

Nonreinforcing Filler-Elastomer Systems. II. Silane-Treated Ammonium Perchlorate in Polybutadiene

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Synopsis

The adhesion between ammonium perchlorate filler and the polybutadiene rubber matrix was investigated. The aggregate composite was modified by surface pretreatment of the filler with various organofunctional silanes. For comparison, the adhesion of glass beads and glass powder, each coated with a fluorocarbon release agent, and carbon black were used as fillers in the cured polybutadiene matrix. Common testing methods used included the determination of Poisson's ratio, photographic analysis, and absorption of water. A new type of stress-strain analysis was introduced. Results closely agreed with established composite theory. The presence of methacryloxy- and amino-functional silanes improved adhesion to the resin system. Epoxy- and vinyl-functional silanes proved to be detrimental at the filler-rubber interface. A major function of the coupling agents appears to be to eliminate the weak boundary layer of surface moisture on the filler particles.

INTRODUCTION

Several formulations are used in the production of solid composite propellants. All have two basic ingredients, an oxidizing agent to supply oxygen for combustion and a binder which functions as part of the fuel. The most widely used formulations include ammonium perchlorate as the oxidizer and polybutadiene as the fuel. Unfortunately, the adhesion between these components is unsatisfactory. This fact has been a cause for concern in the rocket motor industry since poor adhesion may result in void formation at the filler-matrix interface when stress is applied. As a result, the propellant burns inefficiently and combustion is not stable.

The purpose is to study the adhesion between ammonium perchlorate and polybutadiene and to improve it while maintaining good chemical characteristics for use. In an earlier study, Granatstein¹ used model systems which, while yielding useful information, suggested that a composite approximating more closely the actual propellant should be used. Such a simple mixture of ammonium perchlorate and binder is the basis of the present study. All other ingredients, such as aluminum (5-10% by weight), stabilizers, and plasticizers (1% by weight), used in propellant formula-

tions were omitted so that any improvement in adhesion can be attributed to an increase in compatibility between the surfaces of the two major components. Also, instead of using 80% by weight of ammonium perchlorate, as is the case for propellant manufacture, only 10% by weight of the composite was oxidizer. This measure not only ensured safety during mixing and handling but also greatly reduced the possibility of interaction between filler particles while allowing better contact of filler to rubber.

The filler-rubber interface was varied by surface pretreatment of ammonium perchlorate with several organofunctional silanes. The feasibility of using silane-modified systems for solid propellants has been reported in the literature. Reed² has effectively used difluoroamino-substituted silanes as plasticizers in solid propellant formulations. Silane polysulfide polymers have been developed and tested by Schwarz and Lowrey.³ They reported a 50% increase in propellant burning rate.

With the advancing of composite material production in the last few years, there has not been time to set specific testing procedures for studying the adhesion characteristics of heterogeneous systems. For fiber-reinforced composites, shear testing is regarded as satisfactory in observing the nature of adhesion between fibers and matrix. In aggregate-filled systems, different approaches were undertaken aimed at adhesion analysis. Oberth and Bruenner⁴ were interested in the tear phenomenon around solid inclusions in a rubber matrix. By means of tensile testing they were able to show that differences in adhesion occur if the same elastomeric matrix is in contact with solid surfaces having different surface energies. Sekhar and van der Hoff⁵ measured volume changes on elongation of crosslinked rubbers filled with poly(tetrafluoroethylene) powder or small glass beads. The degree of cavitation in these systems of poor adhesion was found by saturating the samples with various gases. Wang et al.⁶ examined the criteria of craze initiation in aggregate composites by means of photographic studies. It was found that strain is the major factor for craze formation. Smith⁷ studied the effect of volume-per cent glass beads in poly(vinyl chloride) on Poisson's ratio. Smith et al.⁸ correlated the adhesion of glass spheres to epoxy resin with the shape of the stress-strain curve. For good adhesion between filler and matrix, the initial slope of the curve must be steep and be maintained to a high stress level. For systems in which poor adhesion occurs, the initial slope is not as steep and the stress level is low.

By the use of simple models of filled rubbers, Nielsen⁹ has predicted both qualitatively and semiquantitatively the stress-strain properties as a function of filler concentration for the two cases of perfect adhesion and no adhesion between the filler and polymer phases. In the case of perfect adhesion, it was found that the strain to break, ϵ_b , of the filled system relative to the unfilled polymer is

$$\epsilon_b(\text{filled})/\epsilon_b(\text{unfilled}) = 1 - V_f^{1/3} \quad (1)$$

where V_f is the volume fraction of filler.

In the case of no adhesion between filler and polymer, the particles cannot carry any of the load. The predicted relative strength is given by

$$\sigma_b(\text{filled})/\sigma_b(\text{unfilled}) \doteq (1 - V_f^{2/3})S \quad (2)$$

where S is the stress concentration factor which can have a maximum value of 1.0 when there is no stress concentration, and σ_b is the stress at break of the system.

Nielsen has also derived the relationship between relative strength and volume fraction of filler in the case of perfect adhesion using the Eilers-Van Dijk equation.¹⁰ Curves representing these equations can be found in Nielsen's paper.⁹

EXPERIMENTAL

Preparation of Samples

Thiokol's HC-434, a low molecular weight carboxyl-terminated polybutadiene (CTPB), and Thiokol's EH-330 hardener, 2,4,6-tri(dimethylaminomethyl)phenol, were poured respectively into a reaction vessel and were slowly mixed by an electrically driven stirrer. A given filler was then added in small portions for approximately 10 min. When complete mixing was assured, the curing agent, Shell's EPON 828 (bisphenol A/epichlorohydrin-based epoxy resin), was introduced quickly, and the speed of the rotating blade was increased since curing of the rubber begins almost immediately resulting in increasing viscosity. The contents were poured into a dumbbell-shaped aluminum mold which had been pretreated with a fluorocarbon release agent. All samples were oven cured at 60°C for 48 hr. Each composite contained 71.0% by weight HC-434, 3.50% EH-330, 10.0% filler, and 15.5% EPON 828.

Filler Pretreatment

Ammonium perchlorate, as prepared by DREV (Defence Research Establishment Valcartier) for solid propellant specification, was treated with Silanes A-174, A-186, A-1100 (Union Carbide), and Z-6075 (Dow Corning). The chemical formula of each silane is shown in Table I. The silane loading was 5% by weight, based on the weight of the filler, a considerable excess over that normally used to treat glass fibers, for example, to assure complete surface coating. Enough benzene was added to produce a slurry, and the components were stirred for 30 min and placed in an oven at 60°C for 16 hr. The benzene, and any alcohol that may have been produced by hydrolysis of the silane, were evaporated. Weight measurements showed that the silanes remained with the ammonium perchlorate particles.

