

# Use of Carbon Fibril Additives to Reduce the dc Resistivity of Elastomer-Based Composites

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## SYNOPSIS

We have prepared inert model solid rocket propellants of two kinds, polycaprolactone (PCP) networks highly (60%) plasticized with triacetin and hydroxyl-terminated polybutadiene (HTPB) cross-linked with isophorone diisocyanate, both filled with over 65% NaSO<sub>4</sub> and Al powders as well as traces of fine carbon fibrils 100 Å thick and several micrometers long. Sheets of these dielectric composites were used for dc surface and volume electrical resistivities near room temperature. Addition of less than 1% fibrils in the PCP composites reduces volume resistivity by a factor of 10. The amount required for HTPB is only 0.1%, leaving processability unaffected; resistivity reduction rises from one to nearly four orders of magnitude as potential difference is increased from 10 to 500 V. Addition of fibrils to HTPB composites is a promising candidate for minimizing the incidence of dangerous electric discharge events. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Composite materials based on a rubbery matrix containing dispersed solids tend to be relatively good electrical insulators. High-volume dc resistivity often persists to the maximum filler loadings compatible with required mechanical integrity, even when the filler particles themselves are good conductors. Although this attribute is usually harmless and often desirable, there are significant instances in which it presents substantial hazards. These are mainly connected to possible inadvertent buildup and subsequent discharge of static electricity combined with the composite's own chemical reactivity. The most egregious examples are solid rocket propellants,<sup>1</sup> whose compounding, casting, curing, and subsequent handling<sup>2</sup> may be attended by frictional charging, further increasing the danger of these operations and, significantly, of deploying and operating the assembled motors.<sup>3</sup>

One conceivable remedy calls for an attempt to increase the composite's resistivity further, confin-

ing static charge-discharge episodes entirely to its surface, which may be appropriately protected by highly conductive coatings; this goal is generally considered unattainable. The more practical opposite approach is to decrease the volume resistivity to the extent required to prevent substantial charge buildup by enabling continuous internal discharge. This may be accomplished by addition of highly conductive filler particles, e.g., carbon black. However, the amounts required tend to be larger than tolerable in a compound already highly optimized<sup>2,4</sup> to meet stringent requirements of combustion energy, burn rate, smoke production, and mechanical strength. Even the processability of the mixture prior to curing may be adversely affected.

This disadvantage may be overcome by altering the shape of the conductive particles from approximately spherical to highly prolate, permitting the volume and weight fractions to be greatly reduced for the same resistivity reduction.<sup>5,6</sup> Aspect ratios of several hundred are attainable, in principle, through the use of chipped metallic wire. Ideal from a chemical as well as mechanical perspective would be thin carbon fibrils with a tendency to bend or curl to minimize rupturing during processing; the minute quantity needed might be substituted for an equal

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**Table I** PCP-based Propellant and Model Propellant Formulations

Propellant Formulation		Model Propellant Formulation	
Material	Nominal Wt (%)	Material	Nominal Wt (%)
Polymer (PCP or PEG)	9.1	Polymer (PCP)	9.2
Plasticizer (nitroglycerine)	22.6	Plasticizer (triacetin)	23.1
Curing agent (Des N-100)	1.6	Curing agent (Des N-100)	1.9
Cure catalyst (TPB)	0.01	Cure catalyst (TPB)	0.05
Aluminum powder	20.0	Aluminum powder	19.7
Ammonium perchlorate	46.7	Sodium sulfate	46.0

weight of carbon black now added to fine-tune processability. Such fibrils of the necessary small size have recently become commercially available.

We show that the addition of trace amounts of microscopic carbon fibrils to model solid rocket propellants can reduce the dc volume and surface electrical resistivities by several orders of magnitude, particularly at higher electrical potential, and we offer tentative interpretations of the mechanisms involved. Preliminary reports of parts of this work have been given.<sup>7-11</sup> This article is based in large part on the MS thesis of C. W. Farriss II, University of Akron (Physics), 1993 (unpublished).

