offered the best possibility as these polymers were close to commercial production, could be terminated in a variety of functional groups, and were known to give narrow molecular-weight distributions [2]. The prepolymers were prepared by The General Tire and Rubber Company from both butadiene and isoprene. Table 1 shows the structure and some of the properties of the prepolymers. The prepolymers generally ranged from 1500 to 2000 number average molecular weight and were terminated in carboxy, primary hydroxy, or secondary hydroxy groups. The pendent group content expresses as per cent 1,2 addition in the case of butadiene and as per cent 1,2 and/or 3,4 addition in the case of isoprene was readily varied, but the more extreme variants were studied.

The relations between molecular weight, Brookfield viscosity, and temperature were determined at The General Tire and Rubber Company. Figure 1

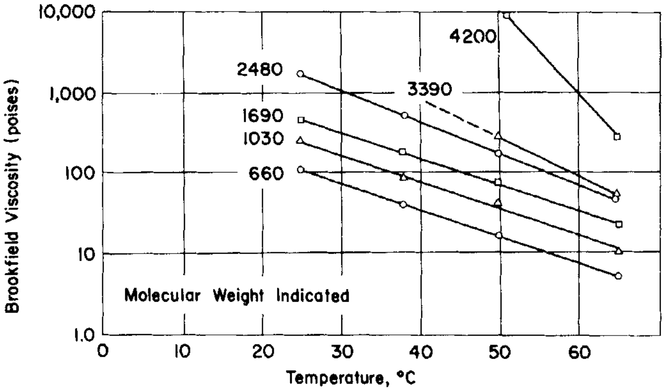


Fig. 1. Viscosity vs. molecular weight saturated carboxy-terminated polybutadiene.

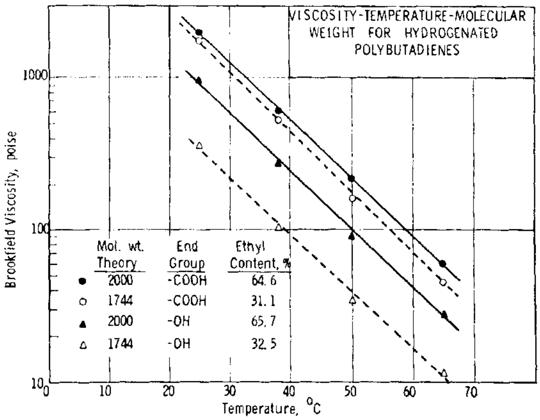


Fig. 2. Reaction of hexanoic acid with DER-332 in toluene with 83 wt% NH_4ClO_4.

shows the relation for carboxy-terminated polybutadienes. Saturated prepolymers in the range of 5000-6000 molecular weight, which are commonly used in solid propellants, were solids too viscous for propellant application. A limit of 50°C for propellant processing when using advanced oxidizers or fuels and a Brookfield viscosity not greater than about 100 p, a figure based on experience, restricted the prepolymer molecular weight to about 2000. It was also apparent that the viscosity increased with the pendent ethyl content and was greater for carboxy than for hydroxy termination (Fig. 2). The effect of pendent groups on the viscosity of carboxy-terminated prepolymers was not as great as in the case of the hydroxy-terminated ones. This was probably because the viscosity of the carboxy-terminated prepolymer was due mainly to the association of the terminal groups. Association was not as serious with the hydroxy-terminated prepolymers [3]. In general, the saturated polyisoprenes were more viscous than the saturated polybutadienes of the same molecular weight.

The accurate determination of the molecular weight of the prepolymers, and consequently their functionality, was a problem, though not an unexpected one. Association of the functional groups was one cause of this difficulty, especially for the carboxy-terminated prepolymers. Early studies of the molecular weight of carboxy-terminated polybutadienes in benzene by vapor phase osmometry were in gross error. Aerojet adopted the use of methyl ethyl ketone and The General Tire and Rubber Company used ethyl acetate as solvents to prevent association of groups during molecular weight