Other fillers investigated include glass beads, glass powder, untreated ammonium perchlorate, and carbon black. A fluorocarbon release agent (MS-122, Miller-Stephenson) was applied to the glass fillers until an excess amount was observed. Table II lists the size and density of each filler.

TABLE I
Nomenclature and Chemical Formula of Each Silane
Under Investigation

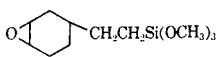
Silane	Nomenclature	Chemical formula
A-174	γ -methacryloxypropyl-trimethoxysilane	$\text{CH}_2=\text{C} \begin{array}{l} \text{O} \\ \parallel \\ \text{C} \end{array} \text{O}(\text{CH}_2)_3\text{Si}(\text{OCH}_3)_3$ $\quad \quad \quad $ $\quad \quad \quad \text{CH}_3$
A-186	β -(3,4-epoxycyclohexyl)-ethyltrimethoxysilane	
A-1100	γ -aminopropyltriethoxysilane	$\text{NH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$
Z-6075	vinyltriacetoxysilane	$\text{CH}_2=\text{CHSi}(\text{OOCCH}_3)_3$

TABLE II
Filler Size and Density

Filler	Tyler mesh	Size, mm	Density, g/cc	Supplier
1. Ammonium perchlorate	80-100	0.15-0.18	1.95	DREV
2. Glass beads	80-100	0.15-0.18	2.6	Chromatographic Specialities
3. Glass powder	200	0.074	2.6	Fisher Scientific
4. Carbon black (ELFTEX 5)	—	2.7×10^{-5}	0.16	Cabot Corp.

Instron Analysis

Method A. The width and thickness of each sample were measured by a caliper, and a line was drawn across the width at the center. A microscope capable of horizontal and vertical movement was placed directly in front of and 3 ft away from the center line on the sample which had been clamped in the jaws of the Instron tensile testing machine. Prior to testing, the initial length between the jaws was recorded. The strain rate was maintained at 0.5 cm/min for 1 min and was then instantaneously reduced to zero rate of strain. The width of a sample was now measured by the microscope at the center line and the increased length between the jaws was tabulated. During this time (approximately 3 min), the sample relaxed somewhat. This was followed by an immediate increase in strain rate to 0.5 cm/min for 1 min, and the width was measured again during the relaxation period. This loading pattern was repeated until fracture of the specimen.

Method B. The rate of strain remained constant at 0.5 cm/min until fracture of the samples. Width measurements were omitted.

Microscopy

A detailed photographic analysis was made using the Reichert ME F, an optical microscope equipped with transmitted and reflected polarized light. Due to translucency of the samples, photographs of the filler-matrix interface were taken below the surface of the composite prior to and after subjection to testing on the Instron tensile instrument. The fractured surfaces of all tensile specimens were thoroughly investigated by means of the scanning electron microscope. A thin layer of aluminum metal (approximately 200 Å thick) was evaporated onto the specimen in order that the rubber sample (an insulator) would not build up any charge.

Water Absorption Study

After tensile and photographic studies, two small sections were cut by a razor blade from each composite. One section contained the tensile fracture surface, the other was adjacent to the former section and away from the fracture surface. All sections were approximately similar in their respective dimensions, i.e., 0.64 cm cut length \times width of mold (1.30 cm) \times depth of mold (1.26 cm). Each section was dried at 50°C for 2 hr and weighed before immersing in distilled water. Since the density of the composites was slightly less than 1 g/cc, the sections were placed in a manner that the end closest to the fracture surface was beneath the water level. Weight measurements were conducted to calculate the per cent water absorbed after 2 hr, 20 hr, 6 days, and 12 days. The water temperature was 50°C for the 2-hr and 20-hr tests and was at room temperature for the 6-day and 12-day tests.

RESULTS AND DISCUSSION

Poisson's Ratio

Preliminary studies for analysis of adhesion between filler and rubber involved the determination of Poisson's ratio. The only difference between the systems investigated was the type of silane coating for the ammonium perchlorate particles. The volume fraction of filler ($V_f = 0.06$) and the matrix (CTPB) was common to each system. Also, since the preparation of all samples was conducted under the same conditions, any noticeable change in Poisson's ratio can be attributed to the silane coating. Poisson's ratio ν is defined as¹¹

$$\nu = \frac{-d \ln \lambda_2}{d \ln \lambda_1} \quad (3)$$

where $\lambda_1 = L/L_0$ and $\lambda_2 = W/W_0$. The initial lengths L_0 and initial widths W_0 are constants. Also, λ_1 can be considered a constant at a specific time during the experiment since width measurements were observed after each 1-min interval of specimen elongation. Poisson's ratio is then proportional to changes in widths for this study.

TABLE III
Summary of Poisson Ratio Results for Various Pretreated Ammonium
Perchlorate Systems. Instron Analysis—Method A

Filler system	Poisson's ratio
CTPB (no filler)	0.50
A.P. (untreated)	0.48
Z-6075	0.48
A-186	0.44
A-1100 (prestressed)	0.40
A-1100	0.38
A-174	0.37

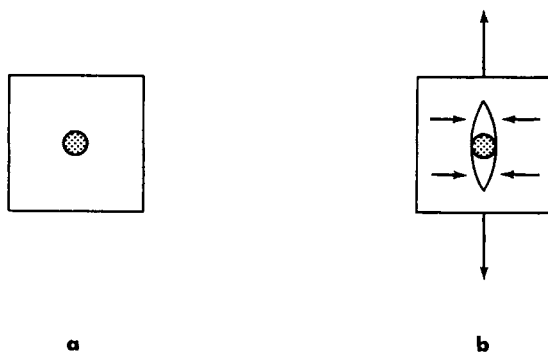


Fig. 1. A schematic representation of (a) an unstressed aggregate composite and (b) a stressed composite.

Now, consider what occurs when an aggregate composite is subjected to tensile stresses. If poor adhesion exists between filler and matrix, voids form around the particles and stress concentrators are present. The stressed composite will "strive" to reach an equilibrium position. This can be accomplished partly by stress relaxation and by the internal release of forces operating perpendicular to external tensile forces and in the direction of the voids, as shown schematically in Figure 1. These lateral forces cause the stressed specimen to decrease in width. In a system of poor adhesion, the change in width is largely due to the numerous voids present. If filler and matrix adhere well to each other, there is a minimal presence of voids, and the relative changes in widths corresponding to given changes in lengths are small. This leads to the conclusion that higher values of Poisson's ratio indicate poor adhesion between components, whereas better adhesion gives ratio values which are lower. Results of the investigation are reported in Table III.

