FIBER REINFORCEMENT OF GUN PROPELLANTS

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ABSTRACT

The basis for this paper is the hypothesis that explosive reactions of gun propellent charges subjected to gross damage from attack by shaped charge (SC) or kinetic energy (KE) rounds are the result of catastrophic grain failures; i.e., that as a result of this type of event, the reactive surface area is increased by many orders of magnitude. Thus, given a propellant ignition by the impact of the SC or KE round, the reaction rate will also be orders of magnitude greater than that for which the propellant was designed. To obviate this sequence of events and thus produce mild reactions to these types of stimuli, it was proposed that propellant grains be made stronger through the addition of small percentages of high strength-to-weight-ratio materials; e.g., graphite fibers. It was anticipated that these reinforcing elements would assume the stress, and because of their extremely large elastic moduli would tend to limit the strain experienced by the propellant material. This in turn would tend to limit the damage, in particular the fracturing experienced by the propellant grains, and thus limit the reaction rate. Representative fibers and propellants were selected, mixed, and tested for sensitiveness and mechanical properties. Response to standard sensitiveness tests was relatively unaffected by fiber addition; mechanical properties of a Low Vulnerability Ammunition (LOVA) propellant, CAB/RDX, were enhanced while those of a standard propellant, M-30, were degraded.

INTRODUCTION

The objective of this work was to determine the feasibility of reducing the sensitiveness of propellant charges so that if they were subjected to hypervelocity impact, they would react mildly. The particular hypervelocity impact threats under consideration were SC jets and KE projectiles. Other pertinent threats are projectile fragments and behind armor debris. Since the Army carries gun propellant into battle in

NOTE: Most figures and tables are omitted because of space and time constraints, but will be presented at the ADPA meeting, May-Jun 82.

armored vehicles, these are commonly experienced threats. Current gun propellants often react violently, exhibiting high order deflagration or, in extreme cases, detonation, when exposed to these threats.

One potential mechanism for these undesirably violent reactions, the mechanism that this research was intended to obviate or vitiate, is as follows: Explosive reactions of propellant charges subjected to gross damage from attack by SC or KE rounds are the result of catastrophic grain failures; i.e., as a result of this type of event, the reactive surface area is increased by many orders of magnitude. Since the reaction rate varies directly as the surface area, the reaction rate will also be orders of magnitude greater than that for which the propellant was designed. The purpose of this task is to obviate this mechanism and thus reduce the violence of gun propellant reactions initiated as described above.

The concept proposed for accomplishing this goal is that of enhancing the toughness of gun propellants through the addition of small amounts of high strength-to-weight-ratio materials in the form of fibers. Toughness in this context is defined as the integral of stress with respect to strain from zero to breaking strain:

$$T = \int_0^{\varepsilon_b} \sigma(\varepsilon)\,d\varepsilon \qquad (1)$$

T = Toughness

σ = Stress (Force/Area)

ε = Strain (Elongation/Length)

ε_b = Strain at Breaking Point

Figure 1 is a typical stress/strain curve, which serves to illustrate this concept.