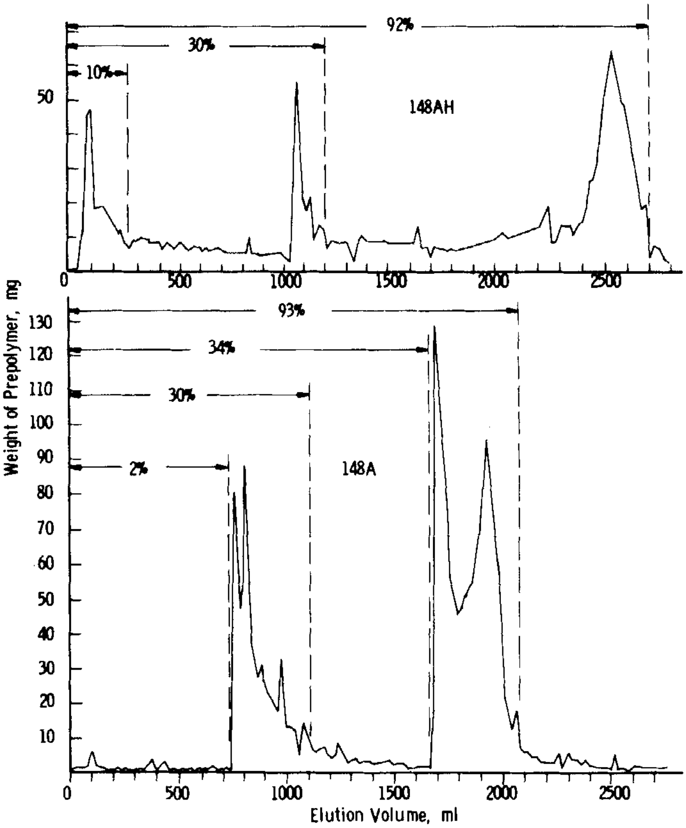


Fig. 3. Chromatographic fractionation of prepolymers 148A and 148AH on SiO_2

determinations. Other workers have used dichlorobenzene at 130°C to prevent association [4]. These workers also established a higher functionality for a saturated, hydroxy-terminated prepolymer by rigorous pumping at a low pressure. Thus, another cause of poor functionality is the presence of low-molecular-weight, probably nonfunctional material.

The question of functionality has been successfully pursued by workers at Esso, who separated non-, mono-, and difunctional fractions by silica gel fractionation of saturated, hydroxy-terminated polybutadiene. Similar fractionations carried out at Aerojet are shown in Fig. 3, which shows the fractionation of a saturated (148AH) and an unsaturated (148A) prepolymer.

Except that the unsaturated prepolymer contained no nonfunctional material, the elution profiles are similar. The nonfunctional fraction may arise from the monofunctional units through hydrogenolysis.

There is apparently some deficiency, not yet fully understood, in the use of the molecular weight to equivalent weight ratio for formulating polymers with saturated prepolymers. This is because the measured or observed cross-link densities of the polymers are greater than calculated. For example, prepolymer 19.3 (Table 1), with a molecular weight to equivalent weight ratio of 1.45, should not be cured with a trifunctional isocyanate. Yet, in fact, it was cured even with a mixture of di- and triisocyanates. The idea of a practical or effective functionality was derived based on the cross-link density of cured binders.

If a polymer is formulated at a one-to-one ratio of reactive groups and complete reaction is obtained, the cross-link density, X_D, as moles of branch points per gram can be obtained and is given in Fig. 4. This equation holds only for f values between 0 and 3. The functionality of the curing agents is accepted as the molecular weight to equivalent weight ratio because well-characterized, easily purified curing agents are used for the determination. Table 2 shows a comparison of practical and apparent functionality for a number of the saturated prepolymers.

$$X_D = \sum_{i=1}^{n} \frac{(f_i - 2)W_i}{f_i E_i}$$

n = number of different reactants.

i = the individual reactants; values 1 to n.

f = functionality of the reactant; known for all ingredients except prepolymer; and not to exceed 3 in value.

W = weight fraction of ingredients.

E = equivalent weight of ingredients.

Fig. 4.

Table 2. Practical and Apparent Functionalities of Saturated Prepolymers

Prepolymer no.	Functionality	
	Practical	Apparent[a]
19.3	1.72	1.45
21.7	1.73	1.77
25.7	1.74	1.71
41.2	1.67	1.90
43.2	1.72	1.76
242AM-148AH	1.98	1.62 (1.75[b])

[a] Molecular weight to equivalent weight ratio.

[b] Values obtained at Esso after removing volatiles.

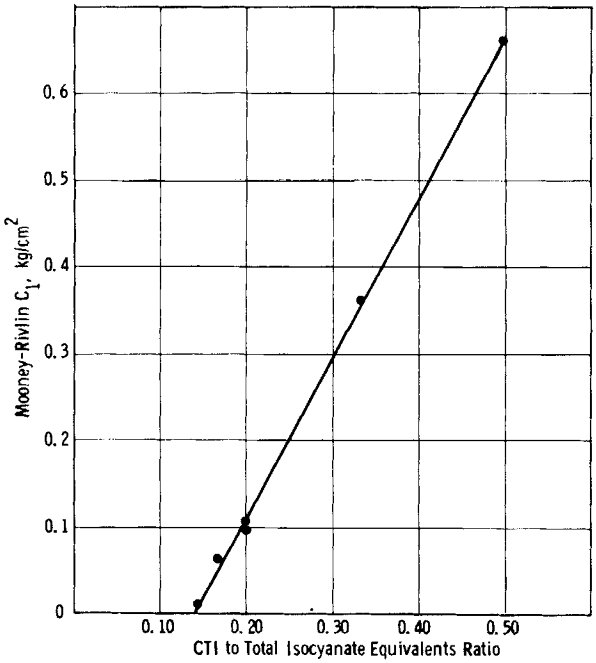


Fig. 5. C_1 constant vs. CTI to isocyanate ratio for Telagen S (242 AM - 148 AH).