The range in values between individual systems is very small, as Table III suggests. However, the overall range from 0.48 to 0.37 is large enough to indicate which silanes improved adhesion between filler and matrix. A composite containing ammonium perchlorate treated with Silane A-1100 was prestressed to 60% strain and allowed to relax for 48 hr to return to its

original length. Poisson's ratio for the prestressed composite was then found to be 0.40. A value above 0.38 (as found from the nonprestressed sample containing Silane A-1100) was obtained because voids had been introduced and adhesion between filler and matrix had been reduced in the prestressed composite. Therefore, it was decided that values lower than 0.40 represented better adhesion in these silane-modified systems.

From a qualitative standpoint, it appears that ammonium perchlorate pretreated with Silanes A-174 and A-1100 adhere better to cured CTPB than do particles treated with Silanes A-186 and Z-6075. In fact, from Table III, it can be deduced that the latter compounds give no improvement in adhesion since their Poisson's ratios are similar to the system containing untreated ammonium perchlorate.

Instron Analysis—Method A

A typical recorder output of Instron analysis, method A, is shown in Figure 2. Each output was converted to a continuous stress-strain curve by first calculating the stress and strain at points corresponding to the initial time of each stress-relaxation stage and then joining these points. The final results of this procedure are presented in Figure 3.

It can be observed that at a given strain, unfilled CTPB can accommodate the greatest stress. This is not unusual since ammonium perchlorate (80–100 mesh) is not a reinforcing filler, and hence any such composite will exhibit a stress-strain curve which is lower in position than a similar curve representing the unfilled rubber. Further investigation reveals that the prestressed sample of ammonium perchlorate coated with Silane A-1100 is the weakest composite.

In order to bring these results into clearer perspective, similar experiments were conducted with composites containing glass beads (80–100 mesh) and glass powder (200 mesh). Both types of glass fillers were coated with a fluorocarbon release agent so as to satisfy the criteria for a poorly adhering system. Two mesh sizes were selected because composites with small-sized fillers tend to improve strength. However, if the adhesion between filler and rubber is very poor, the size of filler is not significant.

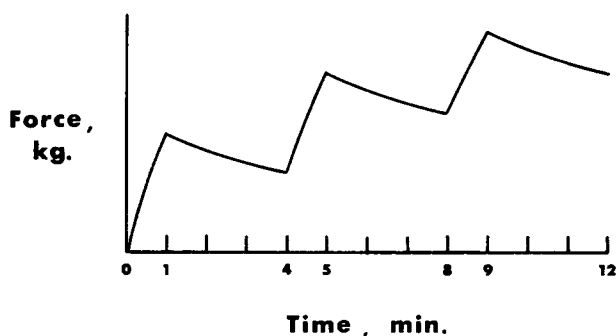


Fig. 2. Typical recorder output, Instron analysis—method A.

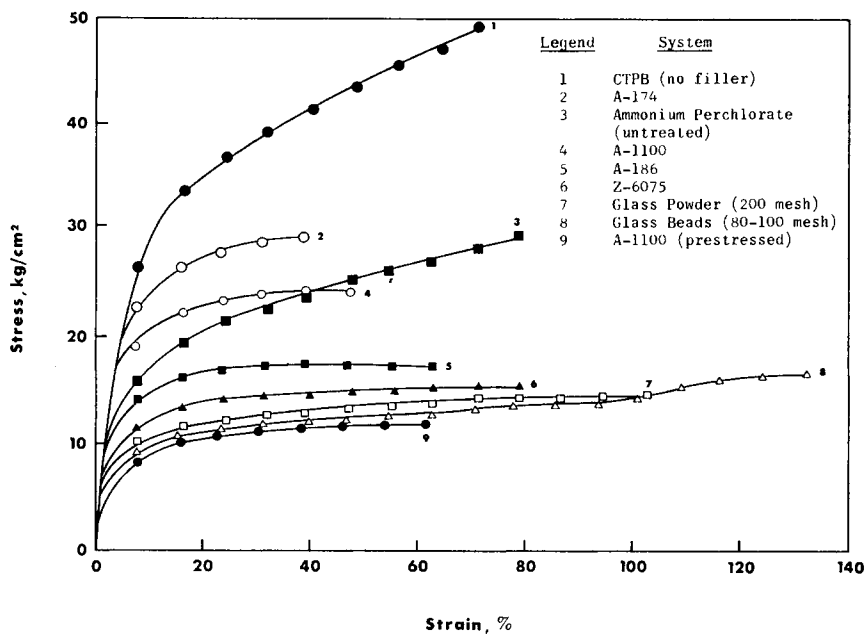


Fig. 3. Stress-strain results from Instron analysis—method A.

As expected, curves for both glass systems practically coincide. Curves in this region of Figure 3 undoubtedly reveal systems of poor adhesion. The curves representing glass-fluorocarbon systems are in close proximity to curves for Silanes Z-6075 and A-186. Adhesion is not improved in these systems, and the presence of these silanes proved to be detrimental at the filler-matrix interface since untreated ammonium perchlorate systems can experience greater stress and undergo greater strain. However, Silanes A-1100 and A-174 improve the adhesion between filler and rubber. These conclusions, if drawn solely upon the shape of the stress-strain curve, are in complete agreement with the glass-epoxy composites studied by Smith et al.⁸

Photographic Analysis

A photographic study was undertaken to investigate void formation within stressed aggregate composites and to identify the nature of the fractured surface.

Figure 4 shows total debonding of CTPB from a glass bead coated with a release agent. Not only is the void present in the immediate vicinity of the bead but it also extends beyond the poorly adhering filler. As the composite undergoes greater strain, more voids appear until finally the voids reach a critical size and number resulting in catastrophic failure. Ammonium perchlorate is highly polar and hydrophilic. As a result, its crystals aggregate to form large particles when in contact with moisture. The particles also tend to aggregate thereby preventing the liquid pre-



Fig. 4. Void formation after tensile testing around a glass bead coated with a fluorocarbon release agent (magnification 300X).