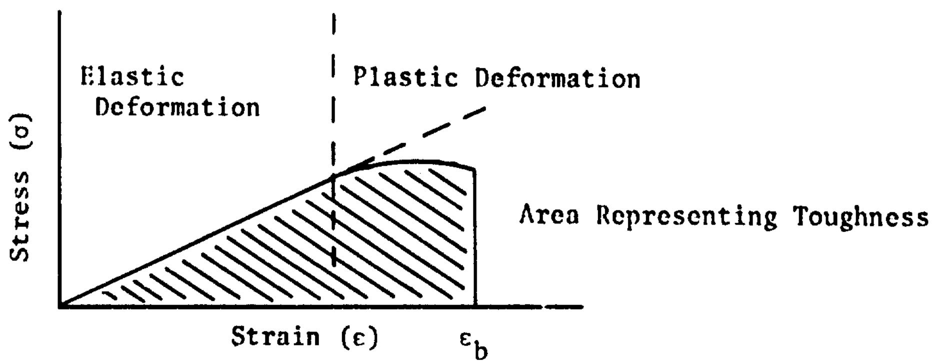

Fig. 1. Typical Stress/Strain Curve

It was anticipated that these reinforcing elements, fibers, would assume the stress since they would be intimately bonded to the matrix of propellant and since their breaking strain is an order of magnitude greater than that of the propellant. Fig. 2 is a stress/strain curve for a graphite fiber, Celanese GY-70. Previously measured physical characteristics of this fiber type include Young's Modulus (E) of $3.8 \cdot 10^7$ psi, and an ultimate tensile stress (σ) of $3 \cdot 10^5$ psi (ref. 1). The changing slope at the toe of this curve, $\epsilon \sim 10^{-3}$, was caused by the straightening of the fiber as stress was applied. The following linear portion yielded Young's modules of $3.29 \cdot 10^7$ psi, relatively near to the value referenced earlier. The ultimate tensile stress, measured at the break point, of $1.29 \cdot 10^5$ psi fell far short of the referenced value. This was because the fiber pulled out of the epoxy used to hold it in the Instron chuck. This behavior indicates a potential problem — that of providing adequate bond strength between fibers and gun propellant so that applied stress can be transferred to the imbedded fibers.

Two values are indicated on the abscissa of Fig. 2, the strains at which TNT and composition-B fail. Since fiber strain at failure is approximately one order of magnitude greater, these fibers could hold these materials together for strains considerably greater than their normal failure strain. TNT and composition-B are not the materials considered here, but were only used in a generic sense as being representative of organic, energetic materials.

Since propellant performance is likely to be slightly degraded by addition of fibers, the proportion used should be kept small. The Blake Code was used to aid in determining the fiber level to be included in the M-30 and CAB propellants. Typical theoretical data such as the graphite fiber level vs impetus for these two propellants are shown in Fig. 3. At the 2% level, there appears to be about a 40 joules/gram loss for both propellants. To be effective, the fibers should be well dispersed throughout the propellant volume. To satisfy both of these requirements, the mean fiber length should be small. The optimum fiber length depends upon the bond strength between fibers and propellant. Fiber length for a given bond strength should be such as to ensure that fiber failure (fracture) and bond failure (pull-out) occur at approximately the same strain state.

In order to assess the validity of this concept, representative fiber and propellant types were selected. Wetting studies were performed on the fibers using TNT as a generic, organic, energetic simulant. Laboratory scale hand mixes were made to assess the processibility of these blends. Small-scale mixes, 5 lb in a 2-1/4 gallon mixer, were made and tested for mechanical properties, safety, and sensitiveness. Results were analyzed and materials selected for large-scale formulation and testing. This large-scale work still remains to be done. The above described study will be discussed in detail, test results presented, comparisons made, and conclusions drawn.

PROPELLANT SELECTION

The rationale for selecting gun propellants for use in this study was as follows: For the sake of cost and time required, the number was restricted to two. It seemed desirable to use one standard propellant and one novel propellant, one that would likely be used in the near future. The propellants chosen should be designed for use in tank guns since their exposure to the threats described earlier is greater than that for other propellants.

With these concepts in mind, the standard tank gun propellant, M-30, and the LOVA candidate, CAB/RDX, were selected. M-30 is a triple-base propellant, having the formulation shown in Table 1; the formulation of the LOVA (CAB) propellant is shown in Table 2.

FIBER SELECTION

In the context of this study, a fiber is defined as a material object having a large fineness (length-to-diameter) ratio and small diameter. The Celanese GY-70 fiber has a nominal diameter of 10 μm, so a 1 mm length of this fiber has a finess ratio of 100:1, quite large for so short a fiber.

