

Nonreinforcing Filler-Elastomer Systems. I. Experiments Based on Model Systems

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Synopsis

Five methods were modified to test for interactions between binder and filler of composite solid propellants. Methods based on uncured binder or model compounds were rate of solution of binder from composite mixtures; centrifugal separation of binder from the filler of composite mixtures; measurement of the contact angle between binder and filler; and adsorption of binder or model compounds by filler from solution. Stress-strain-birefringence was measured on cured binders containing small amounts of filler. In addition to the polymers used as binders and the model compounds, three physical forms of aluminum, and the additives tris[1-methylaziridinyl]phosphine oxide (MAPO) and a polysebacate of methyl-N-diethanolamine were included in the study. The filler was ammonium perchlorate in all experiments. The polysebacate was an effective adhesion improver in the polyurethane-ammonium perchlorate composite. MAPO was not as effective in the system polybutadiene-ammonium perchlorate. Fibrous forms of aluminum result in a weaker propellant than does powdered aluminum. Nonfunctionally terminated polymers were poorer in adhesion, contact angle, and adsorption tests compared with carboxyl- and hydroxyl-terminated types. The nonpolymeric model compounds yielded inconclusive data.

INTRODUCTION

Some solid-fuel rocket motors use composite propellants with binders such as liquid low molecular weight polybutadiene with carboxyl endgroups cured to an elastomeric solid with epoxy or aziridine compounds. Solid-propellant processing techniques use the liquid binder, plasticizer, and curing agents (15% by weight) as carriers for the ammonium perchlorate oxidizer and the aluminum powder which make up about 85% by weight of the propellant. In spite of this high solids content, the viscosity of the uncured mixture must be low to enable satisfactory processability. After the initial processing stages of mixing and casting, the propellant is cured by heating for a prolonged period. The cured binder must adhere to the solid fillers. A failure in adhesion between the components could allow voids to form during the use of the propellant. These might expand violently and lead to instability or demolition of the motor at the operating conditions during combustion. Thus, the binder is important in determining the

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processing characteristics and subsequent mechanical properties of a solid-propellant composition. The propellant is bonded to the case at least on the sides and often at the ends. During the curing cycle and subsequent cooling, shrinkage may introduce strain into the propellant. The final product must have the strength to withstand temperature changes and mechanical shock. Thus, the propellant grain must have suitable viscoelastic properties over a wide temperature range and not creep or fracture under normal manufacturing, storage, or operating conditions.

The propellant may be considered a highly filled elastomeric compound in which the fillers, ammonium perchlorate and aluminum powder, are non-reinforcing. The binders must be sufficiently strong to bond the propellant together, but the propellant need not have long-range elasticity or great tensile strength. Good adhesion between the binder and filler is desirable for uniformity of performance. However, the binder is such a small proportion of the total volume that its mechanical properties must be good. The binder in the presence of the large volume of filler should not stiffen or crystallize during storage at low temperatures or on elongation. Most of these requirements can be met by polybutadiene.

A comprehensive survey of filler-polymer interaction is not attempted. Only the pertinent papers will be quoted. Various studies on methods of improving the adhesion of the binder to the oxidizer have been reported. One was to add a low molecular weight polymer, a polysebacate of methyl-N-diethanolamine.¹ Klager and Wrightson,² in a study using polyurethane filled with steel balls, indicated that vacuole formation, the first visual appearance of adhesive failure, was initiated completely within the binder and not at the interface. They concluded that an improved system would be one which hindered vacuole formation by preventing the voids reaching the filler particles. They suggested a strong boundary layer at the interface, for example, a layer with higher modulus than the bulk of the binder. Others^{2,3} appear to have reached similar conclusions.

Our studies were related to several additional fields which need not be reviewed completely. These included wetting⁴⁻⁷ and adsorption.^{5,8-11} The approach in the preliminary experiments was to take the binder and perchlorate separately and to study the interaction in uncured or model systems. Later, a technique of utilizing a cured system was tested with success, and this became the subject of a more extensive investigation.¹²

EXPERIMENTAL

Rate of Solution of Uncured Composites

It has been proposed¹³ that an inert filler will separate macromolecular chains causing a decrease in chain interaction and a diminution in strength of the mixture, whereas an active filler will form additional bonds between the filler and the macromolecular chains limiting the mobility of the chains and increasing the strength and rigidity of the system. An experiment was devised to test various fillers for activity, that is, whether or not they

showed good adhesion to the polymer. Four- or five-gram portions of polybutadiene (Taktene 1202) were dissolved in toluene, mixed with fillers and adhesion improvers, and films cast by allowing evaporation in poly-(tetrafluoroethylene) (PTFE)-lined muffin tins. (Trade names are identified as to product and owner in the list of polymers and model compounds.)

The samples were discs 40 mm \times 3 mm. Each was placed in 100 ml toluene in a stoppered flask at room temperature. The mixture was stirred at constant speed using a PTFE-coated magnetic stirring bar. At 10-min intervals, the temperature was recorded, and a 1-ml sample was pipetted into a weighed 1-dram vial. This procedure was continued until solid, undissolved polymer was no longer visible. The vials were set aside to allow the toluene to evaporate and then reweighed to determine the amount, and hence the per cent, of the total polymer dissolved versus time in minutes. Control experiments were with unfilled polymer discs of the same weight.

In the experiments of Gorshkov et al.¹³ the polymer disc was suspended from a torsion balance in a wire mesh cage. This proved to be inaccurate since solvent became trapped in the cages.

Centrifugal Separation

The method of determining wetting characteristics outlined by Perrault¹⁴ was modified by putting a weighed amount of polymer-filler mixture along with other ingredients to be tested into a coarse fritted glass Gooch crucible. The crucible was suspended in a centrifuge tube by a piece of plastic tubing. The International Equipment Company Model EXD centrifuge was employed at about 2000 rpm to spin eight crucibles at a time. Weighings of the crucible and contents were taken at intervals until equilibrium was reached, and the quantity of polymer retained by the solid ammonium perchlorate filler was calculated. This number is related to the wetting ability of the binder and the various improvers added. Although an exact number cannot be given for the wetting ability of a filler due to mechanical retention and entrapment of binders and the effects of viscosity, it is assumed that these errors will be the same for any given system and data can be compared.