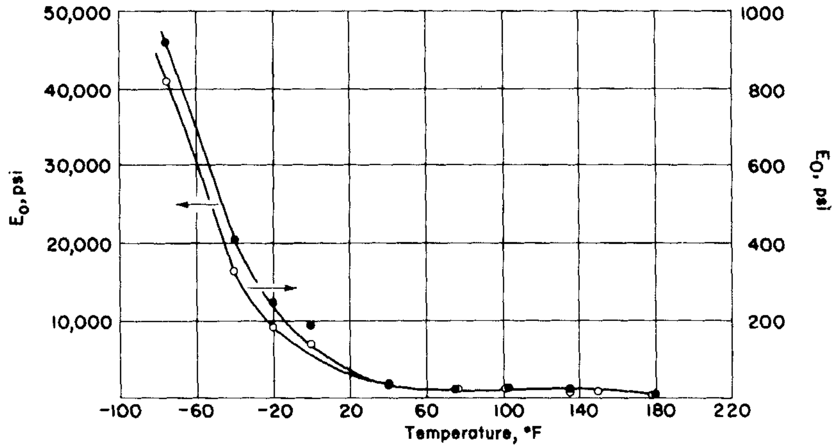


Fig. 6. Variation of binder and propellant moduli with temperature.

A good method for determining practical functionality has been to plot the Mooney-Rivlin, C_1 [5], vs. the tri- to difunctional curing agent ratio, as in Fig. 5. The intercept at $C_1 = 0$ (or $X_D = 0$) gives all the necessary information for calculating functionalities. This method is recommended for application to hydrocarbon prepolymers because of their variable and unpredictable character.

The elastomers made with the saturated, butadiene prepolymers gave propellants with relatively poor low-temperature properties. Figure 6 shows that the temperature variation of the mechanical properties of the polymer and propellant have the same form and, therefore, the low-temperature properties of the propellant are not the result of filling the binder. Glass transition temperatures were determined by temperature-volume change, differential thermal analysis, and by nuclear magnetic resonance. Table 3 indicates some transition temperatures by the temperature-volume method. The transition temperature did not correlate with the nature or amount of pendent groups. Propellants made with prepolymers 21.7 and 19.3 had transitions at -86 and -76°F, respectively.

Differential thermal analysis and NMR gave more information. DTA showed two second-order transitions in both the saturated prepolymer and its cured polymer. These transitions were generally at -60 and -35°C for the prepolymers and at -55 and -20°C for unplasticized binders. In contrast (Fig. 7) the corresponding unsaturated prepolymer and binder have only one second order transition. This fact was used to demonstrate that

Table 3. Glass Transition Temperatures of Saturated Binders by Temperature-Volume Method

Prepolymer no.	Pendent group		Curing agent	Cross-link density, 10^5 moles chain/cc	Tg. °F
	Type	Content, %			
21.8	C_2H_5	59	Epoxide	9.0	-47
23.2	C_2H_5	28	Epoxide	1.5	-57
25.7	C_2H_5	66	Isocyanate	5.4	-63
43.2	i-C_3H_7	44	Isocyanate	3.6	-67
35.2	i-C_3H_7	35	Epoxide	2.0	-72
19.3	C_2H_5	37	Isocyanate	18.5	-83
23.2	C_2H_5	28	Epoxide	4.1	-94
21.7	C_2H_5	58	Epoxide	5.9	-115

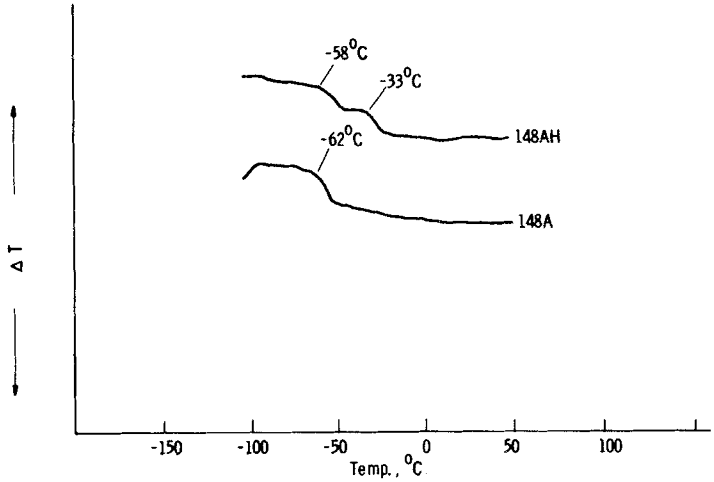


Fig. 7. Differential thermal analysis of prepolymers in N_2 at low temperature (heating rate, 10°C/min; ΔT, 1°C/in.^{2}).

a supposedly unsaturated prepolymer had been mislabeled and was, in fact, saturated. Four propellants made with saturated prepolymers showed second-order transitions at about -75°C, but these were not well defined.

The transition in the NMR line broadening with temperature for this type of prepolymer and its binders was also determined. These transitions have been related to the glass transition temperatures of polymers [6]. There is only a single transition at -11 and -27°C for the hydroxy-terminated prepolymer (33% pendent ethyl groups) and its unplasticized cured binder (Fig. 8). The NMR transition occurs at -52°C for binders plasticized with 25% isodecyl pelargonate.

Examination of initial modulus temperature curves of plasticized binders indicated a glass transition temperature of -30°C. If the rubbery region lies 50°C above the glass transition point, then poor mechanical behavior would begin to be observed in the region 0-20°C, which is consistent with the facts.