Carbon and graphite fibers are manufactured by drawing long filaments from polymerized hydrocarbons such as rayon or polyacrylonitrile. The fibers are chemically treated to stabilize their structure and then baked in an inert atmosphere. At baking temperatures below 1800°C, the fibers are characterized as carbon; above 2500°C, graphite crystal structures are formed. Carbon and graphite fibers are typically 0.004 to 0.020 millimeters in diameter and resemble extremely fine strands of black fiberglass. Because of their small diameters, the fiber filaments are packaged into tows or yarns containing several hundred to many thousand individual fiber filaments. The industrial importance of carbon and graphite fibers lies in their mechanical properties, their extremely high strength-to-weight-ratio.

There exists a plethora of fiber types with a wide variety of characteristics. A fairly complete list of those that were commercially available in 1973 is shown in Table 3. More have become available since then.

Desiderata for these fibers are as follows: They should be strong and tough, but not brittle. Their breaking strain should be greater than that for the propellant matrix. They should bond well to the matrix and be chemically compatible with it. They should also be relatively inexpensive and available.

The process of fiber selection was to compare the properties of available fibers against the list of desired properties, and to select a group that best fits the needs. Small-scale mixes with the associated mechanical properties and sensitiveness tests were used to further narrow the group, to two fiber types. Large-scale tests, yet to be performed, will be used to make the final selection.

A first step in this process was to determine wettability of fibers since wettability is related to bond strength. TNT was used as a generic, organic, energetic, simulant. Fig. 4 shows a set of seven fibers that were dipped into molten TNT, held for a couple seconds, and withdrawn. Numbers under the tows correspond to those in the legend indicating the fiber types used. Scanning electron micrographs (SEM's) were then made of these tows at the interface between the fibers and the upper end of the frozen TNT. A representative set of SEM's is shown in Fig. 5. The photo at 50X shows the entire meniscus; that at 350X, the left side; at 380X, the right side; and at 780X, the only part of the interface that shows any wetting is displayed with great magnification. In general, this fiber type shows almost no affinity for TNT, the meniscus even appears to indicate repulsion. Also, single fibers were dipped into molten TNT, with results shown in Fig. 6. Kevlar was the fiber type used here. A periodic strcture of globules resulted. One was selected and displayed at several magnifications. Again, wetting was very poor.

A third method of assessing wettability was used: A single fiber was suspended horizontally across a microscope slide mounted on the programmable hot stage of a Nikon optical microscope. Powdered TNT was sprinkled onto the fiber. The stage was slowly heated from ambient, through the melting point of TNT, and slowly cooled, while observations were made. Figure 7 depicts the results of one such experiment. Again, Kevlar was used. The droplet shown resulted from a TNT flake melting onto the fiber and then solidifying. The droplet is shown from several perspectives to display contact angles formed between the Kevlar and TNT. In this experiment, wetting appears good.

A slight modification of this method yielded the results shown in Fig. 8. A small pile of powdered TNT was placed at one end of the single fiber suspended on the microscope hot stage as described above. The temperature was cycled as before and behavior observed. As the TNT melted, the meniscus was seen to form; surface tension drew the TNT far up the fiber, blending asymptotically with it. Wetting was very good. The fiber type here was Celanese GY-70, a high modulus graphite fiber.

Fibers were selected to cover a wide range of properties and materials (Table 4).

TABLE 4

Candidate Fibers

Fibers	Length	Comment
3004-S	<1 mm	Heat cleaned glass
612-A4	$\gtrsim$1 mm	Producer's finish, glass
Kevlar	1.5 mm	Aromatic polyamide, DuPont Kevlar 29 Pulp Type 1979
Kynol	∿.9 mm	Cross linked amorphous phenolic polymer, Harbison-carborundum
Nylon Flock	∿1 mm	Claremont grade 572, natural color
GY-70	∿1.5 mm 10 mm*	Lab chopped graphite fiber, Celanese

*10 mm for pilot plant mixes

The selection spans from high modulus, brittle graphite down to low strength nylon flock. Typical examples are shown in Figs. 9 and 10.