Contact Angle, Wetting

When several substances wet a surface, the angle which a drop of each makes with the surface at the point of contact will determine which substance wets the surface better.^{15,16} The smaller the angle the better the wetting. It follows that if a polymer will not wet ammonium perchlorate, then adhesion will be poor and vacuoles will form under stress as the phases separate.

Accordingly, a fine wire with a 1-mm loop at the end was suspended in a hot, saturated aqueous solution of ammonium perchlorate. The solution was stirred slowly and allowed to cool to room temperature overnight.

The process was repeated with the same solution using a wire to which small crystals had adhered. The resulting larger crystals were dried. Those chosen for use had flat unflawed faces of at least 3×3 mm. These were glued to a piece of cardboard, and an approximately 1-mm-diameter drop of polymer or polymer-wetting improver mixture was placed on each. The drops were allowed to come to equilibrium under the influence of gravity for $2\frac{1}{2}$ hr. The drops were then photographed in profile through an horizontally mounted Leitz Wetzlar Ortholux microscope under $25\times$ magnification. The negatives were projected onto a screen where the contact angles were measured with a protractor. This value would be the advancing angle in air since the polymers were viscous, involatile liquids.

Adsorption from Solution

The study was carried out similarly to that of Koral et al.¹⁰ Solutions of polymers, model compounds, or curing agents were made to various concentrations. The solvent was carbon tetrachloride except for a few tests with toluene and benzene. Five or six samples covering the concentration range were prepared and mixed with ammonium perchlorate in the ratio of 5 g perchlorate to 20 ml solution. The entire set of samples was put on the Burrell Wrist Action Shaker and shaken 20–30 hr to ensure equilibrium. The samples were removed and analyzed for unadsorbed material with a Beckman IR5 or IR9 double-beam infrared spectrophotometer. Peak height was measured for a peak representative of the sample under analysis and equated to concentration using the reference solutions. The peak heights obtained from the test solutions were then related to concentrations, and plots of adsorption (milligrams of polymer per gram ammonium perchlorate) versus concentration were made. Analyses were done also using an Abbé 3-L refractometer (Bausch and Lomb) in a similar way.

Stress-Strain-Birefringence

This method was an attempt to determine what effect various inclusions, for example, aluminum fiber or powder, had on the molecular orientation. Also various factors such as prepolymer endgroups, molecular weight, and cure system were compared using stress-strain measurements to determine their effect on the strength of the cured polymer system.

Polymer films, usually about 1 mm thick, were cast in PTFE-lined baking tins, degassed, and cured in a vacuum oven. Strips about 7.5×35 mm were cut with a razor blade and two lines, separated by about 1 cm, were drawn in ink in the central region. The sample was suspended in a glass constant-temperature cell by a clamp. The stress-optical equipment¹⁷ was constructed of Gaertner components. A high-pressure mercury arc lamp and a system of filters supplied monochromatic mercury green light with a wavelength of $546.1 \text{ m}\mu$, which was plane polarized before passing through the sample. Birefringence was measured by the movement of the zero-

order fringe in a Babinet compensator in a telescopic eye piece following the analyzer. Elongation (strain) was measured between the two inked lines perpendicular to the direction of stress by use of a cathetometer. Load was applied by weights suspended from the lower clamp. After a load was applied, the sample was allowed to elongate for 10 min before strain and birefringence measurements were taken. Graphs were plotted of stress versus strain and stress versus birefringence.

Polymers and Model Compounds

Polysar Taktene 1202-X2, 98% cis polybutadiene, \bar{M}_n approx. 100,000; Polysar XPRD-B-441-3, Br-terminated polybutadiene, \bar{M}_n approx. 3,500; Polysar XPRD-B-241-7, Br-terminated polybutadiene, \bar{M}_n approx. 5,000; Polysar XPRD-C-113, carboxy-terminated polybutadiene, \bar{M}_n approx. 5,000; and Polysar XPRD-C-114, hydroxy-terminated polybutadiene, \bar{M}_n approx. 5,000; all from Polysar Limited, Sarnia, Ontario, Canada.

QX-3812 (AHE-530) perchlorate-modified amine-terminated polyglycol, amine hydrogen equivalent weight 566; Dow Chemical Co., Midland, Mich.

Butarez CTL (II) (2278), carboxy-terminated polybutadiene, \bar{M}_n approx. 5,200; Butarez HT Sec. (T-5593), hydroxy-terminated polybutadiene, \bar{M}_n approx. 6,300; and Butarez NF (3AE6), nonfunctionally terminated polybutadiene; all from Phillips Petroleum Co.

Adiprene L-100 (856), capped polyether, 4.2% isocyanate, E. I. du Pont de Nemours and Co., Wilmington, Delaware.

Hycar CTB (2000 \times 156) (22), carboxy-terminated polybutadiene, \bar{M}_n approx. 2,000; Hycar HTB (2000 \times 161) (V74), hydroxy-terminated polybutadiene, \bar{M}_n approx. 7,900; both from B. F. Goodrich Chem. Co., Cleveland, Ohio.

HC-434 (121M), carboxy-terminated polybutadiene, \bar{M}_n approx. 3,600; Thiokol Chemical Corp., Trenton, New Jersey.

R-15-M (707203), hydroxy-terminated polybutadiene, \bar{M}_n approx. 4,700; R-45-M (803311), hydroxy-terminated polybutadiene, \bar{M}_n approx. 4150; CS-15 (611301), hydroxy-terminated 75/25 butadiene-styrene copolymer; all from Sinclair Petrochemicals Inc., New York, New York.

Ricon 100, P-1543, \bar{M}_n approx. 700; Ricon P-1544, \bar{M}_n approx. 2,300; and Ricon 1997, \bar{M}_n approx. 2,400; all 80/20 butadiene-styrene copolymers with 70% pendant 1,2-vinyl units from the Richardson Co., Melrose Park, Illinois.

Ricon 150 P-1611, \bar{M}_n approx. 1,600; Ricon P-1562, \bar{M}_n approx. 1,900; Ricon 1928, \bar{M}_n approx. 2,000; and Ricon 1924, \bar{M}_n approx. 2,500; all polybutadienes with 70% pendent 1,2-vinyl groups from The Richardson Co., Melrose Park, Illinois.