## EXPERIMENT

### Model Propellant Ingredients, Formulations

Two cross-linked propellant formulations were examined: a high-energy version based on hydroxyl-terminated polycaprolactone (PCP) highly plasticized; the other, a conventional formulation based on hydroxyl-terminated polybutadiene (HTPB). For laboratory use, closely equivalent inert ingredients were substituted for the volatile and energetic materials used in live propellants: nitroglycerine and ammonium perchlorate were replaced for the model compounds by triacetin and sodium sulfate, respec-

tively. The nominal quantitative formulations of both the operational and model versions are recorded in Tables I and II.

The ingredients used in the PCP-based model propellant were as follows: PCP was supplied as TONE 0260 Polyol by Union Carbide Corp. and used as received; its molecular weight average  $\bar{M}_n$  was near 3000 g/mol. The curing agent Desmodur N-100 was supplied by Mobay Corp., with the cure catalyst triphenyl bismuth from Boulder Scientific Co. The plasticizer triacetin Kodaflex was manufactured by Eastman Chemical Co. and vacuum-distilled to obtain the middle boiling fraction. These materials were all kept refrigerated in a dry  $N_2$  atmosphere prior to specimen preparation. As for the solid fillers, the aluminum powder had a particle size ranging between 1 and 10  $\mu\text{m}$ , whereas the sodium sulfate, to resemble the original ammonium perchlorate, had particle sizes between 37 and 420  $\mu\text{m}$ . These solids were supplied to us by Thiokol Corp. and were degassed *in vacuo* for 1 h at 50°C prior to compounding.

Most of these materials were also used in the preparation of the conventional model propellant; the butadiene polymer, manufactured by Arco Chemical Co. as R-45, also had a nominal  $\bar{M}_n$  near 3000 g/mol. In this formulation, the curing agent was isophorone diisocyanate (IPDI), provided by Hüls AG; because of its short effective shelf life, its

**Table II** HTPB-based Propellant and Model Propellant Formulations

Propellant Formulation		Model Propellant Formulation	
Material	Nominal Wt (%)	Material	Nominal Wt (%)
Polymer (HTPB)	12.73	Polymer (HTPB)	27.2
Curing agent (IPDI)	2.24	Curing agent (IPDI)	2.30
Aluminum powder	14.76	Aluminum powder	14.6
Ammonium perchlorate	65.0	Sodium sulfate	55.9
Inert ingredients	5.27	—	—

containers were kept flooded with dry N<sub>2</sub> gas and refrigerated below 0°C.

The microscopic carbon fibrils were supplied by Hyperion Catalysis International, Inc. (Lexington, MA) as a recent proprietary product development with initial applications to structural reinforcement. The highly crystalline graphitic (> 98% C when untreated) fibrils take the form of hollow cylinders with outer diameters between 0.007 and 0.07 μm; electron micrographs reveal their modest tendency to curl with loop diameters at least 50 times the fibril diameters. The fibrils' uncoiled lengths exceed their diameters by factors of between several hundred and several thousand. Although the electrical and thermal conductivities of individual fibrils of these dimensions are prohibitively difficult to measure with confidence, both appear to approach those of graphite. (Preliminary characterization of the fibrils was supplied by the manufacturer.) Because of their tendency to trap liquids and atmospheric vapors, the fibril batches as received were flushed with dry N<sub>2</sub> gas and stored in a desiccator, with appropriate aliquots vacuum-oven-dried near 50°C prior to use.

### Fabrication of Model Propellants

Preparation of a PCP-based model high-energy propellant was described previously<sup>12,13</sup> in connection with studies of morphology, mechanical properties, and molecular mobility, but this standard procedure had to be modified here<sup>7,8</sup> to permit the introduction of fibrils in excess of 0.2 wt %. At the higher concentrations the triacetin, PCP, TPB, Desmodur, and fibrils were combined and heated to 50°C to melt the PCP powder. Dispersal was achieved by mixing for 15 s in a Sorvall Omni-Mixer, whereupon the solids were added and the aggregate stirred manually, followed by low-shear mixing with a rubber mill for 30 min at room temperature. The paste was vacuum-molded in a nonadhesive sheet mold at 100°C and 2.2 at. static ram pressure, and allowed to cure for 24 h. This procedure resulted in 2 mm-thick sheets, which were free of granular regions, voids, and cracks up to fibril fractions in excess of 1 wt %. Unfilled networks, gumstocks, with and without fibrils, were easily prepared by using the earlier procedure.<sup>12,13</sup>

