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On the Elastomers Derived from Polybutadiene-Acrylic Acid-Acrylonitrile Terpolymer as a Fuel Binder

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Some characteristic properties of a polybutadiene - acrylic acid - acrylonitrile terpolymer (PBAN) and of the elastomers derived from it were determined to obtain the fundamental information as fuel binders for propellants. The chemical composition of the prepolymer (RF-2) was determined to be:

$$[\{\text{-CH}_2\text{-CH=CH-CH}_2\text{-}\}_{84.0}\{\text{-CH}_2\text{-CH(CN)-}\}_{12.6}\{\text{-CH}_2\text{-CH(COOH)-}\}_{3.4}]_n,$$

and it was found to be a Newtonean fluid. Since the prepolymer was found to be, on the average, 1.2 functional, much mono- or non-functional portion is probably included in it. The tensile properties of the elastomer, based on the cured PBAN, were not as good as those of telechelic elastomers, as far as the same curing agents were concerned. This may be attributed to the influence of the random distribution of the cross-linking sites and to that of the resultant terminal sections of the elastomer. The ultimate tensile strength and ultimate elongation of the PBAN elastomers were in the range of 3—6 kg/cm^2 and 100—400% respectively. It should be remembered that the elastomers contained as much as 30—50% sol fractions.

Polybutadiene, with a high specific impulse and excellent mechanical properties at low temperature, is a promizing fuel bender for a solid propellant. Among the butadiene-based polymers, the polybutadiene-acrylic copolymer (PBAA), the polybutadiene - acrylic acid - acrylonitrile terpolymer (PBAN), and the carboxy-terminated polybutadiene (telechelic polybutadiene) are familiar binders; all of them show a suitable fluidity at the processing temperature, allowing formulation with 80—85% (by weight) of solid ingredients possesing a suitable castability. Because of the functionality of the incorporated carboxyl groups, the systems which contain a prepolymer are easily cross-linked with epoxy- or imine-type curing agents at relatively low temperatures. However, it is still interesting to compare these carboxyl-containing polybutadienes as fuel binders for a solid propellant, because scarcely no systematic information concerning them has been reported. Since these prepolymers have very similar chemical constituents, their combustion characteristics might be on the same level, so it is preferable to criticize them in terms of their mechanical properties, though some aspects of the elastomer based on the telechelic polybutadiene have already been described by the authors.[1,2]

This work will deal with the PBAN prepolymer and the elastomer derived from it. Relative to the telechelic polymer, the PBAN is cross-linked by means of the pendent carobxyl groups. Because of the random distribution of the cross-linking sites, the mechanical properties of the PBAN-elastomer should be influenced by the relatively irregular structure of the network and of the terminal of the resultant macromolecules. The curing agents for the telechelic prepolymer were also found to be effective with PBAN. The elemental analysis and the determination of the carboxyl group were carried out in order to fix the chemical composition of the PBAN prepolymer. The number-average molecular weight and the viscosity were measured by means of a vapor pressure osmometer and a viscometer of the cone-plate type respectively. The derived elastomers were characterized by the results of tensile and swelling tests.

Experimental

Apparatus. *Vapor Pressure Osmometer.* Mechlolab Inc., Model 301-A.

Cone-plate-type Viscometer. Kobayashi-Riken KK., V-1204.

Infrared Spectrometer. Nippon-Bunko-Kogyo K. K., Type IR-S.

Nitrogen Analyser. Coleman, Type No. 29.

Tensile Tester. Toyo-Sokki K. K., Tensilon UTM-1.

Raw Materials. *PBAN Prepolymer.* Naugatuck Chem. Div., U. S. Rubber Co. (Commercial Name: RF-2).

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[1] K. Yamazaki and H. Tokui, This Bulletin, **38**, 2174 (1965).

[2] H. Tokui and K. Yamazaki, *ibid.,* **39**, 2290 (1966).

HMAT. Interchemical Corp. Hexa[1-(2-methyl)-aziridinyl]triphosphatriazine.

MAPO. Interchemical Corp. Tris[1-(2-methyl)-aziridinyl]phosphine oxide.

Epoxide A. (3, 4-Epoxy-6-methylcyclohexylmethyl-3, 4-epoxy-6-methylcyclohexane carboxylate) U. C. C. (Commercial Name: UNOX-201)

Epoxide B. Epoxidized linseed oil. (Epoxy-value: 190)

These materials were used without any further treatment.