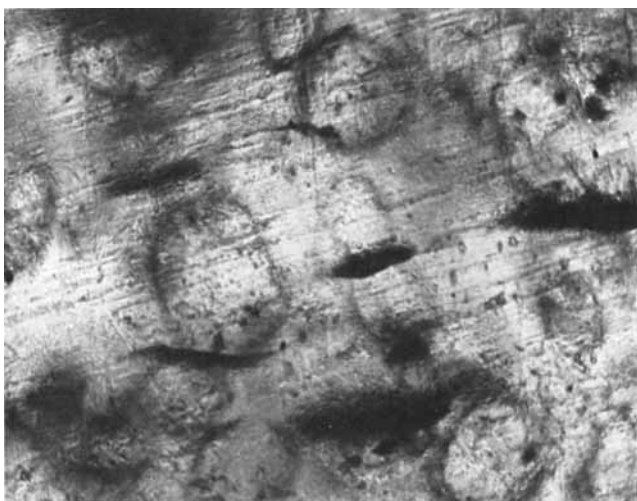


Fig. 5. Large void formation between most neighboring particles of ammonium perchlorate after tensile testing (magnification 120X).

polymer from properly wetting the filler. Hence, when the composite is stressed, void formation appears between neighboring particles, as shown in Figure 5. This suggests that in order to minimize the presence of voids, ammonium perchlorate particles must remain at some distance from one another so that complete wetting of the polymer may be possible. As previous discussions infer, coating the filler with Silane A-174 meets the above requirement, and Figure 6 confirms the other experimental observations. In contrast with the untreated ammonium perchlorate system, a composite containing ammonium perchlorate that has been pretreated with

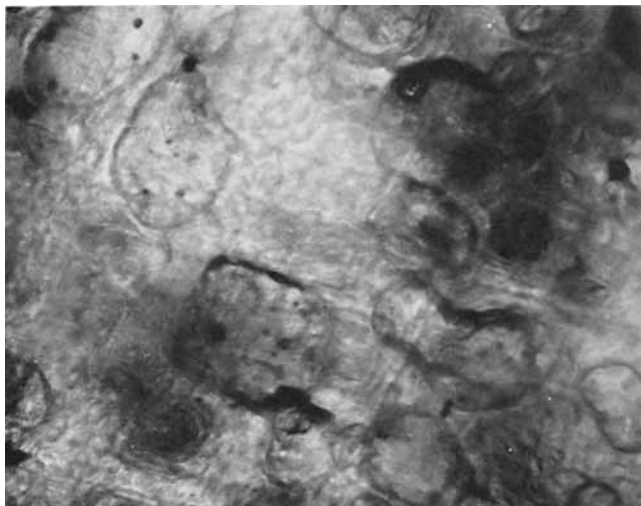


Fig. 6. Small void formation between some neighboring ammonium perchlorate particles coated with Silane A-174 after tensile testing (magnification $120\times$).

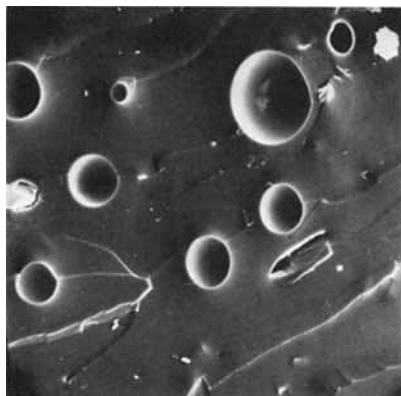


Fig. 7. Debonding of fluorocarbon-coated glass beads from CTPB at fracture surface (magnification $55\times$).

Silane A-174 produces smaller and fewer voids between neighboring filler particles. Better wetting has been accomplished which results in an improvement of adhesion between filler and rubber.

As illustrated in Figure 7, debonding of rubber from fluorocarbon-coated glass beads is severe. No resistance to fracture is offered by the poorly adhering filler. However, this is not the case for ammonium perchlorate systems. Voids are present at the filler-matrix interface, as Figure 8 suggests. A closer examination reveals that the voids partly surround the filler. Pretreatment with Silanes A-186 and Z-6075 (Figs. 9 and 10) produces voids that completely surround ammonium perchlorate particles. Previous discussions concerning Instron analysis, method A, show that

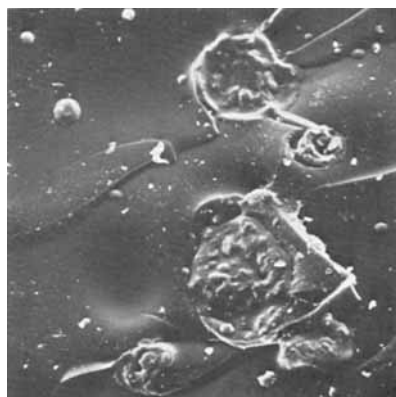


Fig. 8. Fracture surface of untreated ammonium perchlorate in CTPB (magnification 50 \times).

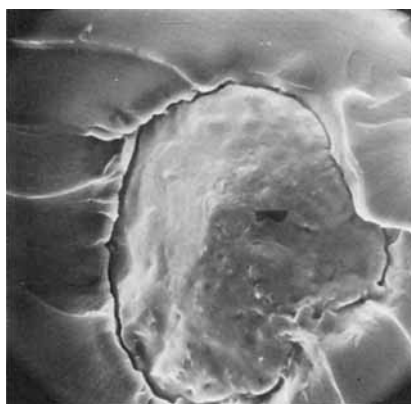


Fig. 9. Void formation around an ammonium perchlorate particle pretreated with Silane A-186 in CTPB at fracture surface (magnification 300 \times).

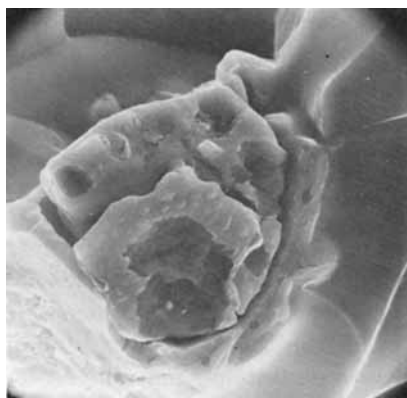


Fig. 10. Fracture surface showing void formation around an ammonium perchlorate particle pretreated with Silane Z-6075 in CTPB (magnification 550 \times).

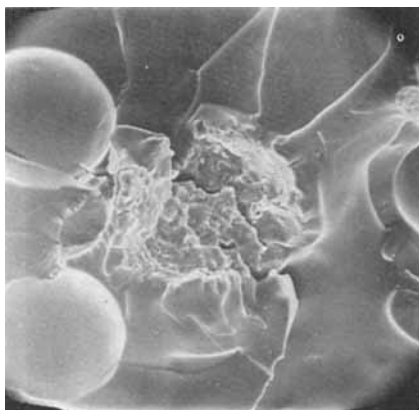


Fig. 11. Fracture surface of an ammonium perchlorate particle coated with Silane A-1100 in CTPB (magnification 100 \times).

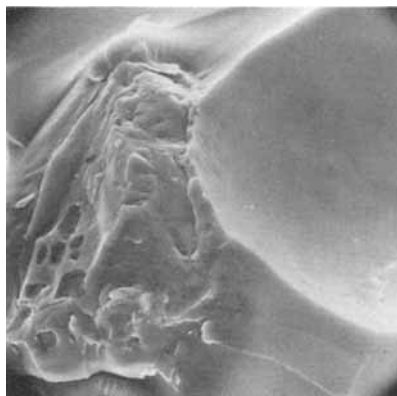


Fig. 12. An ammonium perchlorate particle coated with Silane A-1100 in CTPB at fracture surface (tilt 23 $^{\circ}$, magnification 330 \times).

these silanes prove to be detrimental as a surface coating for ammonium perchlorate and cause deterioration in adhesion between filler and rubber. These photographs indicate that the polymer "prefers" untreated ammonium perchlorate particles rather than filler that is pretreated with Silane A-186 or Silane Z-6075.