Four lines of evidence exclude crystallinity as a cause of the poor low-temperature behavior. First, the NMR studies made to determine line broadening with temperature did not show the characteristic NMR spectra of a crystalline polymer. The value of NMR to measure polymer crystallinity has been challenged [7], however. The DTA thermograms showed no first-order transitions between room temperature and -90°C. An

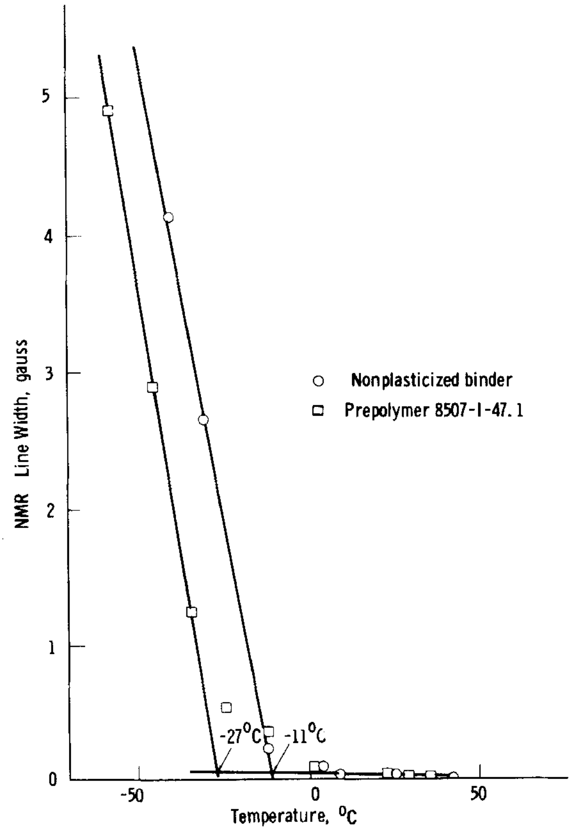


Fig. 8. NMR line width vs. temperature for Telagen S prepolymer and nonplasticized binder.

isothermal dilatometry study of an unplasticized, cured binder at -10°C showed no volume change over a period of 1 week. The dilatometer would have detected a volume change of 0.1%. Similarly, no crystallinity could be detected by X-ray diffraction. Binders from both carboxy- and hydroxy-saturated prepolymer were studied. The results are shown in Table 4. No crystallinity was detected in the binders made with prepolymers of high and low content of pendent groups and cured with either epoxide or isocyanate, nor was crystallinity observed in an elastomer strained to 75%.

All these data indicate that polymer crystallization is not a problem. If crystallization occurred, it would not involve more than 0.1% of the polymer

Table 4. X-Ray Investigation of Tendency of Saturated Hydrocarbon-Based Binders to Crystallize

Prepolymer				
Pendent group	%	Curing agent	Conditions	Remarks
Ethyl	28	Epoxide	-4°C	No crystallization observed
Ethyl	28	Epoxide	75% extension, ambient temp.	No crystallization observed
Ethyl	58	Epoxide	-4°C	No crystallization observed
Ethyl	35	Isocyanate	-4°C	No crystallization observed

Table 5. Methyl Rotational Energy Barriers [9]

Saturated	Energy, cal/mole	Unsaturated	Energy, cal/mole
$CH_3CH_2CH_3$	3400	$CH_2{=}CHCH_3$	1950
$CH_3CH_2CH_2CH_3$	3550	$CH_3CH{=}CHCH_3$ (trans)	1950
		$CH_3CH{=}CHCH_3$ (cis)	600
$CH_3CH(CH_3)_2$	3600	$CH_2{=}C(CH_3)_2$	1500
CH_3OCH_3	2700	CH_3COCH_3	900
CH_3SCH_3	2000	CH_3COOCH_3	900

Table 6. Plasticizers Studied

Plasticizer	Nature
Nujol	Saturated hydrocarbon
Oronite 6	Polyisobutylene
Light circo oil	Naphthenic hydrocarbon
Squalene	Unsaturated hydrocarbon
Citroflex A2	Carboxylic ester
Dioctyl azelate	Carboxylic ester
Dioctyl sebacate	Carboxylic ester
Isodecyl pelargonate	Carboxylic ester
S-141	Phosphate ester
Ansul ether 181	Ether
Arneel OD	Nitrile
n-Dodecanoyl nitrile	Nitrile

at temperatures between -90 and 25°C. Recently, workers at Jet Propulsion Laboratory have supported the idea of crystallization of saturated prepolymers and binders [8]. The most likely explanation of the rapid increase of the elastomer modulus below about 20°C is the onset of the glassy state, which is reached at -30 to -50°C. Elastomers made with corresponding unsaturated prepolymers did not show this type of behavior (which, incidently, is a fact that must be considered when invoking crystallinity as a factor in the low-termperature behavior of such rubbers). Very likely the saturated chain is more rigid than the corresponding unsaturated one. This rigidity arises from the barriers restricting methylene rotation. Consider, for instance, the rotational barriers for methyl groups [9] (Table 5). It is apparent that the very rigid double bond actually reduces the rotational barriers of adjacent groups. It is also apparent that the introduction of a heteroatom or a carbonyl group also relieves the rotational hindrance. This hypothesis predicts that both isobutylene polymers [10] and ethylene-neohexene copolymer [11] presently under development as propellant ingredients will show poor low-temperature mechanical properties.