Toluene. A commercially-available reagent (E. P. Grade) was agitated with concentrated sulfuric acid, decanted, washed with water, dried over calcium chloride, and distilled. The distillate was thoroughly dehydrated over metallic sodium wire, and then redistilled.

Procedures. *Determination of the Carboxyl Content.*3) 0.5—1.0 g of the sample was dissolved in 50 m*l* of a 75/25 benzene-ethanol mixture, and then titrated with 0.1 N alcoholic potassium hydroxide using phenolphthalein as an indicator, in order to obtain the total acidity.

Determination of the Molecular Weight. The calibration factor (K) of the vapor pressure osmometer was determined at 37°C, using benzil as the standard and toluene as the solvent.

Infrared Spectrum. A thin film of PBAN between two rock-salt plates was used for spectrometry.

Elastomer Preparation. The prepolymer and the curing agent were mixed manually, degassed, poured into a cavity formed by two glass plates, and then cured for 7 days in an electric oven to an elastomer sheet about 2 mm thick. The curing temperatures were set at 50°C and 70°C.

Tensile and Swelling Tests. The tensile tests were carried out according to JIS-K-6301. The equilibrium swelling of the elastomer at 20°C was measured in carbon tetrachloride. The details of the procedure have been described in a previous report.1)

Results and Discussion

The constitution of the RF-2 prepolymer was determined to be C, 83.33; H, 10.00; N, 3.23; Ash, 0.00; mol wt (number avg.) 1900; –COOH, 0.062 eq/100 g. Assuming that N and COOH came from acrylonitrile and acrylic acid units respectively, the constitution of RF-2 was determined to be:

$$[\{\text{-CH}_2\text{-CH=CH-CH}_2\text{-}\}_{84.0}\{\text{-CH}_2\text{-CH(CN)-}\}_{12.6}\text{-}\{\text{-CH}_2\text{-CH(COOH)-}\}_{3.4}]_n.$$

Although the C and H contents of the above formula should be 81.97% and 12.96% respectively, none of the noticeable contaminants were detected on the infrared spectrum, as is shown in Fig. 1. From the data on the carboxyl content and the molecular weight, RF-2 should have 1.2 carboxyl groups per molecule (on the average). Since the molecular weight was determined by means of vapor pressure osmometry (V. P. O.), it was questionable whether or not the calibration factor in the region of the molecular weight of benzil (210.23) was invariable in relation to that of RF-2. In order to check this point, the molecular weight of a telechelic polymer (HC-Polymer 434, Thiokol Chem.; carboxy-terminated polybutadiene) was determined by means of V. P. O. and end-group analysis; the resulting molecular weights were 3510 (V. P. O.) and 3840 (–COOH analysis) respectively. It was still doubtful whether or not the carboxy-terminated structure of the material was plausible; however, the observed values were consistent with each other within the error of 10%. In either case, the functionality of RF-2 should be below 2.0, so it was evident that the material was composed from the portions with functionalities of over 2 and of 1 or zero. Indeed, fractionated RF-2 (reprecipitated from the benzene-hexane system; mol wt, 3900) was found to have a functionality of 2.7.

The network of RF-2 should be formed by the polyfunctional fraction with curing agents; however, the coexistent mono-functional molecule would be a powerful modifier to control the formation of the macromolecule. This is proved by the fact that the elastomers derived from RF-2 contained a lot of sol-fractions.

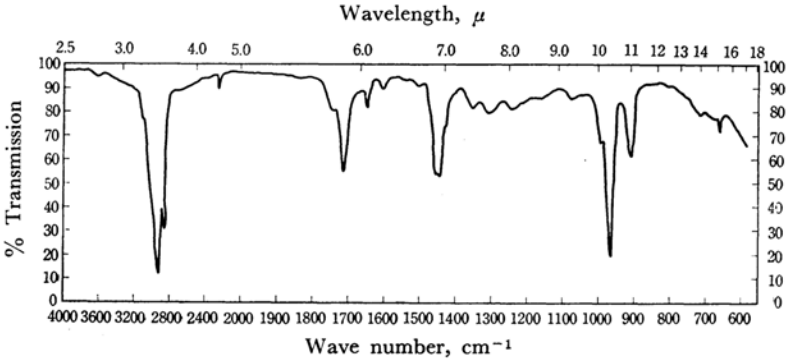

Fig. 1. Infrared spectrum of uncured prepolymer RF-2.