The fractured surfaces of systems containing Silanes A-1100 and A-174 are more complex than the previous systems discussed. Voids are difficult to detect, and the bonding between filler and rubber has greatly improved, as seen particularly in Figures 11-14. The complex nature of the fractured surfaces implies that the silanes provide resistance to fracture and debonding. Also, detection of filler in the composite containing Silane A-174 was difficult. This indicates that fracture may have occurred mostly in the rubber phase instead of at the filler-matrix interface. Some evidence for this occurrence may be found in Figure 14. Fracture in the rubber phase

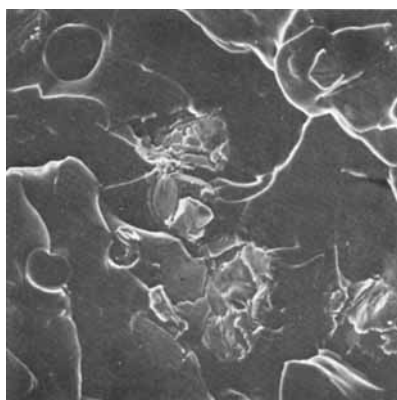


Fig. 13. Ammonium perchlorate particles coated with Silane A-174 in CTPB at fracture surface (magnification $60\times$).



Fig. 14. An ammonium perchlorate particle coated with Silane A-174 in CTPB at the fracture surface (magnification $120\times$).

leads toward a particle at the center of the photograph, but fracture does not extend to the filler interface. Further evidence is supplied in results obtained from the water absorption study.

Water Absorption

In order to obtain a better understanding of adhesion failure between components of an aggregate composite, water absorption tests were conducted. Unlike the photographic analysis which in a strict sense can be regarded as a two-dimensional study, an absorption study involves an investigation into all three dimensions. The following discussion presents several factors which control the extent of water absorption in sections located at the fracture surface and away from the fractured surface.

At Fracture

(i) The fracture surface is "rough" due to the propagation of a crack at the maximum tensile stress. The surface area, available for water absorption, increases.

(ii) Depending upon the extent of adhesion between matrix and filler, failure occurs with either a relatively large or small amount of each component at the fracture surface. Since water "penetrates" ammonium perchlorate more readily than CTPB (the former compound is soluble in water), the degree of absorption varies with the composition of the surface at fracture.

(iii) Fracture occurs at this location (near the center of the dumbbell specimen) because it is here where the composite is subjected to the greatest strain. Again depending upon the strength of the matrix-filler interface, fracture occurs when the critical number and size of voids are reached. The amount and size of these "flaws" decrease at locations further away from the surface fracture.

Away From Fracture

(i) The new surface, as prepared by a razor cut, is "smooth," and hence the exposed area in contact with water is slightly less than the area produced by a crack at the fracture surface.

(ii) Since all samples were prepared in the same manner, it is assumed that each specimen contains an equivalent proportion of matrix and filler at the new surface. Hence the degree of water absorption is influenced more by the relative resistance to penetration at the filler-matrix interface than by the composition.

(iii) The concentration and size of voids are smaller at this particular location in the specimen, since fracture occurs elsewhere.

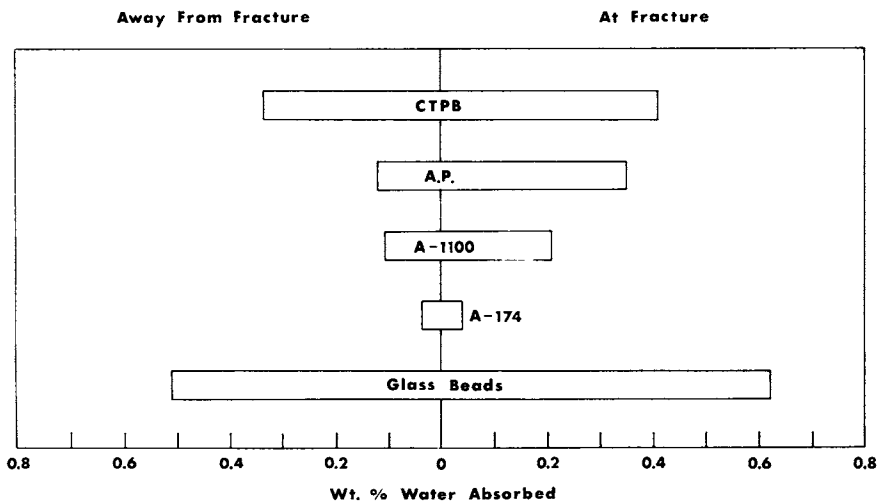


Fig. 15. Water absorption results for several composites after immersion for 2 hr.

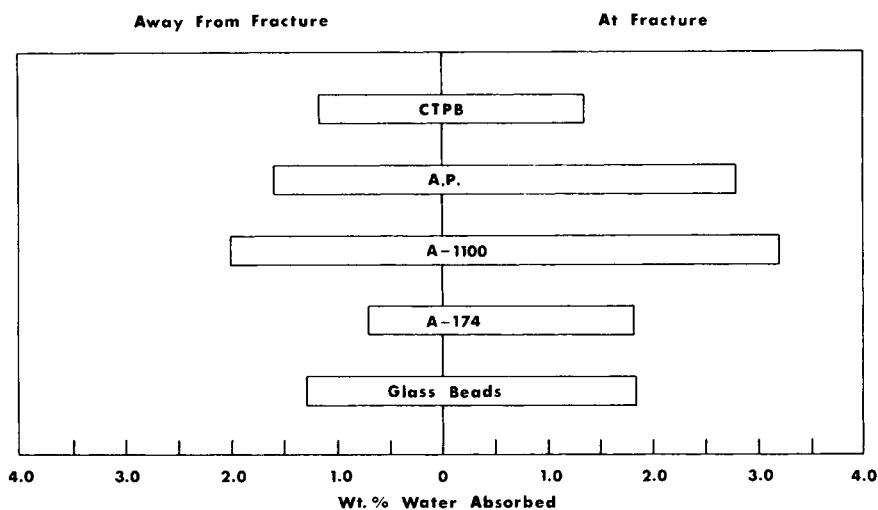


Fig. 16. Water absorption results for several composites after immersion for 20 hr.

