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POLYMER DISPERSION BASED SHEAR THICKENING FLUID-FABRICS FOR PROTECTIVE APPLICATIONS

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ABSTRACT

Previous studies have shown that impregnating a shear thickening fluid (STF) composed of hard, submicron silica particles into fabrics such as Kevlar® can improve their puncture and low velocity ballistic performance. A portion of this improvement is due to restricted mobility of the yarns in the woven fabric architecture. Microscopy of these fabrics after testing have shown pitting and damage to the Kevlar filaments caused by the hard silica particles used in the STF. In the present study, we investigate a shear-thickening fluid made from PMMA particles that are softer than both the previous colloidal particles and the Kevlar filaments. Monodisperse PMMA spheres were synthesized, purified, and transferred into polyethylene glycol to form an STF. Particle softness is evident in a post transitional shear thinning in the STF. The STF was successfully intercalated into Kevlar fabric. Quasi-static spike testing and single layer V_{50} ballistic testing of these STF-fabrics was performed. Interestingly, this composite shows improved performance compared to neat Kevlar under quasi-static spike testing, but exhibits significantly less improvement under low velocity ballistic testing. Microscopy shows little evidence of fiber pitting or significant filament damage, but indicates that the spherical PMMA particles are deformed significantly during loading. The results demonstrate the role of particle hardness in STF-fabric performance.

KEY WORDS: Armor Technology, Materials - Fabric/Textile Reinforcement

1. INTRODUCTION

Shear thickening fluids (STFs) have been used to improve the performance of woven fabrics for protective applications in ballistics and stab [1-5]. Previous work has shown that silica-based STFs (S-STFs) can impart dramatic improvements to the protective properties of Kevlar® fabric, but that the particles abrade the fibers in the damage zone. It is possible that this particle-fiber abrasion is an enabling mechanism for stress transfer between the STF and the fabric, such that particle hardness will have a measurable effect on the performance of STF-fabrics. In this work, we replace the hard silica particles used in previous STFs with PMMA (poly methyl methacrylate) particles that are less hard than the aramid Kevlar fibers. These PMMA-based

STFs (PMMA-STFs) are rheologically characterized, and then intercalated into Kevlar fabrics for puncture and ballistic testing.

2. EXPERIMENTAL METHODS

2.1 Materials Shear thickening fluids used in this study consisted of relatively monodisperse PMMA particles in polyethylene glycol 200 M_w polyethylene glycol (PEG, ρ=1.12 g/cm^3, η=0.049 Pa·s). The PMMA particles were produced via the methanol-water synthesis of Shim et al., in a batch of 1 L total reaction volume at a reaction temperature of 70°C for 3 hours[6]. This reaction mixture was dialyzed against water for 3 exchanges of at least 24 hours each to remove unreacted monomer, methanol and other impurities. Transfer from water to PEG was done by centrifuging the particles into a cake, re-dispersing them with about 1 mL of supernatant for every 4 mL of particle cake, then adding the appropriate amount of PEG and evaporating the water in a vacuum oven at 50°C. Vacuum was broken and the samples were stirred about every 2 hours; the samples were in the vacuum oven for about 24 hours. The desired volume fractions were verified by solution densitometry of diluted STF samples.

The STF-fabric composite (PMMA-STF-Kevlar) was produced using the PMMA in water after dialysis. This mixture was concentrated to 20.7%wt solids by centrifugation, and then an appropriate amount of PEG was added to give a final product of 52%wt or 50% by volume PMMA in PEG, once other solvents were removed. An additional small amount of ethanol was used as a co-solvent to bring the mixture to 3:1 by volume, solvent:STF (or water+ethanol:PMMA+PEG). This mixture was intercalated into 38.1 cm × 38.1 cm panels of Kevlar fabric by spreading the mixture over the fabric and allowing it to soak for 30 seconds, then squeezing the excess fluid out with a steel roller. The fabric was allowed to air dry for 45 minutes before being placed in an oven at 60°C for 30 minutes. The final fabric was dry to the touch and the STF loading on the fabric was 14.1±1% addition by weight. It is important to note that the silica-based STF-Kevlar samples that are compared to this sample in quasi-static spike and ballistic experiments are 20% addition by weight. For all STF-fabric samples, Hexcel Reinforcements (Anderson, SC) scoured Style 706 fabric was used, consisting of 600 denier KM-2 Kevlar yarns in a plain woven construction of 34 × 34 yarns per inch.