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3) Thiokol Chem., *Standard Testing Procedure.*

The viscosities of RF-2 were determined to be as follows:

Temperature, °C	Viscosity, poise
30	260
40	114
50	90
60	46
70	32.5

The sample was found to be a Newtonean fluid from the fact that the shearing stress was proportional to the rate of shear.

The formulation of elastomers and their tensile properties are compiled in Table 1. In Figs. 2 and 3, the tensile properties are plotted against the equivalent ratio of the curing agents for RF-2. The tensile stress reached their maximum values with an amount to two times the amount of curing agent. Similar results were obtained in the case

TABLE 1. TENSILE PROPERTIES OF RF-2 ELASTOMERS

No.	Formulation		Curing temp. °C	Tensile strength kg/cm²	Elongation at break point %	Stress at 100% elongation kg/cm²	Stress at 300% elongation kg/cm²	Hardness
(1)	RF-2	80	50	2.93	148	2.05	—	13.8
	HMAT	3.6						
(2)	RF-2	80	50	4.01	77	—	—	32.8
	HMAT	7.2						
(3)	RF-2	80	50	4.02	89	—	—	29.3
	HMAT	10.8						
(4)	RF-2	80	50	1.73	404	0.45	1.25	0
	Pyridine	0.8						
	Epoxide B	10	70	3.93	178	2.43	—	17.8
(5)	RF-2	80	50	3.13	213	1.62	—	12.0
	Pyridine	0.8						
	Epoxide B	20	70	3.60	98	3.60	—	24.2
(6)	RF-2	80	50	2.79	196	1.58	—	9.6
	Pyridine	0.8						
	Epoxide B	25	70	4.26	143	3.15	—	21.8
(7)	RF-2	80	50	2.59	208	1.37	—	9.5
	Pyridine	0.8						
	Epoxide B	30	70	3.40	140	2.58	—	18.2
(8)	RF-2	80	50	2.14	297	0.81	—	1.8
	Pyridine	0.8						
	Epoxide B	40	70	3.27	192	1.86	—	13.9
(9)	RF-2	80	50	1.74	1230	0.10	0.27	0
	Accelerator	4						
	MAPO	4	70	2.07	742	0.27	0.57	0
(10)	RF-2	80	50	4.25	373	1.26	3.33	6.2
	Accelerator	4						
	MAPO	6	70	3.95	274	1.64	—	11.2
(11)	RF-2	80	50	4.80	358	1.41	3.86	8.9
	Accelerator	4						
	MAPO	8	70	4.13	197	2.31	—	17.8
(12)	RF-2	80	50	4.40	323	1.46	4.05	9.8
	Accelerator	4						
	MAPO	10	70	—	—	—	—	—
(13)	RF-2	80	50	3.44	319	1.16	3.23	6.0
	Accelerator	4						
	MAPO	12	70	3.46	293	1.22	—	8.9
(14)	RF-2	80	50	3.26	326	1.05	2.95	5.6
	Accelerator	4						
	MAPO	14	70	—	—	—	—	—
(15)	RF-2	80	50	2.97	375	0.81	2.28	2.0
	Accelerator	4						
	MAPO	16	70	2.50	310	0.57	—	4.3
(16)	RF-2	80	50	3.55	655	0.58	1.41	2.8
	Accelerator	4						
	Epoxide A	16	70	6.19	817	0.55	1.70	1.2
(17)	RF-2	80	50	3.12	905	0.25	0.70	0
	Accelerator	4						
	Epoxide A	24	70	5.56	1290	0.30	0.56	0
(18)	RF-2	80	50		Undercured			
	Accelerator	4						
	Epoxide A	32	70	6.04	1510	0.19	0.38	0

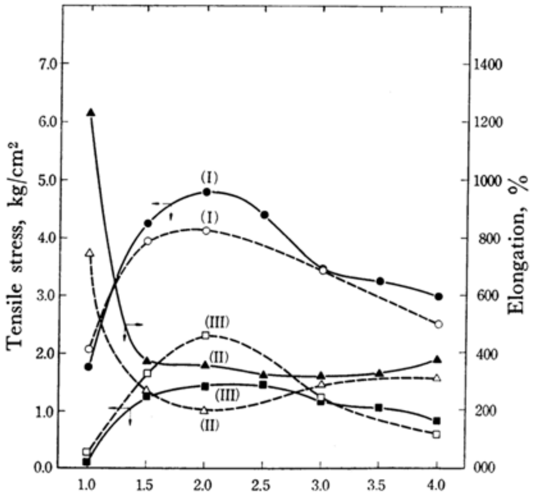

Fig. 2. Tensile properties of RF-2 elastomers (MAPO-cured).
(I) Tensile strength
(II) Elongation at break Pt.
(III) Stress at 100% elongation
—— 50°C cure ---- 70°C cure