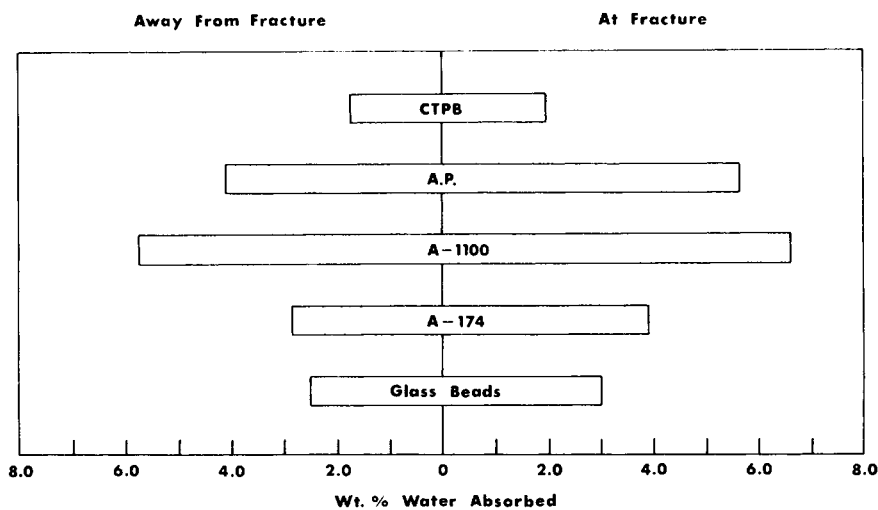


Fig. 17. Water absorption results for several composites after immersion for 6 days.

The results of the water absorption study are presented in Figures 15–18 for immersion times of 2 hr, 20 hr, 6 days, and 12 days, respectively. The samples under investigation were (1) unfilled CTPB, (2) untreated ammonium perchlorate (A.P.) filler, (3) A.P. pretreated with Silane A-1100, (4) A.P. pretreated with Silane A-174, and (5) glass beads coated with fluorocarbon.

Several general observations can be made. As immersion time increases, the amount of water absorbed in each sample increases while the rate of water absorption decreases. Also, in most cases, the “at fracture” samples (henceforth designated A.F.) absorbed more water after 2 hr than did their

TABLE IV
Water Absorption Study Indicating the Influence of Surface Roughness
and Void Formation on the Absorption Process

Time	Ratio of per cent water absorption	
	Surface roughness [CTPB (A.F.F.)/ CTPB (A.F.)]	Void formation [CTPB (A.F.F.)/ glass beads (A.F.F.)]
2 Hours	0.83	0.66
20 Hours	0.86	0.67
6 Days	0.90	0.69
12 Days	0.95	0.71

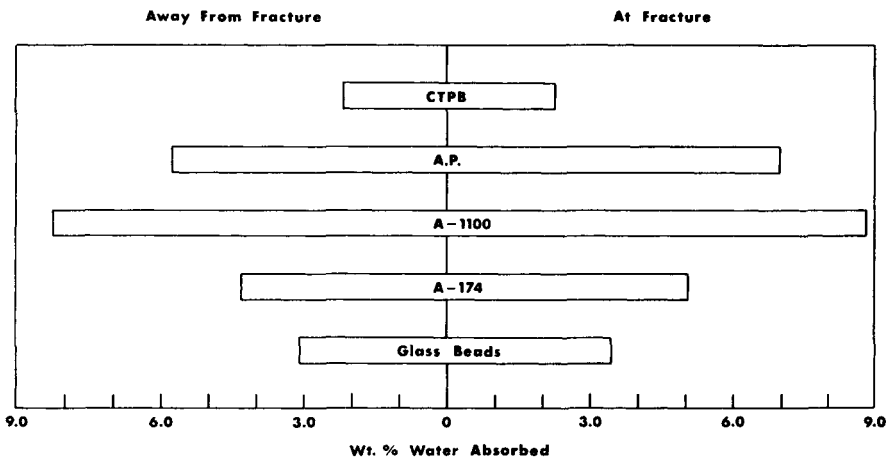


Fig. 18. Water absorption results for several composites after immersion for 12 days.

“away from fracture” counterparts (A.F.F.). The only exception was the system containing ammonium perchlorate pretreated with Silane A-174 where per cent water absorption at both locations was minimal.

By comparison of specific systems, the following discussion reveals the influence of surface roughness, extent of void formation, and filler pretreatment on the absorption process.

The effect of surface roughness on water absorption is best illustrated in a comparison of CTPB (A.F.) with CTPB (A.F.F.). Rigorous weight and volume determinations as well as density measurements (as described in ASTM D 792-66, reapproved 1970) and photographic studies confirmed that void content was negligible in these systems. Hence any difference that is observed in the results is due to surface roughness. Table IV gives the ratio of per cent water absorption of CTPB (A.F.F.) relative to CTPB (A.F.). After 2 hr of immersion, the ratio has a value of 0.83. As immersion time increases, the ratio also increases. After immersion for 12 days, the ratio approaches the value of unity, which indicates that the effect of surface roughness is negligible after this period of time.

When investigating the effect of voids on water absorption, it is best to compare the sample containing glass beads (A.F.F.) with CTPB (A.F.F.). The surface roughness variable has been eliminated since both samples exhibit "smooth" surfaces. Also, since the filler in this case is glass, there is no water absorption into the filler. Table IV lists the ratio of per cent water absorption for CTPB (A.F.F.) relative to glass beads (A.F.F.). As expected, the ratio increases with time of immersion. However, the ratios are much lower than those obtained for surface roughness indications, and the rate of increase of the ratio is also less. It may be concluded, therefore, that the presence of voids has a great influence on the degree of water absorption and that surface roughness is only of minor importance.

To complete this study, the effect of pretreatment of ammonium perchlorate with Silanes A-1100 and A-174 must be discussed in comparison with the untreated filler system. A quantitative analysis is not possible because variables such as surface roughness and extent of void formation cannot be selectively eliminated, while a new variable, namely, the relative solubility of treated and untreated ammonium perchlorate, must also be considered now. Therefore, a qualitative discussion is presented to determine the effect of silane pretreatment in a study of water absorption.

First, in order to appreciate the power of water penetration or capillary action into ammonium perchlorate-filled systems (solubility of filler in cold water is 10.74 g/100 cc and 42.45 g/100 cc in hot water), one should consider the results of untreated ammonium perchlorate (A.F.) and glass beads (A.F.). Both systems exhibit "rough" surfaces and each contains voids. The former system, however, is more readily penetrated by water because its filler is capable of being dissolved. Observations made after 20 hr, 6 days, and 12 days emphatically denote this tendency. At these times of immersion, the per cent water absorbed in the ammonium perchlorate composite is greater than the amount present in the glass-filled system. In fact, the differences in per cent by weight of water absorbed in these systems becomes consistently greater as immersion time increases. The only exception to this tendency occurs at the 2-hr reading. Initially, there is more absorption taking place in the glass-filled composite because its surface area at fracture is larger. Figures 7 and 8 confirm this observation. Hence, surface roughness is an important factor which influences the amount of water absorbed only during the initial stage of an absorption test.