PRELIMINARY HAND MIXES

Hand mixes were made at the Ballistic Research Laboratory (BRL) by incorporating fibers into previously cured gun propellants with the aid of solvents. This was done to provide preliminary data on dispersion and integrity of fibers during mixing as well as to obtain some safety properties. Since the fiber containing mixes were examined optically, the standard M-30 gun propellant presented some problems. In the processing of M-30, usually a graphite glaze is applied to the surface of the propellant, which opacifies the propellant during the redissolving step. In all future M-30 mixes, the graphite glaze will be eliminated to facilitate ease of optical examination of the modified propellants. Most of the hand mixes therefore were made utilizing CAB standard propellant. All fibers dispersed fairly well, considering that they were hand mixed. Most fibers, with the exception of GY-70, showed no dimensional change from mixing. GY-70 did break down to about .3 mm long.

Drop weight impact tests all were in excess of 500 mm, which is considered low sensitivity. Because of the limited capability to make gun propellant at BRL at this time, all of the propellant preparation beyond the preliminary hand mixes, and most of the testing were carried out by the Navy at NOS, Indian Head.

SMALL-SCALE MIXES

All of the small-scale mixes were mixed in a 2-1/2 gallon Baker-Perkins horizontal mixer. Five pounds of each composition (Tables 1 and 2) were prepared.

Mandatory hand mixes

Prior to making any propellant formulations in the pilot plant at Indian Head, it was mandatory from safety that small laboratory mixes be made with all of the same lots of raw materials that were to be used in the pilot plant compositions. Laboratory formulated propellants were prepared and samples were tested on the Differential Thermal Analyzer (DTA). The data, Table 5 for modified M-30 propellants, have a significantly lower peak exotherm ($\sim 188^{o}C$) compared to modified CAB propellants ($\sim 250^{o}C$), which would be expected based on the ingredients in each composition. However, within a given composition the exotherms vary very little, showing that the addition of any fiber to an M-30 or a CAB composition does not lower the modified propellant's exotherm. M-30 compositions had exotherms that ranged from $186^{o}C$ to $193^{o}C$, with the exotherm of the control propellant being $188^{o}C$. The CAB propellants' exotherms ranged from $240^{o}C$ to $250^{o}C$.

Cab (LOVA) procedure

All CAB pilot plant mixes were mixed at 120°F, with blowdown at 70°F. The propellant was removed from the mixer to the extruding operation area. The M-30 propellant mixes were started at 90°F and raised to 120°F; after blowdown the propellant take off temperature was 70°F.

TABLE 5

DTA Data of M-30 and LOVA Propellants

	Exotherm Peak °C	
Sample Identity	M-30	LOVA
Control	188	250
Kynol	188	242
Kevlar	187	247
GY-70	193	250
Nylon	186	240
3004-S	187	249
612-A4	186	250

Extrusion

All propellants were blocked under vacuum twice in the extruder, extruded through a 16 mesh screen at nominal 700 psig. Then the screened material was blocked again twice, and finally extruded as 7 perf gun propellant. The CAB propellants were extruded at a nominal starting pressure of 2000 psig and ambient temperature; the M-30 propellants were extruded at a nominal starting pressure of 1300 psig. The gun propellant was cut into pellets after a suitable drying time. The cut pellets are usually dried 1 day at ambient and 2 days at 140°F. Kevlar-containing pellets tended to have elliptical perfs if the cutting tool was not extremely sharp.

Examination of finished grains

At BRL, samples of all mixes were examined optically, after being cut parallel to the perfs. The fibers were evenly dispersed, and oriententcd parallel to the perfs. Only GY-70 and Kynol fibers broke up during processing of the propellant composition. GY-70, for example, initially was hand cut to 10 mm long. Kynol, as received, was a 0.9 mm long fiber. After processing the compositions through to the finished pellets, the GY-70 fibers were 0.3 mm long and the Kynol were 0.6 mm long. This was determined by dissolving the propellant, filtering and measuring the fibers. Weight -% of fibers in the propellants was also confirmed to be at the 2% level. Fig. 11 is a typical example of what was observed. Table 6 shows these results.