Polysebacate of methyl-N-diethanolamine, \bar{M}_n approx. 1,440; ammonium perchlorate (Trona) (5209), and aluminum powder SA-26, propellant grades; all from Defence Research Establishment Valcartier, Courcellette, Quebec, Canada.

Aluminum fiber straight (2140) ($0.005 \times 0.005 \times 0.125$ in.) and aluminum fiber curled (2120) ($0.001 \times 0.003 \times 0.250$ in.); both from Fiberfil Division, Rexall Chemical Co., Evansville, Indiana.

Tris(1-methylaziridinyl)phosphine oxide, MAPO RD (824172), Interchemical Corp., Carlstadt, New Jersey. Dried over molecular sieve 5 \AA before use.

1,4,9-Decatriene, 1,7-octadiene, and 1,5-cyclooctadiene; all from Columbian Carbon Co. Inc., Princeton, New Jersey.

2,4-Tolylene diisocyanate, Mondur TDS (E-003-7-005), and triphenylmethane triisocyanate, Mondur (F-057-8-002); both from Mobay Chem. Co., Pittsburgh, Pennsylvania.

Bis(2-ethoxyethyl) ether (Diethyl Carbitol), tris(hydroxymethyl)aminomethane, (THAM), 2-hydroxymethyl-2-methyl-1,3-propanediol (THE), and 1,4-butanediol; all from Fisher Scientific Co.

DER 332 (320 BO5) bisphenol A-type epoxy resin; Dow Chemical Co., Midland, Michigan.

1,3-di(4-pyridyl)propane, (DiPyr), and di-4-picolyamine were donated by Polysar Limited, Sarnia, Ontario, Canada.

Other chemicals were laboratory grade.

RESULTS AND DISCUSSION

Rate of Solution of Uncured Composites

During the experiments, room temperature and hence the initial temperature of the toluene varied between 21.2° and 33.5°C . There appeared to be no need to control the temperature. Two discs of polybutadiene were dissolved in toluene at initial temperatures of 24.0° and 33.5°C , and the results are those for samples 1 and 3 of Table I. Although at the higher initial temperature, a larger percentage of the polymer dissolved in the first 30 mins, the end results for the two conditions compared well. It is difficult to define an exact basis for which to compare the data since low molecular weight fractions will be extracted first and the supernatant will become more concentrated and more viscous so that the rate will become diffusion controlled. Since the curves were S-shaped with quite linear early portions, it was decided to compare the data in the central, linear region between 30 and 60 min, and near the leveling-off portion at 120 min. Table I contains the results.

Considering samples numbered 4, 5, 8, 12, and 13 in which tris[1-methylaziridinyl]phosphine oxide (MAPO) was an ingredient, no bonds which strongly alter the dissolution rate are formed between MAPO and either polybutadiene or aluminum powder. There is no effect on the addition of aluminum straight fibers, sample 8, instead of powder, sample 4. A comparison of samples 5 and 13 indicates that MAPO and ammonium perchlorate combine to interfere slightly with the solution of polybutadiene. However, this occurs only when perchlorate is the major ingredient (as it would be in a typical solid propellant). Comparing samples 12 and 13 shows

TABLE I
Solution of Uncured Polymer from Composites

Sample no.	Composition			Room temp., °C	Solution					
	Poly bd, ^a g	Amm. perchl., ^b g	Other, g		After 30 min		After 60 min		After 120 min	
					Dissol., %	Temp., °C	Dissol., %	Temp., °C	Dissol., %	Temp., °C
1	2.61	—	—	32.5	60	34.1	84	34.5	89	34.6
2	1.34	2.6	0.8 ^c	30.0	50	31.6	79	33.3	93	34.3
3	2.72	—	—	24.0	48	24.6	81	26.8	95	28.8
4	2.56	—	0.01 ^d	21.2	26	22.7	65	24.7	97	25.4
			0.3 ^e							
5	2.82	0.3	0.01 ^d	23.9	22	24.9	61	26.9	90	29.4
6	2.48	2.6	—	22.6	39	23.6	73	25.4	92	26.9
7	2.88	—	0.03 ^f	21.7	24	22.7	62	24.8	90	27.3
8	2.60	—	0.01 ^d	25.0	29	26.4	65	28.7	87	31.0
			0.3 ^g							
9	1.87	2.6	0.4 ^e	26.9	39	28.5	64	31.2	92	33.4
10	2.51	0.3	—	22.2	41	23.4	67	25.5	89	27.2
11	2.61	—	0.3 ^h	22.6	26	23.1	56	25.2	83	27.8
12	2.35	2.6	0.08 ^d	31.1	47	32.3	67	33.8	88	35.0
			0.08 ^f							
13	2.41	2.6	0.08 ^d	28.8	38	30.1	63	32.1	83	33.7
14	2.60	—	0.3 ^e	21.4	24	22.8	51	25.3	91	28.4
15	2.60	—	0.3 ^e	21.2	18	22.4	43	25.0	81	27.4
16	2.60	0.3	0.03 ^f	22.3	23	23.7	48	26.1	72	28.3
17	1.12	0.3	1.4 ⁱ	21.7	1	22.6	1	25.2	2	27.4

^a Polybutadiene.

^b Ammonium perchlorate (propellant grade).

^c Acetic anhydride.

^d MAPO (tris[1-methylaziridiny]phosphine oxide).

^e Aluminum powder (propellant grade).

^f Polysebacate of methyl-N-diethanolamine.

^g Aluminum straight fiber.

^h Aluminum curled fiber.

ⁱ Nitric acid, 70%.

Defence Research Establishment Valcartier.

that MAPO and the polysebacate of methyl-N-diethanolamine apparently compete for the available "adhesion sites" on the ammonium perchlorate. Since sample 12 has double the total weight of additives compared with sample 13 while each has the same rate of solution, 0.08 g of either polysebacate of methyl-N-diethanolamine or MAPO is sufficient to occupy the available sites on 2.6 g of ammonium perchlorate.