Due to the limited yield of the batch reaction, the PMMA particles impregnated into Kevlar were produced in a different reaction batch from the particles used to produce the STF sample for rheological study. The differences between the two samples (particle size, polydispersity) were minimal and both samples were observed to shear thicken by hand stirring and minimal rheological testing. The final PMMA particles produced had a density of 1.20 g/mL, determined by solution densitometry. The size determined from SEM micrographs was 1050±50 nm; an example micrograph is seen in Figure 1.

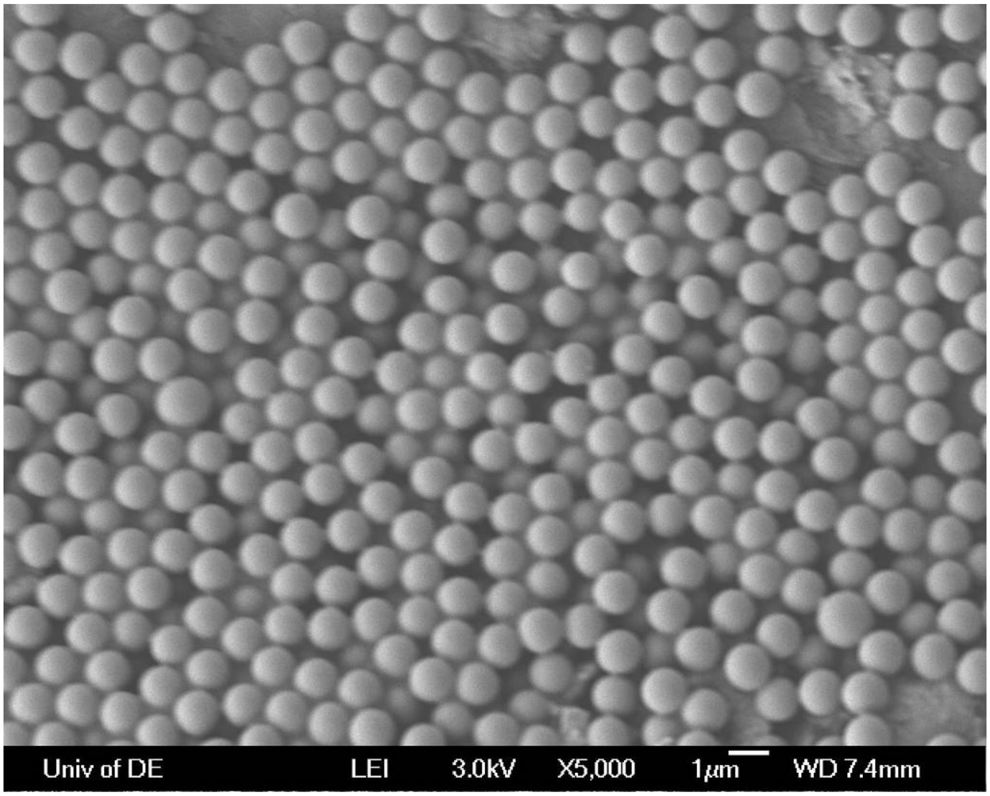


Figure 1: SEM micrograph of PMMA particles.

2.2 Rheometry The shear rheology was measured on a TA Instruments AR-G2 stress-controlled rheometer, with a 40 mm 4° aluminum cone and Peltier plate at 25°C. The samples were pre-sheared to break down any structure from loading by shearing at a constant stress of at least 0.1 Pa for 1 minute. Higher concentration samples required higher initial shear stresses to begin flowing, with samples pre-sheared at up to 1000Pa to break the yielding behavior and begin flow. After initial flow was established, a continuous ramp was done from 0.1 Pa to 1000 Pa for 3 minutes. Then steady-state stress sweeps from 0.1 Pa to at least 1000 Pa were performed, requiring three 10 second measurements within 5% to reach steady state. Higher maximum stresses, up to 1500 Pa, were investigated in the higher concentration samples. Rheometric slip was checked by the use of disposable 20 mm parallel plates that had been sandblasted to provide a roughened surface, at a gap of 1 mm.