These remarks finally lead to a comparison of silane-modified versus untreated ammonium perchlorate composites. At the 2-hr observation, both silane systems absorb less water than the composite containing untreated ammonium perchlorate. This fact implies that tensile failure occurs near or at the silane-matrix interface thereby producing a "smooth" surface, whereas the untreated ammonium perchlorate composite fails at the filler-matrix interface resulting in a "rough" fracture surface. Also, resistance to water penetration in the system modified with Silane A-174, or its hydrolysis products, is greater than that offered by the composite con-

taining untreated ammonium perchlorate at each time interval. These observations reveal that Silane A-174 serves as a protective coating for ammonium perchlorate particles. This is not the case, however, in the Silane A-1100 system where the per cent water absorbed is generally larger than that for untreated filler. Plueddemann¹² obtained similar results and found that Silane A-1100 does not form a "high polymer" siloxane when aging in aqueous solution but rather remains as a dimer species which retains its water solubility. Unlike Silane A-1100, Silane A-174 is nonpolar and becomes insoluble in water as soon as the dimer unit is formed.

The water absorption study supplied valuable information regarding the extent of surface roughness and void formation in these aggregate composites containing either a dissolvable or nondissolvable filler. Also, provided that the silane does not dissolve in water, this test suggested that a coating can adhere effectively around ammonium perchlorate particles.

A Study in Composite Theory

Each of the previous four methods used to investigate the adhesion between ammonium perchlorate and carboxyl-terminated polybutadiene gives evidence that pretreatment of filler with Silane A-1100 or Silane A-174 improves adhesion characteristics. The purpose of the following study is to finally verify these conclusions from composite theory.

For the case of perfect adhesion, the right-hand side of eq. (1) has a fixed value which depends upon the amount of filler present in the composite. Deviation (below theoretical values) of the quantity of the left-hand side from the fixed value on the right indicates that adhesion is not optimal.

The strain to break of unfilled CTPB is 67%. The strain to break and relative strain to break of filled composites are shown in Table V. The difference between the right- and left-hand sides of eq. (1) for fluorocarbon-coated glass beads is 0.23. Hence, it is safe to assume that systems that show a deviation of 0.23 or thereabouts exhibit poor adhesion between filler and matrix. Once again, it is seen that systems containing untreated ammonium perchlorate, Silane A-186, and Silane Z-6075 can be categorized into the poorly adhering group. Their deviation values are 0.28, 0.15, and 0.27, respectively. On the other hand, composites of ammonium perchlorate pretreated with Silanes A-1100 and A-174 both show a deviation value of 0.04, which classifies these systems into the better adhering group.

All composites investigated thus far have one important feature in common, namely, the fillers are nonreinforcing. In order to appreciate the physical properties of a reinforced aggregate composite, carboxyl-terminated polybutadiene was filled with carbon black ($V_f = 0.40$). The breaking strain of this composite was found to be 42%. Nielsen's theory predicts that at a volume fraction of 0.40, the relative tensile strength is 0.25. But as expected in a reinforced composite, the value of the relative strain to break is high. Indeed, the experimental value for the carbon black system was 0.62. Hence, Nielsen's model does not predict the adhe-

TABLE V
Case of Perfect Adhesion. Instron Analysis—Method B^a

Filler system	ϵ_b , %	$\epsilon_{rel.}$	$1 - V_f^{1/3}$
A.P. (untreated)	22	0.33	0.61
A-174	38	0.57	0.61
A-186	31	0.46	0.61
A-1100	38	0.57	0.61
Z-6075	23	0.34	0.61
Glass beads	28	0.42	0.65
Carbon black	42	0.62	0.26

^a $\epsilon_{rel.} = \epsilon_b(\text{filled})/\epsilon_b(\text{unfilled}) = 1 - V_f^{1/3}$; $\epsilon_b(\text{unfilled}) = 67\%$.

TABLE VI
Case of No Adhesion. Instron Analysis—Method B^a

Filler system	$\sigma_b(\text{filled})$, kg/cm ²	$\sigma_{rel.}$	$1 - V_f^{2/3}$	S
A.P. (untreated)	27.7	0.78	0.85	0.92
A-174	26.1	0.74	0.85	0.87
A-186	27.3	0.77	0.85	0.91
A-1100	22.6	0.64	0.85	0.75
Z-6075	25.4	0.72	0.85	0.85
Glass beads	32.1	0.91	0.88	1.0
Carbon black	40.5	1.14	0.45	2.53

^a $\sigma_{rel.} = \sigma_b(\text{filled})/\sigma_b(\text{unfilled}) = (1 - V_f^{2/3})S$; $\sigma_b(\text{unfilled}) = 35.4 \text{ kg/cm}^2$.

sion between a matrix and a reinforcing filler. In fact, no such prediction is necessary since all reinforced aggregate composites must exhibit excellent adhesion between filler and matrix. Nielsen's model, however, is extremely useful for comparing the adhesion between modified nonreinforced fillers to the rubber matrix.

For the case of no adhesion, the values of all quantities in eq. (2), except for the stress concentration factor S , can be found experimentally. Therefore, assuming the equality of eq. (2), the value of S may be obtained mathematically. An unfilled CTPB rubber can undergo a stress of 35.4 kg/cm² before fracture. Table VI lists the necessary data.

As theory suggests, the maximum value of the stress concentration factor is 1.0 at poorest adhesion.⁹ The carbon black-filled composite gives a value that is greater than unity. This indicates that there is excellent adhesion between components, and as a result eq. (2) is inapplicable. The Eilers-Van Dijk equation relating relative tensile strength to volume fraction of filler is derived from a consideration of good adhesion between filler and matrix. The theoretical relative tensile strength value at volume fraction of 0.40 is 1.01. The experimental value was found to be 1.14, which closely agrees with the theoretical model.

For the remaining composites, Nielsen's theory may be applied. The poorest adhering filler must be the fluorocarbon-coated glass beads. The stress concentration factor has a value of 1.0 for this composite. As the value of S decreases from unity, the adhesion between filler and matrix improves. Hence, the order from poorest to best adhesion system is (1) glass beads, (2) untreated ammonium perchlorate, (3) A-186, (4) A-174, (5) Z-6075, (6) A-1100.