Procedures for producing cured HTPB-based composites have also been described in connection with other research objectives,<sup>14-16</sup> although the identity and content of the solid fillers differed substantially from those in use here. Wide-ranging adaptation of these methods failed to result in acceptable specimens for the highest fibril fractions

to be tested unless the solids fraction was reduced from the desired 80-70 wt %. Table II, consequently, reflects this reduction for the present study of HTPB model propellants. However, the results of the resistivity measurements to be described will make it clear that the amount of fibrils needed in practice will easily be low enough to permit processing by the established methods to produce compounds containing at least 80% solids as required. The formulation of Table II is tailored to minimize diffusing sol, i.e., to maximize the fraction of the binder network obtained, taking into account the surface chemical reactivities of the solid ingredients. The techniques used for this purpose, and their results, have been described in earlier reports.<sup>15,16</sup>

The preparation method evolved for the present work<sup>9,10</sup> called for combining the R-45 and fibrils in the high-shear mixer for 1 min and the mixture to be degassed for 30 min at 85°C. IPDI was stirred into the mixture under dry N<sub>2</sub> gas flow and allowed to react for 30 min. The fillers, also degassed earlier, were then added under flowing nitrogen, and the aggregate was mixed in a sealed Sorvall Omni-Mixer at 16,000 rpm for 1.5 min, which caused some heating. Vacuum molding resembled the process described for the PCP-based composites except that here curing took place for 36 h at 85°C.

Circular disk samples, 10 cm diameter, for the resistivity measurements were cut from flaw-free portions of the molded sheets. To remove occasional surface bloom of polymeric or unreacted liquid material particularly on the PCP composites, the resistivity specimens were mechanically cleaned and abraded with 600-grade sandpaper. All specimens were maintained dry and in darkness at 50°C before and between measurements. The glass transition of the PCP binder had been measured<sup>12</sup> to be 42°C; this was verified for several of our specimens.

### Resistivity Measurements

The dc resistivity measurements were performed with a Hewlett-Packard high-resistance meter, Model 4329A, connected through low-noise leads to a matching resistivity cell, Model HP-16008A, the latter capable of being switched between volume and surface resistivity modes. The cell could be operated inside a convection oven for measurements above room temperature. All measurements reported here were made at 20 or 30°C, as indicated. The volume and surface resistivities  $\rho$  (in units of Ω-cm) and  $\sigma$  (units of Ω), respectively, were extracted from the measured resistance  $R$  via their definitions:

$$R = \rho t/A, \quad R = \sigma d/l, \quad (1)$$

where  $t$  is the thickness of the sheet (the average of up to 8 measurements via micrometer);  $A$ , the area of the inner contact plate of the cell;  $d$ , the width of the annular gap between it and the outer contact ring (which also serves as a guard ring for volume resistivity measurements); and  $I$  representing the mean circumference of that gap. The last three quantities were available from the instrument's instruction manual. The resistance readings were either recorded manually at specified times or, preferentially, read from a chart recording made with a Linseis Model 7600 chart recorder. The latter was attached to the analog output of the resistance meter, with voltage levels later converted to resistance via a template calibrated by using standard decade resistors.

Because the measured values of  $R$  for the relatively stiff PCP-based specimens tended to be erratic and dependent on the cell's contact pressure, the use of a contact-enhancing fluid was required. The product ultimately selected as far superior to oil-based emulsions, graphite slurries, and conductive paints was Cor-Gel, a water-based electrolytic gel used in medical diagnostics, e.g., EKG and EEG. Its use entirely eliminated any contact problems, but at the disadvantage of a finite water-evaporation rate, which limited the time available for resistivity runs to approximately 2 h, usually sufficient.

The use of contact gel was unnecessary for the flexible and tacky HTPB-based composites. Because of the far higher resistivity of these samples, small inadvertent motions of the cell or its electrical connections resulted in spurious transient resistance readings; careful immobilization of all components eliminated these effects.