An examination of samples 7, 12, and 16 in which polysebacate of methyl-N-diethanolamine was an ingredient shows that the polymer does not react chemically with polybutadiene (sample 7), but there is physical interaction between polybutadiene and the chemical product of the polymer and ammonium perchlorate (sample 16). From a comparison of samples 5 and 16, the polysebacate of methyl-N-diethanolamine is a more effective ingredient than MAPO. However, in competition for the same sites (samples 12 and 13), the MAPO-ammonium perchlorate reaction is preferred over the polysebacate of methyl-N-diethanolamine-perchlorate reaction.

Samples 6 and 10 show that there are weak physical adhesive forces between polybutadiene and ammonium perchlorate. However, in large quantities (sample 6) ammonium perchlorate tends to separate the polymer molecules and decrease the strength. This would be so in solid propellant formulations. Unless adhesion improvers are added, the highly filled mixture will crumble under small stresses.

The remaining samples showed effects which were not revealing as far as the main purpose of the experiment was concerned. Sample 17, containing nitric acid, had the slowest rate of dissolution. Addition of the acid caused charring of the ingredients, and the heat evolved could have crosslinked the polymer. Samples 14, 15, and 11, containing various forms of aluminum, had slow solution rates. This was due to a dense screen of aluminum fibers around the polymer which hindered solvent-polymer contact. The samples treated with acetic anhydride (2 and 9) were tried in an attempt to introduce carboxylic acid groups which would be attracted by the positive ammonium groups in the perchlorate. Sample 2 showed that no reaction occurred. That a smaller amount of acetic anhydride produced a slightly faster rate of solution may be explained by dilution whereby the greater volume of liquid decreased the viscosity and increased the rate of solution.

Centrifugal Separation

A comparison of MAPO and the polysebacate of methyl-N-diethanolamine as adhesion improvers with polybutadienes and polyurethanes was attempted by this method. Other exploratory experiments were to determine whether the polybutadiene end group affected the adhesive properties and to test a polymer stated to be a perchlorate-modified, amine-terminated long-chain polyglycol.¹⁸ The results in Table II are for maximal retention, the amount added, and the per cent of liquids retained under those conditions.

For the first three tests, a 50-50 polymer-ammonium perchlorate mixture was used due to ease of handling. Identical samples were used to check the reproducibility of results, and it was found that an increase in the liquid

TABLE II
Adhesion of Liquid to Ammonium Perchlorate during Centrifugation

Sample no.	Binder	Composition		Maximal retention			Comment
		Other ^a		At additive concn.	Liquids retained, %		
1	Butarez NF	NH ₄ ClO ₄	MAPO	0.3 phr	4.0	no change with concn.	
2	Adiprene L-100	NH ₄ ClO ₄	polysebacate	0.9	11	increased rapidly above 0.8 phr	
3	Butarez CTL	NH ₄ ClO ₄	MAPO	1.7	5.6	short maximal range	
4	QX-3812				0.2		
5	QX-3812		Al powder	50	20		
6	QX-3812		Al st. fiber	30	3.0		
7	QX-3812		Al curl. fiber	24	2.4		
8	QX-3812	NH ₄ ClO ₄			-10	decomposition	
9	QX-3812	NH ₄ ClO ₄	polysebacate	0.1	-9	decomposition	
10	QX-3812	NH ₄ ClO ₄	MAPO	0.1	-8	decomposition	

^a See Table I for identification.

retained in the crucible at equilibrium in excess of 0.5% could be attributed to an improvement of wetting.

Sample 1 involved the testing of the effectiveness of MAPO in a 50-50 mixture of ammonium perchlorate and Butarez NF, a polybutadiene with nonfunctional endgroups. The data indicate that MAPO has no significant adhesion improving qualities when mixed with a nonfunctional polybutadiene.

The data for Adiprene L-100 liquid polyurethane elastomer (sample 2) with varying concentrations of polysebacate of methyl-N-diethanolamine show a marked increase in the per cent liquid held in the crucible for concentrations of the polymers above 0.8 phr (parts per hundred parts resin). At 0.9 phr, the per cent liquids held has increased by a factor of 2 over that for the polymer-free control. The test was sufficient to show that the polymer did improve the adhesive properties between a polyurethane and ammonium perchlorate.

Sample 3 showed the effect of MAPO with Butarez CTL, a carboxyl-terminated polybutadiene. An increase in the per cent liquids held at equilibrium occurred with a maximum at a MAPO concentration of 1.7 phr. At a much higher concentration (~ 20 phr), there was a decrease in the per cent liquids retained, probably due to dilution whereby MAPO had reduced the viscosity of the mixture sufficiently to facilitate flow from the crucible.

Samples 4 to 10 were composed of QX-3812 with different additives present. Remarkable reproducibility was obtained with this polymer. Samples 5, 6, and 7 compare the performance of QX-3812 with three different forms of aluminum. The aluminum powder retains about seven times as much polymer as the fibers, probably due to the smaller particle size and larger surface areas which allows it to pack into a compact, low-porosity mass which impedes the flow of polymer through it. Samples 8, 9, and 10 show the effect of mixing the polymer in a 50-50 ratio with ammonium perchlorate, and adding 0.1 g polysebacate of methyl-N-diethanolamine or 0.1 g MAPO, corresponding in each case to about 2.25 phr. During mixing, the odor of ammonia was noted. Calculations indicated that at least 10% of the liquid weight must have been given off as ammonia. Since the curing additives could not contribute this much, the ammonia must be from the ammonium perchlorate. No clues as to why so much ammonia would be released were obtained, and the problem was not followed since this reaction with the oxidizer would produce a propellant full of voids and gas pockets.

The method as outlined by Perrault¹⁴ proposed that after 1 hr, the amount of liquids passing through the crucible varied inversely as the molecular weight of the polymer. The method used here attempted to improve the accuracy by measuring the holdup in the crucible and filler and allowing centrifugation to continue until equilibrium is attained to correct for variations in viscosity and the holdup.

Comparing the data, several points are evident. A terminally functional polymer is necessary for MAPO to improve adhesion of polybutadiene. It

is unlikely that significant crosslinking could have taken place at the low temperatures of this test. Weak hydrogen bonds could be formed at the =NH group formed by reaction with MAPO or at the oxygen of the carboxyl groups terminating the polybutadiene or the oxygen in MAPO. Since these are weak and infrequent bonds, only minor improvement in the adhesion would be, and is, observed in mixtures containing MAPO. In the case of polysebacate of methyl-N-diethanolamine, it is suggested that a reaction occurs with a tertiary amine, bonding the polysebacate to the perchlorate crystal face and eliminating ammonia.