An extensive study of plasticizers was undertaken to improve the low-temperature elongations of binders and propellants prepared with saturated prepolymers. The plasticizers included saturated and unsaturated hydrocarbon, carboxylic and phosphate esters, ethers, and nitriles (Table 6). No evidence for a plasticization effect in saturated binders was obtained. While plasticizers lowered the initial modulus and the uniaxial tensile strength at

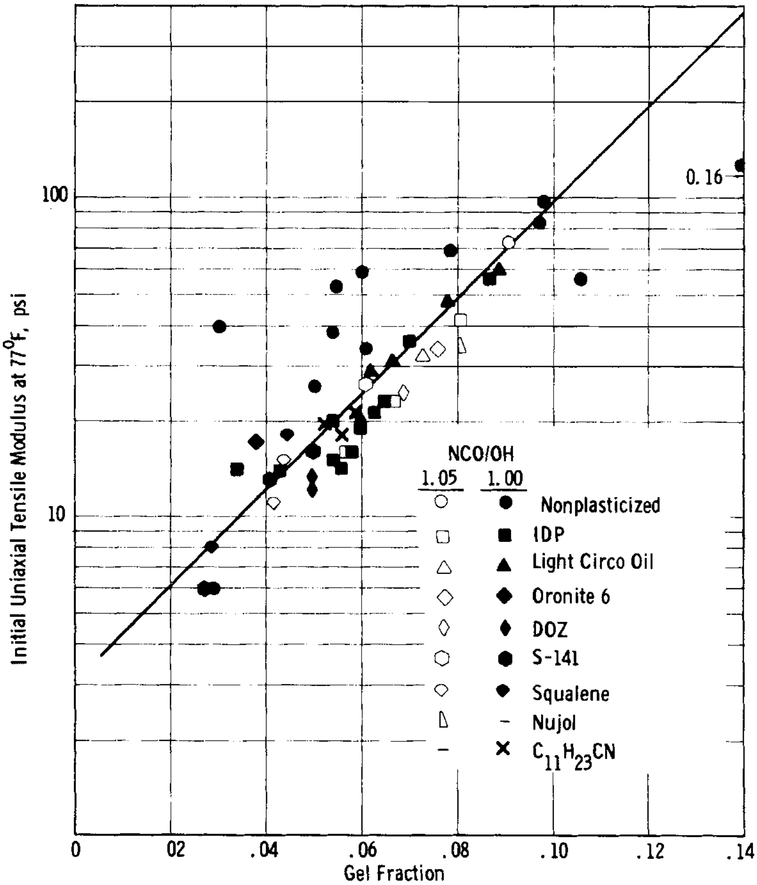


Fig. 9. Initial uniaxial tensile moduli (77°F) vs. the gel fraction of toluene-swollen plasticized binders.

break, the effect was related to the gel fraction of the binder and not to the type or amount of plasticizer (Figs. 9 and 10). The data seemingly indicate that the introduction of a plasticizer decreases the extent of cure and that as a result the binder properties are modified. If the modification of the properties were the result of rubber-plasticizer interaction, one might expect a dependence of properties both on type and amount of plasticizer.

The effect of plasticizer on low-temperature properties also indicated a dependence on the cross-link density or extent of cure of the binder. For instance, Fig. 11 indicates that the initial tensile moduli at high and low

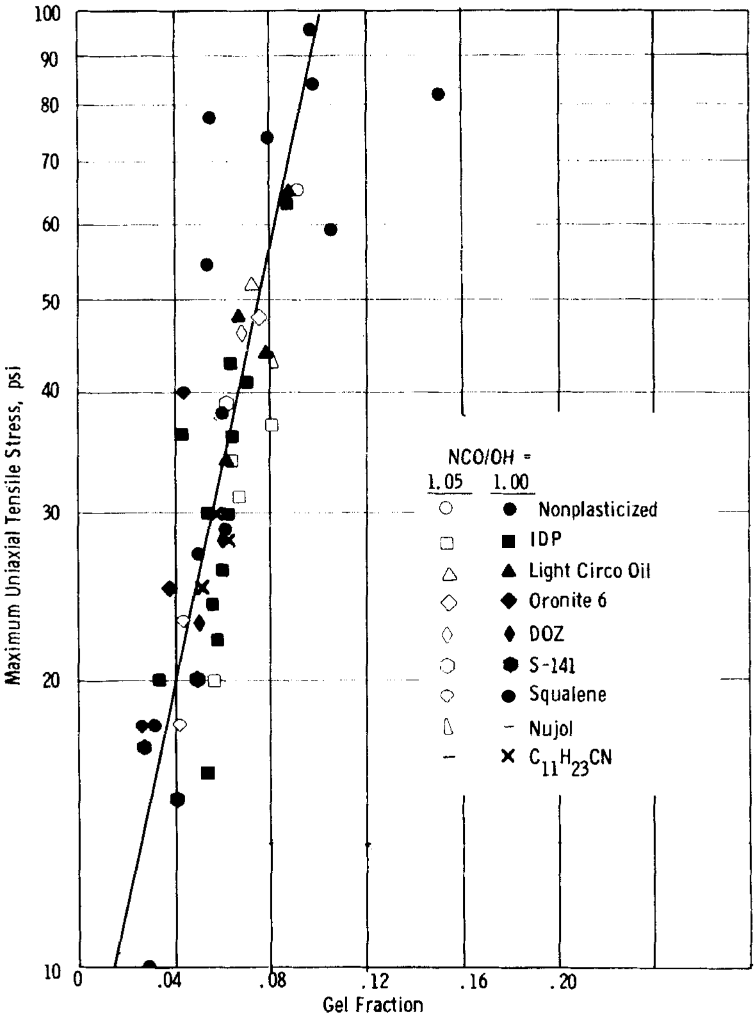


Fig. 10. Maximum uniaxial tensile stress (77°F) vs. the gel fractions of toluene-swollen plasticized binders.