In many specimens of both formulations, the resistivities also were dependent on the applied potential. Therefore, except where indicated, all results reported were collected at the same potential difference of 10 V and, hence, also at constant internal field as the sample geometry was kept very nearly the same among specimens. In many PCP-based composites, both resistivities were, in addition, explicitly dependent on the time from first application of the measuring potential. This effect was clearly evident from the resistance meter's chart recordings. In some HTPB-based samples containing fibrils, the chart recordings registered small but rapid resistance fluctuations having amplitudes not exceeding 10% of the reported readings and frequencies mainly above 0.3 Hz. Use of a digital oscilloscope with Fourier transform capability connected to the cell in parallel with the meter showed that most of the ac spectral power in the two specimens examined (0.25

and 0.75 wt % fibrils) was concentrated between 2 and 45 Hz.

Since each of the reported readings represents an average of at least six separate measurements taken on at least two duplicate preparations, it was important to keep the measuring protocol identical. Thus, all measurements were begun 1 min from the start of the timer at the application of the potential; reported values represent averages over intervals of approximately 5 s. All specimens having time-dependent resistivities returned reproducibly to their initial resistance values within a few minutes after the test potential was removed and the cell contacts grounded via its external switch.

## RESULTS AND DISCUSSION

### PCP-based Model Propellants

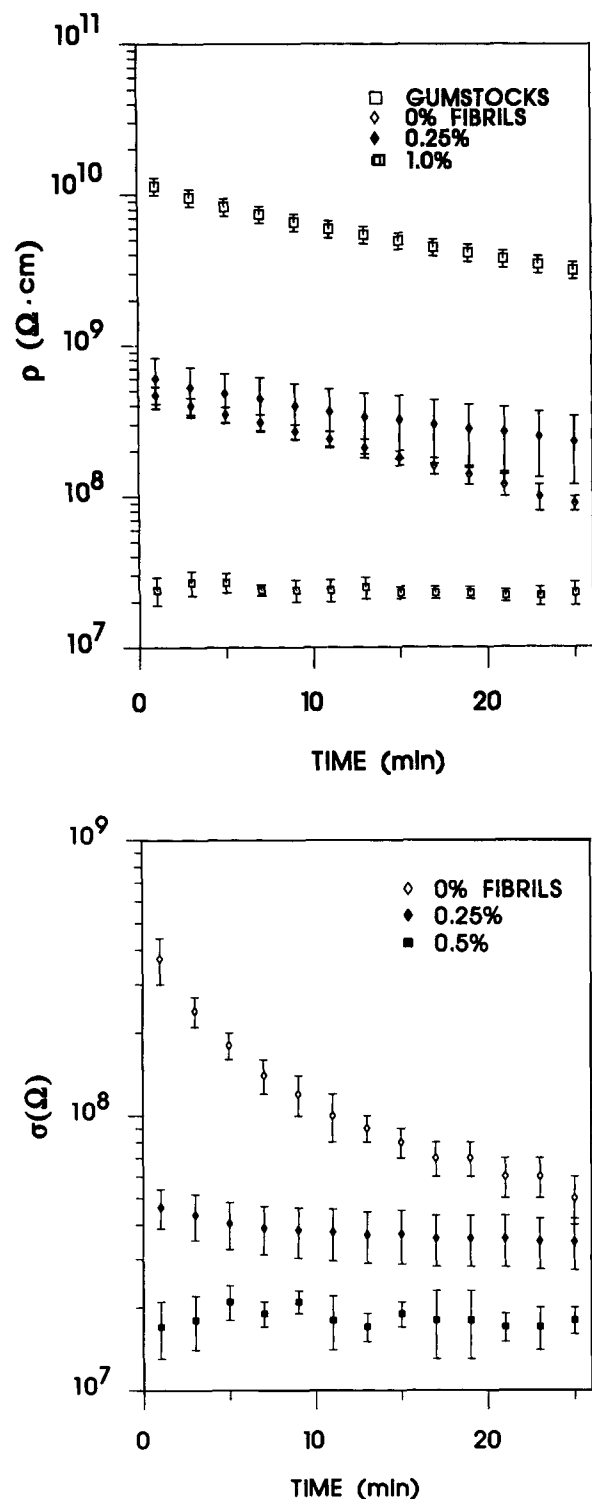
Figure 1(a) shows the volume resistivity in PCP gumstock without fibrils and in model propellant formulation without and with fibrils, as function of time from the application of the 10 V test potential. The values and uncertainties shown represent, respectively, the means and their standard deviations of at least six independent measurements, including several made on duplicate samples. Hence, the uncertainties characterize overall reproducibility rather than the much greater precision of a single measurement.