Ammonia elimination was not noted when mixing these compounds, but the carboxyl endgroup may have reacted with some of it. Since the molecule contains several nitrogen atoms, many links with the crystal face are possible. Also, the polysebacate has approximately the same molecular weight as most of the prepolymers used with it. Thus, a physical intertwining of molecules could occur before the crosslinking stage to lock the perchlorate-polysebacate complex to the polyurethane.

Contact Angle, Wetting

This study was undertaken to determine the effect of various factors on wetting of ammonium perchlorate by the liquid polymers. Among the factors studied was chemical composition, molecular weight, type of endgroup, and adhesion promoters. Table III records the results. Most apparent are the two extremes in contact angle, experiments 3 and 8. Experiment 8 shows that the endgroup is an important factor in wetting. While various hydroxyl- and carboxyl-terminated products yield contact angles of 27° to 38°, the nonfunctional polymer yielded a contact angle of 44.5°. This would imply that much of the adhesion should occur at the ends of the chain. From this, it could be inferred that a lower molecular weight polymer (shorter chains, more endgroups) would show improved

TABLE III
Contact Angle of Polymers on Ammonium Perchlorate Crystal Faces

Experiment no.	Ingredients	Contact angle θ	cos θ
1	Polysebacate of methyl-N-diethanolamine	27°	0.891
2	Adiprene L-100	31.5°	0.853
3	Adiprene L-100 + 4.75 phr polysebacate	24°	0.914
4	Hycar CTB (2000 × 162)	31°	0.857
5	Hycar CTB (2000 × 156)	34°	0.829
6	Hycar HTB	27°	0.891
7	Butarez CTL	37°	0.799
8	Butarez NF	44.5°	0.713
9	Butarez HTS	38°	0.788
10	Sinclair R-15-M	32°	0.848
11	Sinclair R-45-M	33°	0.839

adhesion. Sinclair R-45-M has lower molecular weight and viscosity than Sinclair R-15-M, yet a similar contact angle, as shown in experiments 10 and 11. This suggests that the structure of the polymers (not revealed in most instances) from various sources affects wetting. Endgroups do have an effect since experiments 7, 8, and 9 are on polymers from the same source and could have the same basic structure with the endgroups varying.

Experiment 3 proves that the polysebacate of methyl-N-diethanolamine is an effective adhesion improver in a polyurethane system as the contact angle (24°) is smaller for the mixture than for either of the ingredients (experiments 1 and 2). Little valuable information may be deduced from a comparison of hydroxyl- and carboxyl-terminated polymers as the behavior observed is erratic. For a study of this kind to be useful, characterization of the prepolymers would have to be undertaken. A literature survey revealed no work of this nature having been carried out using propellant components.

Adsorption from Solution

Finding a common solvent for polybutadienes and other compounds studied was restricted when infrared spectrometry was used. Carbon tetrachloride was favored. Other solvents could be used and better reproducibility obtained when refractive index was measured.

Data obtained with tests on model compounds, curing agents, and additives are shown in Table IV, while data obtained using polymers are in Table V. A typical adsorption curve is in Figure 1. The per cent adsorbed should be higher at low concentration and decrease with increasing concentration, while the absolute amount should increase to a maximum. This behavior was observed for MAPO, Diethyl Carbitol, and Thiokol HC-434 in carbon tetrachloride, and Dow QX-3812 in benzene. The zero or negative adsorption observed in the middle of a concentration range could not be explained. In several cases there were chemical reactions. For example, HC-434 in carbon tetrachloride using refractive index for analysis darkened the solution, indicating a reaction. When the data were plotted, the reference and adsorption curves crossed. At low concentrations, reaction caused a greater change in refractive index than did the change in concentration due to adsorption. At higher concentrations, larger amounts could be removed by adsorption and this behavior was reversed. When infrared analysis was used in this case, no reaction was detected from the results, presumably because the reaction did not involve the group whose infrared absorption was being measured.

Ricon 150, a polybutadiene with 70% pendent 1,2-vinyl groups, appears to have the greatest affinity for ammonium perchlorate. Whether it is a suitable ingredient for propellants would have to be determined by formulating and testing a motor. HC-434 appeared to be adsorbed well on perchlorate. This polymer has been tested and is in use in motors. An upper limit for adsorption of Butarez type is about 60 mg/g ammonium perchlorate for the hydroxyl-terminated (HTS) and nonfunctional types

TABLE IV
Adsorption of Model Compounds and Additives in Carbon Tetrachloride

Test liquid	Method of analysis ^a	Adsorption, in mg/g NH ₄ ClO ₄ , taken from curves at concentrations of:				
		2 g ^b	4 g	6 g	8 g	10 g
MAPO	A	0	0	0	0	0
MAPO	B	—	26	34	41	48
1,4,9-Decatriene	A	12	12	6	2	—
1,4,9-Decatriene	B	0	0	0	0	0
Diethyl Carbitol	A	11	20	27	—	—
1,7-Octadiene	A	56	5	0	—	—
1,5-Cyclooctadiene	A	26	4	0	4	22
2,4-Tolylene diisocyanate	A	0	0	0	0	0
2,4-Tolylene diisocyanate	B	0	0	0	0	0
Polysebacate of methyl-N-diethylanolamine	—					reaction

^a A: Beckman IR-9; B: Abbé refractometer.

^b Per 100 ml solvent; 25 g NH₄ClO₄/100 ml solvent.