The only discrepancy existing in this order is the reversed positions of Silanes A-174 and Z-6075. This is most likely due to the fact that Nielsen's theory is based upon an ideal model when equality of eq. (2) is assumed. Composites, however, contain imperfections, and hence the theoretical breaking strain or breaking stress is not usually attained and differences between observed and theoretical values are likely to occur. Fortunately, the discrepancy in this case is very small and may be dismissed from further discussion. However, a word of caution should be interjected if adhesion between components in an aggregate composite is studied at greater volume loadings of filler. Mixing must provide good contact between filler and matrix or numerous flaws will be present in the composite resulting in a poor comparison between theoretical and observed data.

Silanes as Coupling Agents

Silanes are most commonly used as coupling agents in glass-polymer systems.¹³ However, the chemical adsorption of silanes onto glass is not thoroughly understood. Also, no attempt has been made to explain why some metals such as iron and aluminum¹⁴ which do not contain surface silanol groups adhere well to polymers if pretreated with certain silanes. It is generally accepted that the presence of moisture on a substrate is an important factor for reaction of coupling agents. The hydrolyzable groups on the silane react with water to produce silanol groups which react with surface moisture on the inorganic substrate through hydrogen bonding, eliminating a weak boundary layer. Since technology has surpassed scientific research in this area, it is only possible to provide some insight for silane adsorption onto ammonium perchlorate and its involvement in cured polybutadiene rubber by means of several literature references.

Bertolucci et al.¹⁵ have recently investigated the adsorption of organic molecules on a series of synthetic and natural calcium phosphates. By means of infrared spectrophotometry, they were able to observe high-frequency shifts in the band of the P-O bond which contains the surface oxygen atom. Ammonium perchlorate has a structure that is similar to calcium phosphate. Both crystals contain four oxygen atoms surrounded by a central atom. Also, oxygen atoms appear at the surface of each crystal lattice. Similarities in these crystals might suggest that chemical adsorption of certain silanes on ammonium perchlorate is possible. But these observations are speculative, and definite conclusions can only be obtained from experimental work involving the ammonium perchlorate-silane interface.

As in glass-resin composites, it is easier to explain adhesion improvement by means of an examination of the silane-polymer interface. The rubber in this investigation is thermosetting, but the formulation for curing includes polybutadiene, epoxy curing agent, and amine catalyst. Since polybutadiene has vinyl groups along the resin backbone, unsaturated silanes such as methacryloxy- and vinyl-functional silanes are the preferred coupling agents.¹⁶ The presence of epoxy and amine compounds suggested the use of an epoxy- and amino-functional silane to encourage chemical reaction between the coating and rubber matrix. Results show that Silanes Z-6075 and A-186 do not improve adhesion between filler and rubber. In fact, these silanes are detrimental at the interface. This observation is similar to results obtained by Plueddemann¹⁷ which indicate that nonreactive silanes on glass in a thermosetting polymer gives poorer bonding than untreated glass. The organofunctional group of almost all coupling agents has been separated from the silicon atom by at least three carbon atoms in order to preserve its reactivity. As seen from Table I, Silane Z-6075 is an exception, and hence vinyl reactivity is poor. This is in sharp contrast to the improvement in adhesion with the use of Silane A-174. This silane is reactive since the unsaturated functional group is at a distance from the silicon atom, thereby favoring reaction with the pendant vinyl group of the polybutadiene without steric hindrance.

Since an epoxy-amine curing system is used, Silane A-186 should have been able to react with the hardener in the same manner as the epoxy resin. However, results show that this was not the case. Manufacturers of silanes¹⁸ recommend an ethanol/water mixture of ratio 1/3 for the hydrolysis of Silane A-186 because it is insoluble in water alone. An ethanol/water surface layer was not investigated because this procedure deviated from the usual propellant formulation.

Silane A-1100 improves adhesion between the filler and rubber owing to its reactivity in the presence of the amine catalyst (EH-330). However, the amino-functional silane does not reach the standard set by the methacryloxy-functional silane. This may, in part, be due to the fact that there are more vinyl groups present for reaction with Silane A-174 than epoxy groups for Silane A-1100. Also Plueddemann¹² states that amino-functional silanes, when in aqueous media, do not hydrolyze in the normal manner. These silanes partially hydrolyze and form cyclicized structures. The amine group probably forms an ionic bond with the inorganic portion of the molecule. This occurrence not only ties up part of the inorganic portion but also reduces the reactivity of the amino-functional group.

For glass-resin composites, it is recommended that a unimolecular layer of silane be present at the interface for optimal mechanical properties. This corresponds to about 0.1% silane. In this study, an excess was used to allow some of the silane to react with moisture on the surface of the hydrophilic filler while the excess remained as an adsorbed coating. Reactivity with the elastomeric matrix could be dependent upon the organo-functional group in the respective silanes.

CONCLUSIONS

Poisson's ratio values were higher for systems containing an epoxy- or vinyl-functional silane. Low values for Poisson's ratio were observed when ammonium perchlorate was pretreated with either a methacryloxy- or amino-functional silane. It was found that lower values indicated better adhesion between filler and rubber.

Instron analysis, method A, gave a new approach to studying adhesion between components in an aggregate composite. Tests showed that the presence of silanes with epoxy or vinyl groups proved to be detrimental at the filler-matrix interface. This testing procedure identified systems having good and poor adhesion.

The photographic analysis revealed the incomplete wetting behavior of prepolymer onto untreated ammonium perchlorate particles. Pretreatment with epoxy- or vinyl-functional silanes caused total debonding between filler and rubber. Some evidence existed that fracture in methacryloxy- and amino-functional systems is predominantly in the rubber phase.

The water absorption study of samples located "at fracture" and "away from fracture" provided valuable information regarding the extent of surface roughness and void formation in a composite containing either a dissolvable or nondissolvable filler. The amino-functional silane did not serve as a protective coating since it dissolved in water. However, the methacryloxy-functional silane coating was insoluble in water. It was concluded that this test gave added assurance that a silane coating was present around ammonium perchlorate particles as long as it did not further dissolve in water.

Confirmation of the results was made by using Nielsen's composite theory for the cases of perfect adhesion and no adhesion between components. The theoretical principles, which assume flawless composites, closely agreed with experimental results at low volume fraction loading of filler.

It is not yet understood whether adhesion improvement was due to silane coupling onto ammonium perchlorate particles or only to the elimination of a weak boundary layer in the form of moisture. An additional factor could be the coupling of the organo-functional group to the resin adjacent to the layer of silane on the ammonium perchlorate.

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Addendum

Interrupted stress-strain experiments on nylon 6 have been investigated by Rubin.¹⁹ The technique is comparable to Instron analysis, method A, the study of which was completed and the manuscript prepared prior to recognition of the relevance of his contribution.

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