It is seen that incorporation of the solids decreases the resistivity by a factor near 20 and that the addition of 0.25 wt % fibrils provides no significant further reduction. Volume resistivity decreases over time in a manner consistent with

$$\rho(t) = \rho_{\infty} + (\rho_0 - \rho_{\infty})\exp(-t/T) \quad (2)$$

This equation was successfully fitted<sup>17</sup> to the data. The characteristic time constant  $T$  extracted had a value near 15 min; at longer times,  $\rho$  appears to reach imprecisely defined lower asymptotes  $\rho_{\infty}$  dictated by the presence of solid filler but independent of (modest) fibril content. Introduction of 1 wt % fibrils into the composites reduces initial volume resistivity  $\rho_0$  by another factor of 20 and eliminates its time-dependence; more extended measurements (not shown) suggest that the long-term asymptote is unaffected.

Somewhat similar but more pronounced effects may be observed in the surface resistivities in PCP-based specimens, shown in Figure 1(b). Gumstock measurements were not available. The fibril-free composite exhibits a shorter resistive time constant,



**Figure 1** (a) DC electrical volume resistivity and (b) surface resistivity at 20°C in (large open squares) PCP gumstocks and (open diamonds) model propellant without fibrils and containing fibrils in the amounts of (filled diamonds) 0.25 wt %, (filled squares) 0.5 wt %, and (open squares) 1.0 wt %, as function of time since application of the 10 V measuring potential.

near 5 min. The effect of 0.25 wt % fibrils is more pronounced in the surface measurement and eliminates much of the time-dependent decay, which is entirely unobservable at 0.5 wt % filler. (At 1 wt %, the surface resistance was unrecordable, falling just below the meter's lowest range.) Again, a common asymptote may ultimately be approached.

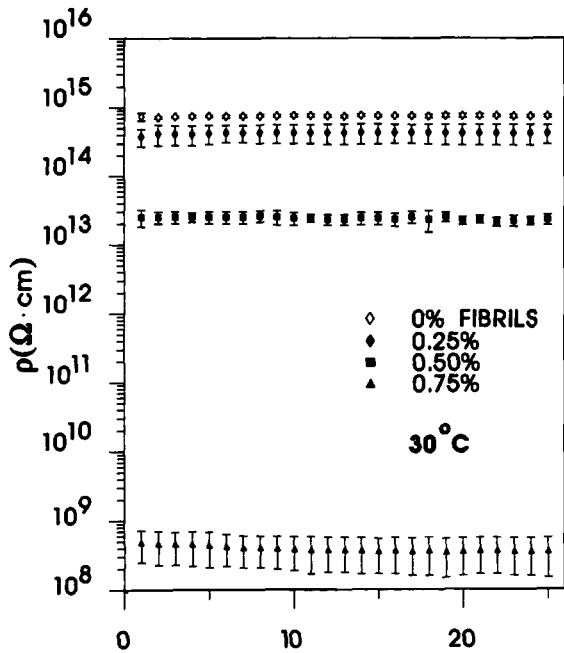
### HTPB-based Gumstocks and Model Propellants

Because electric discharge problems are more severe in the case of conventional HTPB propellants than in high-energy formulations, a more detailed investigation of the effect of fibrils seemed called for. Figure 2 shows volume resistivity in HTPB gumstocks containing between zero and 0.75 wt % fibrils. The resistivity is between four and five orders of magnitude higher than in PCP gumstocks, but no time-dependent decrease is observed in any sample. Although 0.1 and 0.25 wt % fibrils offer no improvement, 0.5 wt % lowers  $\rho$  by a factor of 30, but 0.75 wt % results in a six-order reduction, at the expense of reduced pre-cure processability. Again, the surface resistivity in the same samples (not shown) shows very similar trends.

Samples cured with the mold mounted vertically had significantly but not reproducibly lower resistivities than those with the mold held horizontally. Optical inspection of the translucent gumstocks showed that in the vertically cured specimens the fibrils had a pronounced tendency to cluster, ostensibly as a result of floating downward prior to binder gelation and collecting against obstacles. In the horizontally molded samples, the fibrils appeared randomly dispersed in both directions. Resistivity results obtained in vertically cured specimens are omitted from the present report.