TABLE 6

Particle Sizes of Fibers

	Before Mix	After Mix
GY-70	10 mm	0.3 mm
Nylon Flock	0.9 mm	0.9 mm
612-A4	0.6 mm	0.6 mm
3004-S	0.5 mm	0.5 mm
Kevlar	1.5 mm	1.5 mm
Kynol	0.9 mm	0.6 mm

TESTS

Safety

Results of the safety tests done at NOS, Indian Head (Table 7) were as expected. The addition of fibers to M-30 or CAB gun propellants did not increase their sensitivity to impact, friction or electrostatic discharge compared to the control propellants, those without fibers. It can be noted that M-30 had a medium sensitivity to the drop weight impact test while CAB propellant exhibitied a low sensitivity.

Density

The densities obtained with the modified CAB propellants had a considerable scatter beyond that attributed to the fibers being incorporated into the propellant. Densities ranged from 1.55 g/cc to 1.645 g/cc. The modified M-30 propellants exhibited a much narrower density range, 1.626 g/cc to 1.658 g/cc.

Dimensional stability

Ten pellets were randomly selected from each mix. Their dimensions were measured, averaged, and listed in Table 8 A for CAB and in Table 9 A for M-30. Both propellants were considered to show excessive scatter in physical dimensions.

Parameters such as density and physical dimensions (outer/inner web distance, for example) must be included in with the closed bomb data to have any meaningful results. These data are in the process of being reduced.

Burn rates

The burning rates were obtained on the closed bomb at 5000 psig increments from 5 to 30 thousand psig. Tables 8 B and 9 B show the results. The fibers appear to have little effect, on the burn rate, as was expected.

Drop weight mechanical properties tests

This is a method by which the mechanical properties of a material can be evaluated under high strain rate, compressive loading. The device consists of a standard drop weight tester, normally used for impact sensitivity measurements, that has been modified by placing a force gauge and an assembly that transmits the impact force from the falling weight cage to the sample, in place of the standard anvil. Fig. 12 is a schematic diagram of this device. Results of this test are in the form of stress and strain vs time, and visual observation of damage. A typical set of stress/strain curves is shown in Fig. 13, and post-test photos of fiber-containing grains in Fig. 14.

The maximum stress before failure was measured and the relative amount of damage was noted. M-30 is stronger than CAB/RDX and required a drop height (DH) of 20 cm and a drop weight (DW) of 2 kg for fracture. CAB/RDX required a DH of 11 cm and DW of 1 kg. The results are shown in Table 10.

TABLE 10

Drop Weight Mechanical Properties Test Results

Lot No.	Fiber	Maximum Stress (MPa)	Relative Damage
CAB/ATEC DH = 11 cm, DW = 1 kg			
1072	Kynol	33.6	0
1073	GY-70	37.1	-
1077	Control	33.3	0
1078	Nylon Flock	34.8	0
1079	Kevlar	39.7	-
1080	3004-S	33.1	0
1081	612-A4	37.9	-
M-30 DH = 20 cm, DW = 2 kg			
1170	Control	105	0
1171	Nylon Flock	95.4	0
1172	Kevlar	89.8	0
1173	3004-S	91.6	0
1174	612-A4	106	+
1175	GY-70	103	+
1176	Kynol	93.3	+

Legend: 0 = Damage Level for Control Samples
- = Less Damages Control
+ = More Damage than Control

M-30 lots with fibers all showed more damage than the control lot. For some grains the damage difference was only slight, but the stress before failure in these cases was markedly lower. This indicates that the grains became more brittle upon the addition of the fibers, a condition that will cause more fracture upon failure. In the case of CAB/ATEC, the amount of damage done was either about the same or a little less than for the control lot. For some lots the average stress before failure was higher than for the control lot, but the scatter in the indiviual results reduces the significance of the higher average. The smaller amount of fracture indicates that some fibers may increase the strength of the grain on the order of 10%.