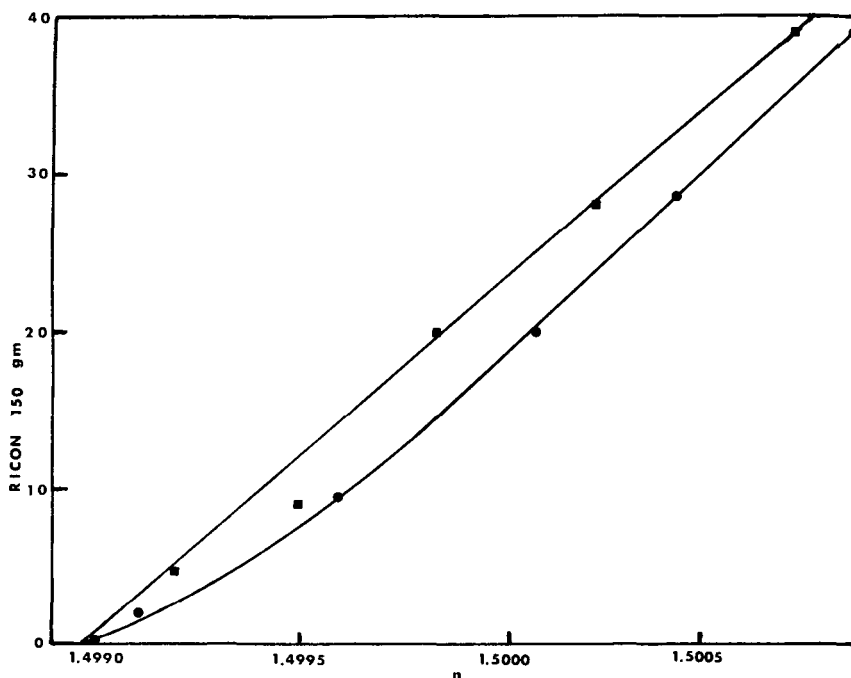


Fig. 1. Concentration of Ricon 150 in g/100 ml benzene as measured by index of refraction of the solution: (●) in the absence of ammonium perchlorate; and (■) after shaking with ammonium perchlorate for 21 hr (9th last sample Table V).

TABLE V
 Adsorption Data for Polymers

Test polymer	Solvent	Method of analysis ^a	Adsorption, in mg/g NH ₄ ClO ₄ , taken from curves at concentrations of:				
			2 g ^b	5 g	10 g	15 g	30 g
Polysar XPRD B-441-3	CCl ₄	A	58	97	—	—	—
Polysar XPRD B-441-3	CCl ₄	B	7	20	53	103	—
Polysar XPRD B-441-3 (dried)	CCl ₄	B	no adsorption				
Polysar XPRD B-441-3 (dried)	C ₆ H ₆	B	no adsorption				
Polysar XPRD B-241-7	CCl ₄	A	no adsorption				
Polysar XPRD B-241-7	CCl ₄	B	no adsorption				
Polysar XPRD B-241-7 (dried)	CCl ₄	B	no adsorption				
Polysar XPRD C-113	C ₆ H ₆	B	0	0	31	35	0
Polysar XPRD C-113	CCl ₄	B	no adsorption				
Polysar XPRD C-114	C ₆ H ₆	B	no adsorption				
Polysar XPRD C-114	CCl ₄	B	18	9	8	8	—
HC-434 ^c	CCl ₄	B	negative		14	36	—
HC-434	CCl ₄	A	26	61	108	125	—
Adiprene L-100	CCl ₄	A	no adsorption				
Adiprene L-100	CCl ₄	B	26	20	24	30	—
Butarez NF	CCl ₄	B	no adsorption				
Butarez NF	C ₆ H ₆	B	48	48	48	48	56
Butarez HTS	CCl ₄	B	no adsorption				
Butarez HTS	C ₆ H ₆	B	36	40	48	62	48
Butarez CTL	C ₆ H ₅ CH ₃	B	no adsorption				
Butarez CTL	CCl ₄	B	no adsorption				
Butarez CTL	C ₆ H ₆	B	52	48	56	68	96
CS-15	CCl ₄	B	0	0	0	36	32
Hycar CTB (2000 × 162)	CCl ₄	B	no adsorption				
Hycar CTB (200 × 156)	CCl ₄	B	no adsorption				
Hycar HTB	CCl ₄	B	0	0	0	0	59
Ricon 150 (Lot 1924)	CCl ₄	B	0	0	17	40	—
Ricon 150 (Lot 1924)	C ₆ H ₆	B	40	90	172	208	184
Ricon 150 (Lot 1928)	CCl ₄	B	0	0	15	35	—
Ricon 150 (Lot P-1562)	CCl ₄	B	15	20	30	0	—
Ricon 150 (Lot P-1611)	CCl ₄	B	0	0	0	30	—
Ricon 100 (Lot P-1544)	CCl ₄	B	0	0	17	24	—
Ricon 100 (Lot 1992)	C ₆ H ₆	B	no adsorption				
Ricon 100 (Lot 1997)	C ₆ H ₆	B	no adsorption				
Ricon 100 (Lot P-1543)	CCl ₄	B	28	14	24	20	—
Dow QX-3812	C ₆ H ₆	B	16	20	24	26	32

^a A: Beckman IR-9; B: Abbé refractometer.

^b Per 100 ml solvent; NH₄ClO₄ 25 g/100 ml solvent.

^c Chemical reaction observed.

(NF), and about 100 mg/g for the carboxyl-terminated type (CTL). Adsorption occurred only when benzene was solvent. These facts indicate that the carboxyl endgroup is preferred for adhesion-adsorption and that benzene is a poorer solvent than carbon tetrachloride or toluene for Butarez types.

The Polysar XPRD samples are not adsorbed. This may be due to improper choice of solvent which may be so also for the Hycar samples and Sinclair CS-15. Dow QX-3812, Ricon 100, and Adiprene L-100 show constant adsorption lower than for Ricon 150, Butarez types, and HC-434.

The data for model compounds and other additives are sketchy, and little information can be gathered from the studies. MAPO might be expected to improve adhesion since it was adsorbed by the perchlorate.

The relative adsorptions of solvents, model compounds, and polymers make the experimental system complex. Koral et al.¹⁰ studied the adsorption of poly(vinyl acetate) on tin, iron, and activated alumina. They investigated the effects of solvent, molecular weight, temperature, and molecular weight distribution and concluded that adsorption is much greater from a poor solvent than from a good solvent, that adsorption increases with molecular weight and is especially pronounced in a poor solvent, and that adsorption increased with an increase in temperature.

Stress-Strain-Birefringence

Design criteria for propellants are a minimum of 5% strain and 100 psi stress at break. No criteria are available for unfilled or lightly filled binders. Therefore, the comparison must be based on relative values.

Table VI lists the data, and Table VII records the formulations and the conditions for curing. Graphs of birefringence versus stress were typical as shown by Figure 2.