2.3 Quasi-static Stab Test An Instron Model 4201 load frame, equipped with a 1 kN load cell, was used to perform the quasi-static stab tests. Tests were performed by mounting a penetrator into the crosshead of the load frame, and then displacing the penetrator into a fabric target (4 layers) at the rate of 5 mm/min. The targets were backed by a multi-layer foam backing, based on the National Institute of Justice (NIJ) standard 0115.0. This backing consists of four layers of 5 mm-thick neoprene sponge, followed by one layer of 31mm-thick polyethylene foam, seen in Figure 2 along with the NIJ spike and knife threats typically used. All quasi-static testing was conducted on four-layer targets using a standard NIJ spike as the threat. Load versus displacement is recorded for each target and penetrator; higher loads indicate higher resistance to penetration.

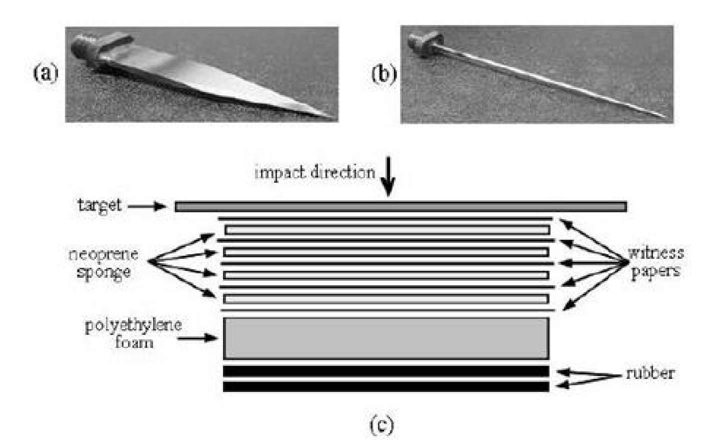


Figure 2: (a) NIJ knife impactor, (b) NIJ spike impactor, (c) foam backing used in the quasi-static stab tests.

2.4 V_{50} Ballistic Test Ballistics testing on the STF Kevlar composites was conducted using a smooth-bore, helium pressurized gas gun. Spherical steel projectiles of 0.22 caliber (5.59 mm diameter) and ~ 0.62 g were used. Two parallel, light-triggered chronographs were used to measure time-of-flight for calculation of impact velocities.

Single layer, 5.1 cm × 19.1 cm fabric samples were prepared and stapled to wooden blocks. These blocks were then lightly tensioned and mounted on a wooden frame (Figure 3). Behind the target was a polyethylene bag that acted as a witness. Each target was impacted one time, at the center of the target. The impact velocity was varied to induce a mixture of partial and complete penetrations. Complete penetrations are defined as impacts that cause the projectile to fall into the witness bag, or penetrate through the witness bag. All other impacts are considered partial penetrations. The V_{50} velocity of a fabric is the velocity at which the projectile has a 50% chance of penetrating through the target. For the neat Kevlar and the S-STF-706, the V_{50} was calculated by taking the five highest velocity partials and five lowest velocity completes (N=10) and averaging these ten velocities; due to a smaller number of samples, only the three highest partials and three lowest completes (N=6) were used for the PMMA-STF-706 V_{50} calculation.

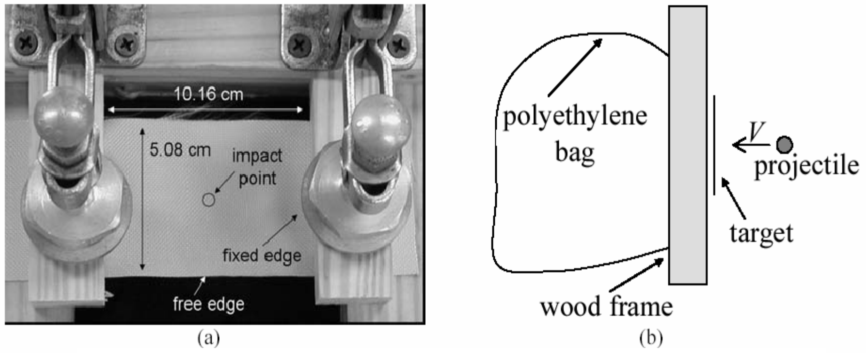


Figure 3: Photograph and schematic diagram of helium gun target.