temperature are related for plasticized saturated binder. Since the modulus of the rubber is related to the extent of cure, the effect observed apparently is a plasticizer-cure interaction rather than a plasticizer-rubber interaction. The data of Fig. 11 include five different plasticizers, the content of

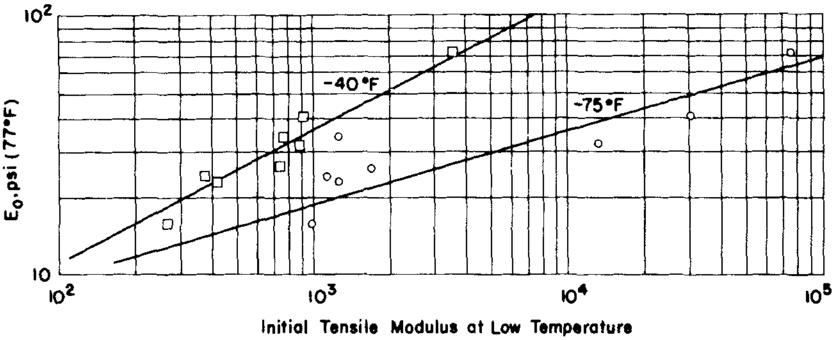


Fig. 11. Initial tensile modulus at 77°F vs. initial tensile modulus at -40 and -75°F for plasticized Telagen S binders.

one of which is varied from 10 to 30%. Since these plasticizer results are limited in number and for only one binder, generalization is not possible. However, it would be of interest to obtain further information of this type for other plasticized systems. Attempts to swell cured binders with plasticizer were not successfully carried out. These data lead to the conclusion that the low-temperature properties of saturated binders cannot be improved by plasticization.

Very detailed swelling determinations were made using 25 solvents (Table 7). While there was considerable data scatter, the cohesive energy density of 80 was indicated (Fig. 12) for a binder based on a CTI-HDI-cured prepolymer (1800 molecular weight, 33% pendent ethyl). A log-log plot of the gel fractions of toluene-swollen binders vs. the cross-link density had a slope of 1.95 (Fig. 13) indicating a χ value of 0.497. The χ value was too close to 0.5 to accurately calculate cross-link density from the gel fraction by the short form of the Flory swelling equation [12]. Cross-link densities were derived from the log-log plot of the gel fraction vs. the cross-link density from the compression modulus of swollen elastomers [13].

The curing agents which were used for the preparation of the saturated elastomers were evaluated for extent and stoichiometry of reaction with a model substrate both in the absence and presence of ammonium perchlorate [14]. The model substrate was a simulant for the prepolymer. The curing agents selected for the binder studies are shown in Table 8. While these experiments were not exhaustive, the isocyanates tested showed much fewer side reactions in the presence of ammonium perchlorate. The

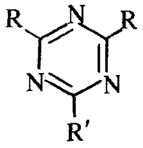
Table 7. Maximum Swelling and the Cohesive Energy Densities (CED) of Solvents

Solvent	CED	Maximum swelling, ml solvent/g binder
Methanol	209	0.062
Nitromethane	159	0.11
Dimethylformamide	147	0.149
Acetonitrile	139	0.05
Isopropanol	132	0.178
Pyridine	112.5	0.678
Nitrobenzene	108.3	0.261
Ethylene dichloride	98.1	0.92
Methylene chloride	97.6	1.62
Dioxane	94.6	0.85
Acetone	93.3	0.168
Chlorobenzene	90.2	2.91
Tetrahydrofuran	86.8	4.70
Chloroform	85.3	3.36
Benzene	83.6	3.42
Methyl ethyl ketone	81.7	0.55
Ethyl acetate	81.6	0.50
Toluene	79.3	4.12
Mesitylene	77.4	3.06
Xylene	77.4	2.86
Carbon tetrachloride	73.6	4.68
Cyclohexane	66.8	3.68
Ethyl ether	59.8	1.52
n-Heptane	55.0	2.38
n-Hexane	52.4	2.32

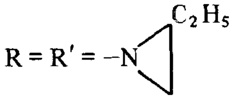
combination of CTI, a triisocyanate, and hexamethylene diisocyanate was selected as the favored curing agent for a prepolymer of nominally 2000 molecular weight, with 33% pendent ethyl groups, and terminated in secondary hydroxy groups. A binder and a corresponding propellant (88 wt% solids) were made and characterized. Their failure envelopes are shown in Figs. 14 and 15. That there was a definite simple relation between the properties of the binder and propellant was illustrated in Fig. 6. At any

Table 8. Curing Agents Used in Binder Study

Aziridines

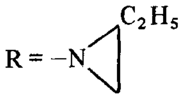


2,4,6-Tri-(2-ethylaziridinyl-1)-s-triazine (TEAT);