From Table VI it is evident that, except for formulations 5 and 6, maximal birefringence and stress occur at the same strain. Nevertheless, results are best compared for the same technique.

Zero birefringence for formulations 1 and 9 is due to nonuniform mixing and incomplete curing which allowed the samples to relax faster than measurements could be taken. This same problem may have existed to lesser extents in other samples. The other 13 tests can be separated into those with birefringence under 100×10^{-6} and those with birefringence over 500×10^{-6} . In the first category are formulations 2, 3, 11, 14, and 15. High birefringence values result when the macromolecular chains align under stress. Formulations 2 and 3, using Polysar XPRD types with ammonium perchlorate and aluminum powder, respectively, indicate that poor adhesion has occurred. If adhesion is poor, voids form between the inclusions and the molecules, and alignment is hindered. The birefringence as a measure of order would be low. The same behavior is evident with formulations 14 and 15 using QX-3812 and aluminum straight fiber and ammonium perchlorate, respectively. Formulation 11 may be in error

TABLE VI
Data from Stress-Strain-Birefringence at Room Temperature (23-30°)

Formulation no.	Modulus, kg/cm ²			Birefringence		Tensile	
	100%	200%	300%	Maximum × 10 ⁶	Corresponding strain, %	Maximum stress, kg/cm ²	Corresponding strain, %
1	6.53	13.71	—	0	—	16.3	228
2	7.42	—	—	33	160	12.3	160
3	—	—	—	14	69	6.1	69
4	3.8	7.7	12.6	2510	420	20.8	420
5	2.18	3.81	5.78	1020	365	38.8	800
6	31.3	63.5	—	3000	32	98	277
7	—	—	—	2170	33.7	7.8	33.7
8	—	—	—	915	15.8	6.5	26.2
9	—	—	—	0	—	2.1	11.1
10	—	—	—	920	15.9	3.2	15.9
11	—	—	—	12.5	51	6.9	51
12	—	—	—	550	21	6.8	37
13	—	—	—	1310	49	5.1	49
14	—	—	—	24	4.0	0.85	4.0
15	—	—	—	78	2.3	2.3	10.1

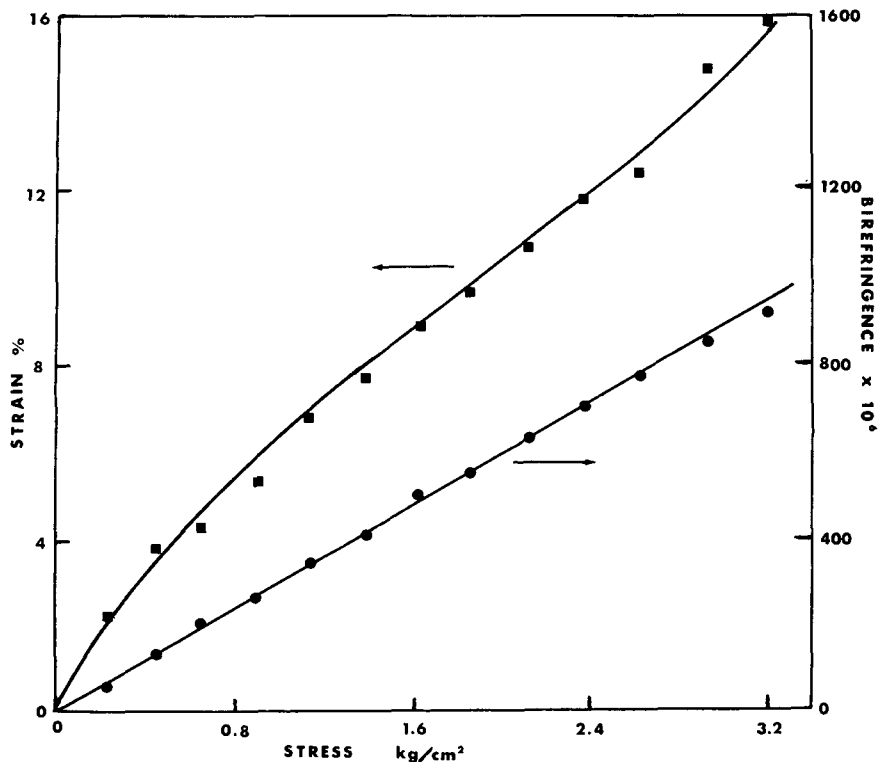


Fig. 2. Strain $100(L - L_0)/L_0$ (●) and birefringence $(n_1 - n_2) \times 10^6$ (■) vs. stress in kg/cm² for the compound Hycar HTB/Mondur TM/ammonium perchlorate (sample 10, Tables VI and VII).

TABLE VII
Formulations of Film for Stress-Strain-Birefringence Measurements in Table VI

Formulation no.	Composition
1	36.12 g Polysar XPRD B-441-3; 0.43 g 1,3-di(4-pyridyl)propane; 0.86 g di-4-picolyamine (20% excess curatives); cure 70 hr, 72°C
2	18.07 g Polysar XPRD B-441-3; 0.22 g 1,3-di(4-pyridyl)propane; 0.439 g di-4-picolyamine (20% excess curatives), 0.54 g ammonium perchlorate (3 phr); cure 67 hr, 72°C
3	20.56 g Polysar XPRD B-441-3; 0.25 g 1,3-di(4-pyridyl)propane; 0.49 g di-4-picolyamine (20% excess curatives); 0.67 g Al powder (3.3 phr); cure 70 hr, 75°C
4	12.5 g Polysar XPRD-B-241-7; 0.11 g 1,3-di(4-pyridyl)propane; 0.22 g di-4-picolyamine (20% excess curatives); cure 72 hr, 72°C
5	55.1 g Adiprene L-100; 0.15 g tris(hydroxymethyl)aminomethane; 2.0 g 1,4-butanediol; cure 3 hr, 100°C
6	48.9 g Adiprene L-100; 0.15 g 2-hydroxymethyl-2-methyl-1,3-propanediol; 2.0 g 1,4-butanediol; cure 3 hr, 100°C
7	28.3 g Hycar HTB; 7.5 g Mondur TM; cure 5½ hr, 90°C
8	28.7 g Hycar HTB; 7.7 g Mondur TM; 1.1 g Al straight fiber (3.82 phr); cure 5½ hr, 90°C
9	30.0 g Hycar HTB; 7.8 g Mondur TM; 1.2 g Al powder (4.0 phr); cure 5½ hr, 90°C
10	28.2 g Hycar HTB; 7.3 g Mondur TM; 1.0 g ammonium perchlorate (3.55 phr); cure 5½ hr, 90°C
11	26.7 g Hycar; 6.0 g Mondur TM (86% theory); 1.0 g Al powder (3.74 phr); cure 18 hr, 90°C
12	27.7 g Hycar HTB; 6.3 g Mondur TM (86% theory); 1.0 g Al straight fiber (3.61 phr); cure 18 hr, 90°C
13	27.9 g Hycar HTB; 6.3 g Mondur TM (86% theory); 1.1 g ammonium perchlorate (3.93 phr); cure 18 hr, 90°C
14	24.2 g QX-3812; 7.4 g DER 332; 1.5 g Al straight fiber (4.74 phr); cure 22 hr, 100°C
15	24.0 g QX-3812; 7.3 g DER 332; 1.5 g ammonium perchlorate (4.78 phr); cure 22 hr, 100°C