All specimens with fibril concentrations in excess of 0.25 wt %, i.e., those in which the fibrils significantly reduce resistivities, show rapid small resistivity fluctuations about the means plotted, e.g., in Figure 2; this observation also extends to the filled model HTPB propellants.

Measurement results for the HTPB composites are shown in Figure 3(a) (volume resistivity) and Figure 3(b) (surface resistivity). As in the HTPB gumstocks, no significant long-term time dependence of either resistivity is observed in any sample. Addition of 70 wt % solid filler, one-third of which is electrically highly conductive, reduces volume resistivity by two orders of magnitude. Addition of fibrils in the amount of 0.5% based on total specimen weight (hence, 1.5% of binder weight) results in a further reduction of over five orders of magnitude,

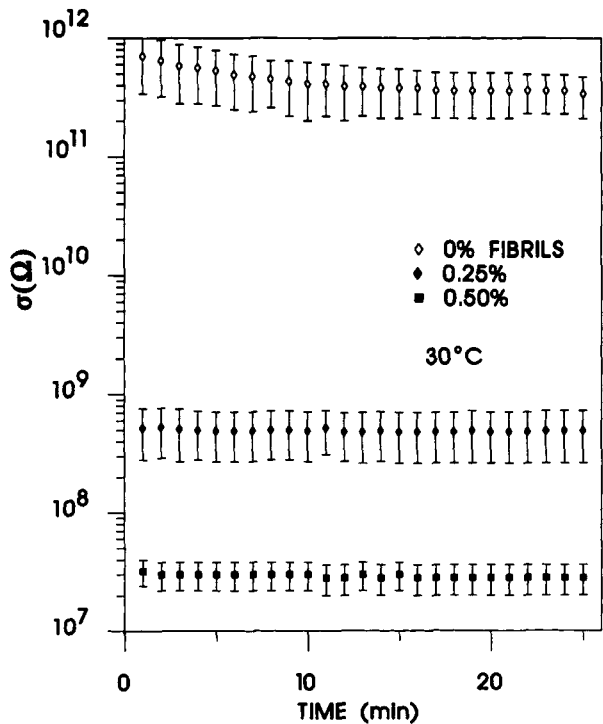
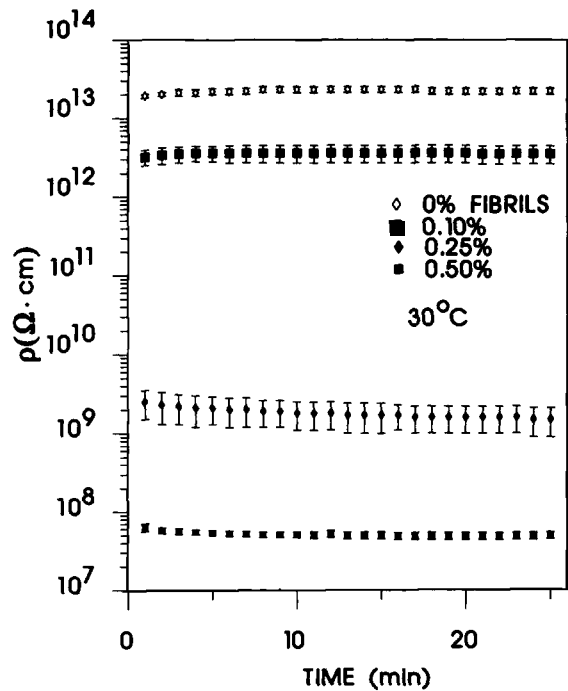


**Figure 2** Volume resistivity at 30°C in HTPB gumstock (open diamonds) without fibrils and (solid symbols) containing fibrils at (diamonds) 0.25 wt %, (squares) 0.50 wt %, and (triangles) 0.75 wt %, as function of time.