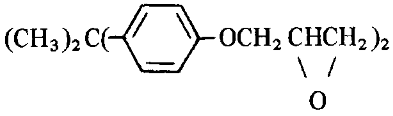
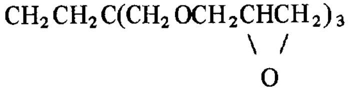
$R = R' = -N$ (aziridine, C_2H_5)

2-Methoxy-4,6-di-(2-ethylaziridinyl-1)-s-triazine (M-DEAT);



$R = -N$ (aziridine, C_2H_5)

$R' = -OCH_3$

Epoxides	
 $(CH_3)_2C(C_6H_4OCH_2\underset{O}{CHCH_2})_2$	2,2-Di-[4-(2,3-epoxypropoxy)phenyl] propane (DER-332)
 $CH_2CH_2C(CH_2OCH_2\underset{O}{CHCH_2})_3$	Trimethylolpropane triglycidol ether (Epotuf 427-60E)
Isocyanates	
$(CH_2CH_2CH_2NCO)_2$	Hexamethylene diisocyanate (HDI)
–	Triisocyanate (CTI), (Aerojet-General Proprietary)

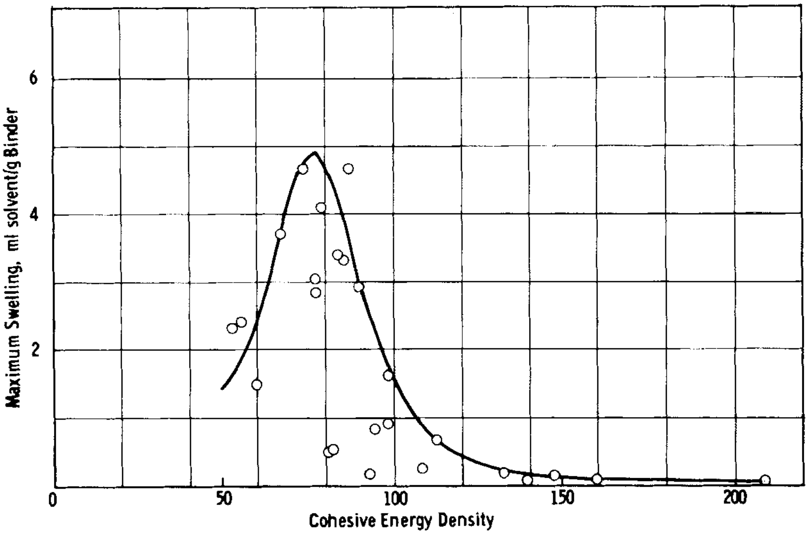


Fig. 12. Maximum swelling and solvent cohesive energy density for an isocyanate-cured Telagen S binder.

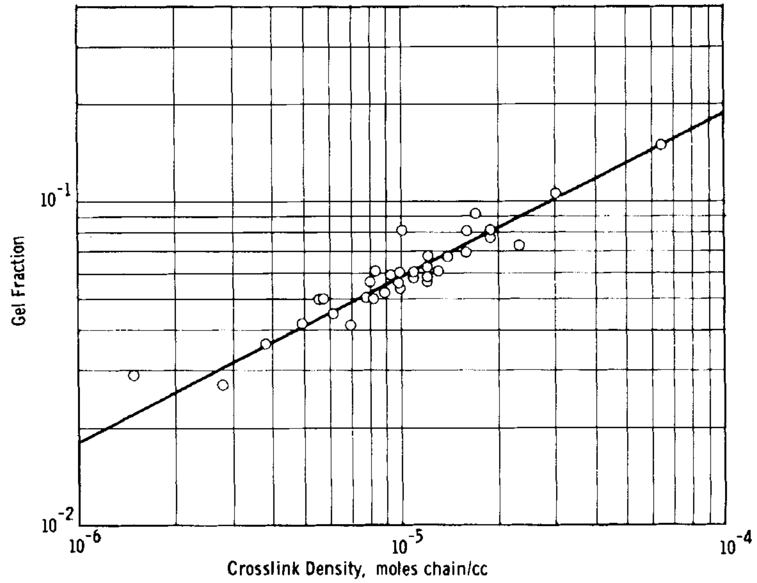


Fig. 13. Gel fraction vs. cross-link density for Telagen S binders.

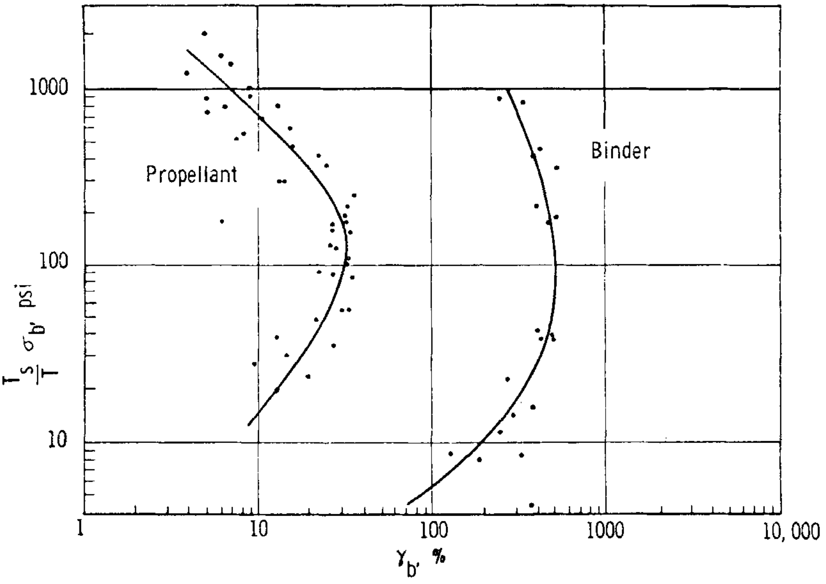


Fig. 14. Failure envelope for workhorse propellant and binder (U).