The main problem with fiber-containing M-30 propellant appears to be with the fiber/propellant bond; this is very weak. Instead of strengthening the propellant, the fibers weakened it, likely by forming void-like inclusions in the material. The proper choice of bonding agent may cause a great improvement in response to this test. Apparently, bonding between fibers and CAB is much better, since these tests exhibit improvement in mechanical properties.

Compression test data

This series of tests was performed on an Instron mechanical properties tester. The principal difference between these tests and those previously described, the Drop Weight Mechanical Properties Tests (DWMPT), is the strain rate used. For the DWMPT, the interval over which stress is applied is a few milliseconds, whereas for Instron tests, this interval is on the order of 1 minute. Data were taken for two temperatures, 20°F and 77°F, for both propellant types, with the control and the six fiber types. The data are shown in Table 11. High compressibility and large compressive force at yield are desired. Fibers did not improve the compressive force at yield for M-30; neither was there significant degradation except for nylon flock and Kevlar, for which there was about 20% degradation. Nylon flock improved the compressibility of M-30 by a small amount. Results were better for fiber addition to CAB/RDX. In almost all cases the compressive force at yield exceeded that for the control, by approximately 12% for nylon flock and Kevlar. Compressibility was also improved by two fiber types, both of glass, 3004-S and 612-A4, but only by about 4%. Unfortunately, the fiber type causing the greatest improvement in the one parameter was not the one causing the most improvement in the other parameter. However, glass fiber type 612-A4 caused a 3.7 improvement in compressibility and 6.2% improvement in compressive force at yield.

SUMMARY

The objectives of this work were to attempt to reduce the sensitiveness of gun propellants to attack by shaped charge jets and long rod penetrators, as well as to all other forms of impact. The approach was to strengthen the propellant so that impact would produce less cracking and fragmentation than in the unmodified state and thus result in a lower reaction rate. All combinations of two propellants and six fibers were made and tested in various ways. Fiber addition had little effect on any of the properties of M-30 propellant except for mechanical properties: compressive force at yield was reduced by ca 20% for two fiber types. Fiber addition to CAB/RDX resulted in some improvement in mechanical properties for several fiber types.

Sensitiveness was not tested except to insure compatibility of fibers with propellant, and safety in processing. These tests included drop weight impact, friction, and electrostatic discharge. Again, no significant changes were noted for the modified as compared with the unmodified propellants. The test which might have shown some effect, the drop weight impact test, was ineffective because the sample grains had to be powdered for this test while the whole purpose of adding fibers was to prevent fracturing of the grains.

The tests discussed earlier were intended as screening tests, to indicate research directions for further and larger scale testing. These indications are that there is some merit to the concept, but that further small-scale research is required before proceeding to larger scale testing. Wetting and bonding agents could be used to improve the fiber/propellant interface bond strength. This then should improve the mechanical properties of the propellant grains. If this work is continued, the shotgun test will be applied to the enhanced materials, as a final screening test. In this test, grains are impacted on a solid obstacle at various speeds. Resulting fragments are then ignited in a closed bomb, and the maximum rate of change of pressure ($\dot{P}max$) recorded. $\dot{P}max$ vs impact speed is plotted and compared with that for the control materials. This test should provide a very sensitive discriminant for fiber desensitization of propellants to impact because it so closely parallels the tactical situation being addressed. Candidates which respond favorably to the shotgun test would then be subjected to shaped charge jets and possibly to fragment and long rod penetrator attack.

REFERENCES

1 R. Lieb, et al, "Impact Mechanical Properties Tester for Gun Propellants," 1981 JANNAF Structures and Mechanical Behavior Subcommittee Meeting, Vol. 1, pp 155-162.