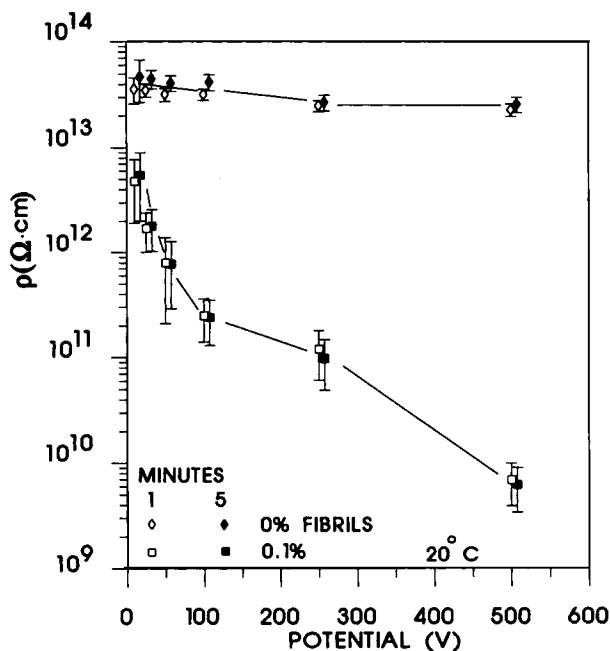
but considerably reduces processability by greatly increasing the viscosity of the precure batch. However, even 0.1 wt % fibrils (i.e., 0.3 wt % of binder), having only a modest effect on batch viscosity, provides a useful conductivity improvement at 10 V. Again, the surface resistivities tell a similar, related, story.

Electrostatic discharge events in solid propellants tend to arise from buildup of potential differences greatly in excess of the 10 V used for the results shown so far. Previous experience<sup>18</sup> showed that resistivities in these materials are somewhat field-dependent. It was therefore of interest to determine whether the addition fibrils would maintain or perhaps enhance the moderate beneficial decrease of resistivity with increasing test potential. The results of our measurements of volume resistivity as function of test potential in composites containing 0.1 wt % fibrils are shown in Figure 4. It is seen that as test potential is increased from 10 to 500 V the monotonic resistivity drop in the base-line composites is less than a factor of two, whereas it reproducibly amounts to three orders of magnitude in three separate specimens otherwise identical except for the addition of 0.1 wt % fibrils. Dramatic decreases of resistivity with increasing field strengths

are customarily taken as evidence of the operation of a dielectric breakdown mechanism even when the changes are reversible and reproducible, as is the



**Figure 3** (a) Volume resistivity and (b) surface resistivity at 30°C in HTPB-based model propellant (open diamonds) without fibrils and (solid symbols) containing fibrils at (large squares) 0.10 wt %, (diamonds) 0.25 wt %, and (small squares) 0.50 wt %, as function of time.



**Figure 4** Volume resistivity at 20°C in HTPB model propellant (diamonds) without fibrils and (squares) containing 0.1 wt % fibrils as function of potential difference between test electrodes. Measurements were taken (open symbols) 1 min and (solid symbols) 5 min after application of the potential.

case here; below, we elaborate on an hypothesis appropriate to the present systems. Measurements in the specimens containing larger amounts of fibrils display even more pronounced decreases; the quantitative results are incomplete because resistance values at potentials exceeding 100 V invariably fall below the measurement capacity of our instrumentation. No time-dependent resistivity trends were observed at any test potential, but the rapid jitter persisted at all potentials.

## DISCUSSION

These observations suggest a coherent picture of electrical conduction in these materials along the following lines: Whereas the conductive filler particles (at least Al) and the fibrils are capable of electronic conduction, the binder (network gel, any sol, and plasticizer) must depend almost entirely on one or more ionic mechanisms<sup>19</sup> including dielectric breakdown. In our composites, neither the filler particles nor the fibrils were present in quantities sufficient to approach the percolation threshold. Conservative rough estimates for the amount of fibrils of stylized geometry needed to provide unin-

terrupted electronic conduction suggest 3–5% by volume of the binder independent of filler content; aside from being energetically unacceptable in a solid propellant, this amount would result in an entirely unprocessable formulation.