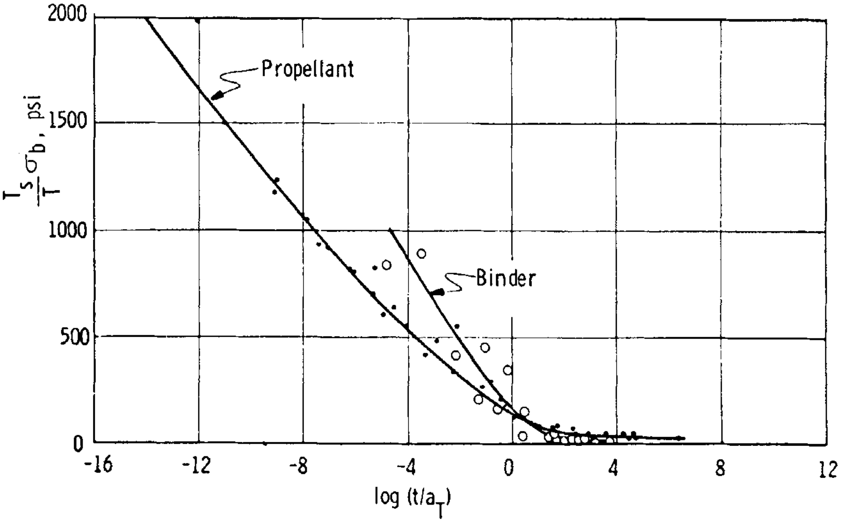


Fig. 15. Failure envelope for workhorse propellant and binder (U).

any temperature between -75 and 180°F, the initial modulus of the propellant was about 50 times that of the binder. Presumably this factor of 50 was characteristic of the volume fraction and type of filler.

The saturated binder should be considered a successful one because it achieved its primary goals—the utilization of saturated hydrocarbons resistant to advanced oxidizers and fuels and elimination of oxidative surface hardening observed in propellants based on unsaturated prepolymers. While the propellant showed rather good mechanical behavior between 0 and 180°F, the poor elongation at very low temperature has impeded its acceptance by the industry.

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Accepted by editor May 27, 1969
Received for publication June 16, 1969

Discussion of Paper by A. J. Di Milo and D. E. Johnson

Saturated-Hydrocarbon Prepolymers for Solid Rocket Propellants

J. Linsk: Since saturated binders are not capable of affording good low-temperature propellant properties, is the approach of potentially saturating the unsaturated prepolymers likely to be useful?

A. J. Di Milo: It is likely that the use of prepolymers with saturations between about 50 and 90% will be suitable for formulation of propellants with both good low-temperature properties and good stability to air oxidation. This work is now in progress. The improvement of low-temperature properties with decreasing saturation has been demonstrated, but the oxidative stability is still to be determined.

J. A. Sauer: Where did the energy barrier values shown in your table for CH_3 and CH_2CH_3 come from? Differences in barriers to rotation of ethyl groups depending on their location on the polymer chain are also evidenced in the low-temperature mechanical relaxation data. For example, in PB, where the ethyl group is directly attached to the main chain, a low temperature γ-type relaxation is found near 150°K. However, if the ethyl group is attached to a D atom further out on the side chain, as in PEMA, or to a C=O group in the side chain, as in PVP region, then the mechanical transition is found at much lower temperatures near 50°K. This is evidence that the barrier to rotation of the pendent ethyl group is much less when attached to a side chain O or C=C atom group than when attached directly to a main chain C.

A. J. Di Milo: Refer to Ref. [9].

L. Bragg: Why aren't the hydrogenated polybutadiene binders more crystalline?

A. J. Di Milo: Probably the crystallinity is inhibited by the presence of the pendent groups.

J. Moacanin: The evidence obtained at JPL supporting crystallinity is as follows: The prepolymer depolarizes light and shows a sharp drop in viscosity at about 40°C. The modulus behavior of the elastomer is characteristic of a partially crystalline system. There is a gradual decrease in modulus as T_g is exceeded, in contrast to the sharp decrease characteristic of amorphous systems. The probable crystallinity content is of the order of 2 or 3.4, which would make it difficult to detect by the methods discussed by Dr. Di Milo. We agree with Di Milo, however, that the major factor on low-temperature properties is the high T_g value.

R. F. Landel: 1) How was the gel fraction varied in the case where you showed a variation of modulus with gel content? 2) Would you amplify on your comment that there is a plasticizer-cure and not plasticizer-rubber interaction?

A. J. Di Milo: 1) The gel fraction variation was the result of changing cross-link density by varying the di- to triisocyanate ratio. 2) I mean that a prepolymer cured in the presence of plasticizer gives a different binder than one cured in the absence of plasticizer. The difference, a result of different gel fractions for the two binders.