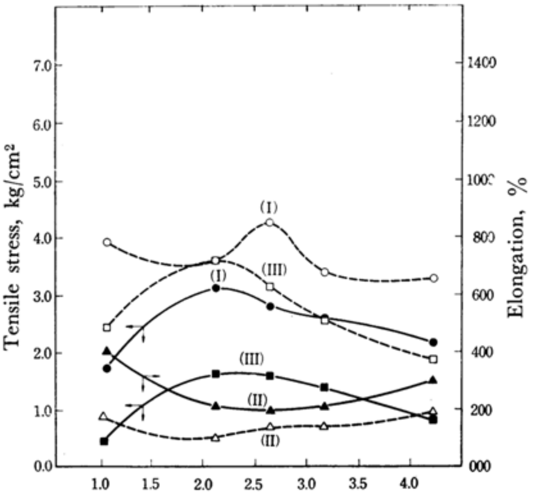

Fig. 3. Tensile properties of RF-2 elastomers (epoxide B-cured).
(I) Tensile strength
(II) Elongation at break Pt.
(III) Stress at 100% elongation
—— 50°C cure ---- 70°C cure

of telechelic polybutadiene.¹⁾

The swelling data of the cured products are compiled in Table 2. The average length of the chain between cross-links, M_c, is given by Eq. (1):⁴⁾

$$\nu \doteqdot 1/M_c = [V_r + \mu V_r^2 + \ln(1-V_r)]/[-\rho V_o(V_r^{1/3} - V_r/2)] + 2M \qquad (1)$$

where ν : moles of effective chain per unit of volume of the elastomer
V_r : Volume fraction of the elastomer in the swollen gel
ρ : density of the polymer
V_o : molar volume of the solvent
μ : polymer/solvent interaction parameter
M : number-average molecular weight of the uncured polymer

When V_r is very small, $V_r^{1/3} \gg V_r/2$, Eq. (1) can be written as Eq. (2), putting $Q_m = 1/V_r$:

$$1/M_c = (1/2 - \mu)/\rho V_o Q_m^{5/3}(1 - 2M_c/M) \qquad (2)$$

The tensile stress of the elastomer, f, is given by Eq. (3):

$$f = \nu \boldsymbol{R} T(\alpha - 1/\alpha^2)(1 - 2M_c/M) \qquad (3)$$

From Eqs. (2) and (3), Eq. (4) is obtained:

$$f = \boldsymbol{R} T(\alpha - 1/\alpha^2)(1/2 - \mu)/\rho V_o Q_m^{5/3} \qquad (4)$$

Accordingly, f should be proportional to $Q_m^{-5/3}$ for a fixed value of α. However, the tensile stress of RF-2 elastomers deviated from this relationship, as is shown in Fig. 4; this deviation was remarkable in the high Q_m range.

TABLE 2. SWELLING DATA OF RF-2 ELASTOMERS

No.	Curing temp.	Sp. gr. at 20°C	Sol-fraction %	Q_m	M_c
(1)	50°C	0.9794	32.39	5.66	787
(2)	50	0.9596	22.78	4.13	679
(3)	50	0.9669	26.69	4.33	699
(4)	50	0.9510	43.73	8.55	869
	70	0.9533	28.72	5.30	767
(5)	50	0.9608	30.91	6.12	809
	70	0.9611	25.54	4.76	732
(6)	50	0.9630	30.96	6.17	808
	70	0.9646	27.61	5.04	751
(7)	50	0.9656	33.42	6.38	817
	70	0.9677	29.61	5.35	774
(8)	50	0.9719	39.53	7.53	853
	70	0.9736	34.35	5.93	803
(9)	50	0.9595	56.04	14.36	920
	70	0.9608	48.45	11.11	898
(10)	50	0.9653	34.01	6.78	831
	70	0.9648	30.45	6.06	806
(11)	50	0.9702	32.15	6.15	810
	70	0.9681	29.45	5.56	783
(12)	50	0.9718	32.85	6.03	808
(13)	50	0.9734	35.42	6.41	819
	70	0.9741	36.65	6.68	827
(14)	50	0.9767	38.15	6.82	839
(15)	50	0.9791	40.25	7.37	850
	70	0.9785	41.37	7.63	853
(16)	50	0.9817	37.90	7.74	857
	70	0.9853	37.97	7.80	855
(17)	50	0.9906	47.29	10.18	894
	70	0.9971	48.75	10.42	897
(18)	70	1.0078	53.05	11.16	901

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4) J. Furukawa and S. Yamashita, *Nippon Gomu Kyokaishi, (J. Soc. Rubber Ind. Japan)*, **30**, 955 (1957).