Both filler and fibrils can reduce bulk electrical resistance by shortening the equivalent dielectric gap length in the binder, both because of the decreased binder volume and the irregular geometry of the electronic conduction paths. (The same mechanisms also decrease the dielectric breakdown strength of the composite.) Because of their extreme aspect ratios, the fibrils are much more efficient per volume than are the solids in short-circuiting local binder regions. In addition, the small dimension of the fibrils subjected to potential differences produces concentrations of electric fields in their vicinity and encourages dielectric breakdown in adjacent binder regions.<sup>20</sup>

We hypothesize that most of the resistance reduction, and all of the resistance jitter, produced by fibrils in HTPB composites arise from repeated infinitesimal charge buildup–dielectric breakdown episodes in numerous separate critical binder regions of the specimens. However, the energy dissipated in these frequent minor episodes is sure to be many orders of magnitude smaller, more widely distributed, and more easily dissipated, than that in macroscopic electrical breakdown; the latter is regarded in the solid rocket industry as an alarming failure of the propellant even when it does not lead to undesired ignition. The absence of jitter in the PCP-based materials then should be a consequence of their much lower intrinsic resistivity, which makes fibrils ineffective except in amounts large enough to result in a smoother averaging over an even larger number of buildup–discharge oscillators. It should be noted that the thermal conductivity of the individual fibrils greatly exceeds that of the surrounding binder, improving the composites' ability to distribute the heat generated by the benign microscopic dielectric breakdown events; these occur where adjacent fibrils almost touch one another or nearby aluminum particles.

The slow initial resistivity decay in the PCP-based formulations is likely to arise from ionization and subsequent migration of plasticizer molecules. Ionization is thought to be produced by concentrated resistive heating near the few initially available ionic conduction paths in the binder material. As conduction consequently increases, the ohmic heating is reduced and distributed over more sites, resulting in the establishment of a reduced equilibrium ionic production rate and thus an asymptotic approach

to a lower resistivity. The presence of substantial amounts of fibrils obviates this mechanism by electronically short-circuiting binder regions otherwise subject to it. In these cases, even the greatest amount of fibrils usable here was sufficient only to accelerate the attainment of equilibrium ionization rates in critical regions, producing an immediately asymptotic resistivity without, however, greatly affecting its magnitude. But in this formulation, in the absence of fibrils, the initial resistivities were already nearly low enough for the probability of electric discharge events to approach acceptability.

## SUMMARY AND CONCLUSIONS

We studied the effect of adding small amounts of microscopic carbon fibrils on the dc electrical resistivities of two rubbery composites intended as models for solid rocket propellant, a highly plasticized high-energy formulation based on PCP and a more conventional HTPB model. We believe that this study is the first to report the use of high-aspect-ratio carbon fibrils to reduce bulk resistivity in a rubber-based composite.

In the PCP-based formulation, we find that the fibrils modify the initial decay of the resistivities without affecting the asymptotic values. The amounts required to effect a significant reduction in the asymptotic resistivity are judged to be too large to result in acceptable processability. Taken together with the only marginal requirement for resistivity reduction in this formulation, we conclude that a further search for improvement along these lines is not worth the effort.

In the HTPB formulations, with their intrinsically higher resistivities and consequent urgent need for modification, the use of miniscule amounts of fibrils resulted in substantial reduction in resistivities. Of particular interest, and benefit, was the pronounced decrease of resistivity with increasing electric potential. Here, the use of such fibrils is highly recommended since the amounts required should call for only minor modifications of the manufacturing process.

Our qualitative and quantitative observations in HTPB specimens are consistent with a picture in which the fibrils, without being able to create connected electric conduction paths, repeatedly discharge local charge buildup in the binder. These episodes are frequent in time, densely distributed in space, and very modest in their liberated and easily dissipated energy, ensuring that the net effect is overwhelmingly benign by comparison with bulk di-

electric breakdown seen in analogous propellant free of fibrils. The net effect of these episodes is to simulate an approximately steady dc resistivity as observed, displaying a rapid drop as fibril content and/or applied potential are increased. It seems clear that no theory treating the test specimen as continuous medium is capable of explaining the set of phenomena observed. The role of plasticizer and sol in the high-energy model propellant formulation is more complex than that of the gel; its contribution to bulk resistivity seems to rely on the ability of its ionized molecules to migrate slowly in response to applied electric fields.

On the basis of the present work, a detailed study of the addition of fibrils to actual conventional HTPB propellants as a means of preventing electric discharge dangers may be confidently recommended. A detailed investigation of the effect of fibrils on the molecular motions of the binder network and sol in these materials is currently in progress in our laboratories, using NMR-based diffusion and conventional solids NMR techniques.

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