owing to incomplete cure since other samples using the same polymer performed well.

Samples with high birefringence, formulations 4, 5, 6, and 7, were unfilled and do not give information about adhesion but show that a high degree of order can be achieved under stress. Samples 8, 10, 12, and 13 indicate that good adhesion has resulted. These samples were Hycar HTB with various inclusions. For formulations 8 and 12, containing aluminum straight fiber, rupture occurred along a fiber. Although birefringence indicates that a high degree of order and good adhesion was achieved, this rupture would indicate that the adhesive forces are weak, and thus aluminum fibers should not be used.

The maximum stress-strain data are an indication of how well the binder will resist stresses. No design criteria are available, but those which broke at less than 100% strain are treated as a group. This would include all Hycar HTB samples and the QX-3812. samples. The Hycar samples

were weak. Those cured with 86% of the theoretical amount of curative showed higher strain at break but were judged to be unsuitable for propellant use. The QX-3812 samples behaved poorly in all aspects and are considered unsuitable.

Generally, the Polysar XPRD and Adiprene L-100 samples showed good stress-strain behavior. However, a good adhesion improver is needed for the XPRD samples. The Adiprene L-100 polyurethane samples show very clearly the problems involved in curing systems. When THAM was used, low stress produced high elongation and moderate birefringence; but when THE was used, high stress produced lower elongation but very high birefringence. Comprehensive studies of curing would be required to compare all of the polymers exactly.

Schwartz¹⁹ conducted stress-relaxation studies on HC-434 and Butarez CTL, using MAPO and Erla-0510 (an epoxide) as curing agents. He reports that under continuous stress relaxation, the polymers are very similar, but under intermittent testing, Butarez is broken down more slowly than HC-434. He notes that when HC-434 is cured with a mixture of curing agents, aging properties are improved, the rate of chain scission is reduced, and stability improved. No tests were done with ammonium perchlorate present, but Schwartz speculates that it may have some catalytic influence on the curing reaction.

While the preliminary data obtained using the five techniques were promising, better and more reproducible results were obtained using more sophisticated equipment, as reported in subsequent studies of Markin.¹²

CONCLUSIONS

Comparison of rates of solution of polymer from the polymer-filler mixture revealed that MAPO and a polysebacate of methyl-N-diethanolamine do not react with polybutadiene unless ammonium perchlorate is present. The reaction product of MAPO and perchlorate forms weak chemical bonds with polybutadiene, and the reaction product of the polysebacate and perchlorate combines physically with polybutadiene. MAPO is less efficient than the polysebacate in improving adhesion. Polybutadiene reacts weakly with ammonium perchlorate unless the latter is present in a large percentage which causes separation of the polybutadiene molecules and decreases the strength. Acetic anhydride does not introduce acid groups into the polybutadiene chain, and nitric acid decomposes the polymer. The method is inconclusive for comparing adhesion to various forms of aluminum.

Using the centrifuge to study the separation of excess or nonadhering liquid prepolymers from the filler yields reproducible data. An increase in the per cent liquids held by contents of the crucible at equilibrium in excess of 0.5% can be attributed to an improvement in adhesion. MAPO has no effect on the adhesion of Butarez NF (nonfunctional endgroups), but yields a slight improvement with Butarez CTL (carboxyl-terminated); with

maximum improvement occurring at a MAPO concentration of 1.7 phr. The polysebacate improves the adhesion of Adiprene L-100 to ammonium perchlorate greatly with polysebacate concentrations in excess of 0.7 phr. QX-3812 underwent a chemical reaction with ammonium perchlorate in which a large amount of ammonia was liberated, making it unsuitable for propellant use.

Measurement of the contact angle of liquids on ammonium perchlorate crystals showed that the wetting of ammonium perchlorate is affected by the endgroup of the polymer. In addition, the chemical structure of the polymer is more important than its molecular weight, indicating that more bonds are formed internally than at the ends. The polysebacate is very effective in improving wetting (adhesion), in conjunction with Adiprene L-100.

The adsorption of liquid polymers and model compounds on solid ammonium perchlorate revealed that the infrared technique had limited use in this method, as reproducibility was poor and the choice of solvents was limited. Better success could be achieved using refractive index as an analytical technique. Ricon 150, Thiokol HC-434, and MAPO showed poorer performance but were suitable nevertheless. Polysar XPRD types, Hycar, and Sinclair CS-15 were unsuitable. Butarez samples gave constant adsorption behavior, with the CTL form adsorbing more. Benzene was a poorer solvent for the Butarez samples than either toluene or carbon tetrachloride and promoted adsorption. Behavior of model compounds was generally inconclusive.

Stress-strain-birefringence studies indicated that cured samples of Polysar XPRD types and Adiprene L-100 had stress-strain behavior suitable for propellant use. Hycar HTB and QX-3812 were unsuited for use in propellants. Polysar XPRD types and QZ-3812 showed low stress birefringence values attributed to poor adhesion. Hycar HTB showed good adhesion except when aluminum fibers were present. These latter are unsuitable as propellant ingredients. Mixing procedures, the type of curatives, and curing procedures must be studied before stress-strain-birefringence data can be suitably interpreted.

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