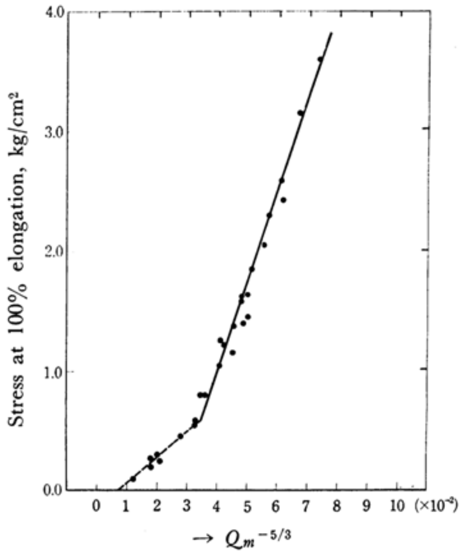

Fig. 4 Swelling data *versus* tensile stress.

The value of M_c listed in Table 2 were obtained by Eq. (1) taking the values of 1900 and 96.61 for M and V_o respectively, and taking 0.264 for the value of μ.[5] Equation (2) induced an error of about 10—13% for the values of M_c when $Q_m=$ 4—5. However, this could not explain the deviation in Fig. 4, since the error has converged to less than 2% when Q_m was increased to more than 10. From the fact that the elasticity of the elastomer with a high Q_m value was unusually poor, it might be deduced that the stress relaxation of the elastomer would be remarkable. The applied strain rate, 500 mm/min, might be too high to obtain the equilibrium stress, thus causing an unexpected increase of the stress. The observed values of Q_m for the RF-2 elastomer are nearly the same as ones of the telechelic polymer, although the tensile stress of the former is remarkably smaller than that of the latter. This fact is undoubtedly due to the effcts of terminal groups and the random distribution of cross-linking sites in the cured RF-2 molecule.

Another distinctive characteristic of RF-2 elastomers was the high sol-fraction content; this may be explained, as has previously been described, by the existence of either a mono- or a non-functional portion in the RF-2 prepolymer. The sol-fraction in the elastomer, S, should be reduced and the tensile stress might be improved as the cross-linking reaction proceeds. Charlesby[6] has deduced that the relationship of the reciprocals of the cross-linking density, $1/q$, *versus* $(S+S^{1/2})$ should be linear when polymers are randomly cross-linked. However, as far as the RF-2 elastomers are concerned, it is expressed as a convex curve. In spite of the fact that the distribution of carboxyl groups in the RF-2 prepolymer might be random, the cross-linking reaction could not take place at random because of the limited number of cross-linking sites.

The values of the tensile stress of the elastomer were estimated from the swelling data by means of Eq. (4); however, they did not agree well with the measured values. This might be attributed to the contribution of a large sol content. It may easily be considered that the dispersed sol in the network structure acts as just a diluent; however, the reinforcing effect of the sol was found to a limited degree in a previous work.[1]

Conclusions

The curing agents for the telechelic prepolymer have been found to be effective for PBAN. Although they have almost the same value of Q_m as the telechelic elastomers, the tensile strength and the modulus of RF-2 elastomers are distinctly poor; this is to be attributed to the effect of the terminal groups of the network structure.

It has been found that the content of mono- or non-functional contaminates in the RF-2 prepolymer was so high that a large amount of a sol-fraction had to be present in the cured elastomers.

The authors wish to express their deep thanks to Mr. Kazuo Kamagata for the viscosity measurements. Gratitude is also due to Professor Hidefumi Hirai and his colleagues for their vapor-pressure osmometry.

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[5] A. G. Shvarts, *Rubber Chem. and Tech.*, **31**, 691 (1958).

[6] A. Charlesby and S. H. Pinner, *Proc. Roy. Soc.*, **A249**, 367 (1959).