3. RESULTS AND DISCUSSION

2.1 Rheology The steady-state rheology of the PMMA-STF was tested at multiple volume fractions corresponding to ϕ=0.40, 0.45, 0.48, and 0.49. The first backward steady state sweep following the pre-shear is shown in Figure 4 (this data was taken at progressively decreasing stresses). Due to the yielding behavior of these samples, the behavior at low shear was not accurately evaluated in the forward sweeps, flow did not occur until stresses above the yield stress. There is a nontrivial dependence of the low shear viscosity on volume fraction observed in this figure that is thought to be a consequence of structure reformation that is beyond the scope of this work.

Of interest here is the post shear thickening behavior of these PMMA-STFs, where a clear shear thinning is observed at the highest shear rates. This is in contrast to the S-STFs that exhibit a discontinuous rise in viscosity at a limiting shear rate [5]. To explore this further, Figure 5 compares the shear rheology of the sample at ϕ=0.48 where roughened (sandblasted) parallel plates were used to eliminate wall slip. The second shear-thinning regime at high shear stresses is also observed a comparable shear rates (note that the parallel plate geometry has a distribution of shear rates in contrast to cone and plate geometry), indicating that the behavior is real and not an artifact of wall slip.

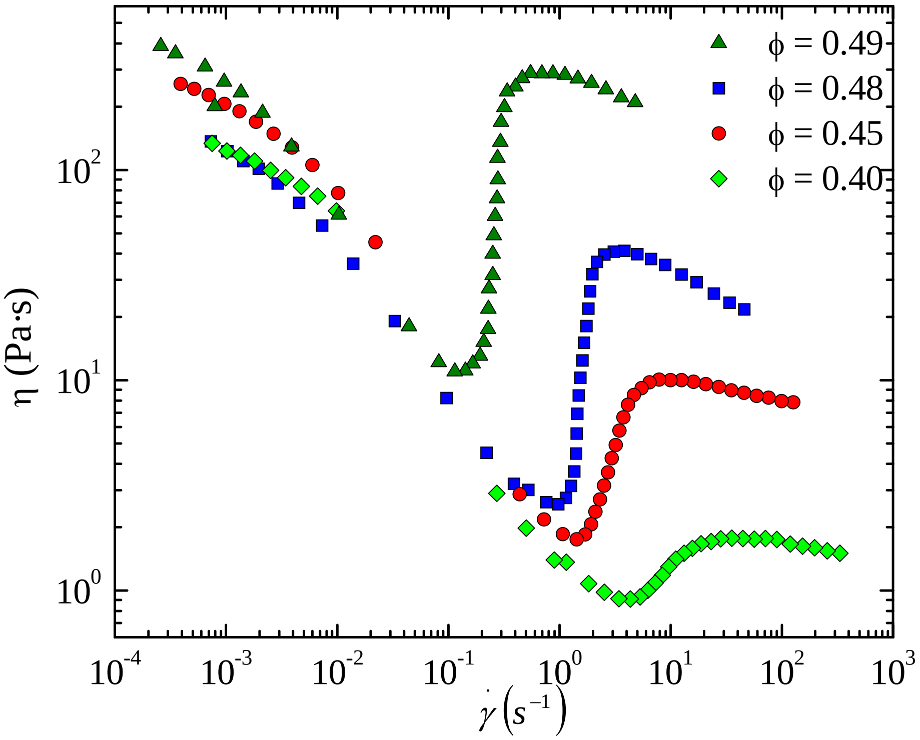


Figure 4: Steady-state rheology data of PMMA-PEG STF at multiple volume fractions. Shown is the first backward steady-state sweep (points taken at decreasing stress).

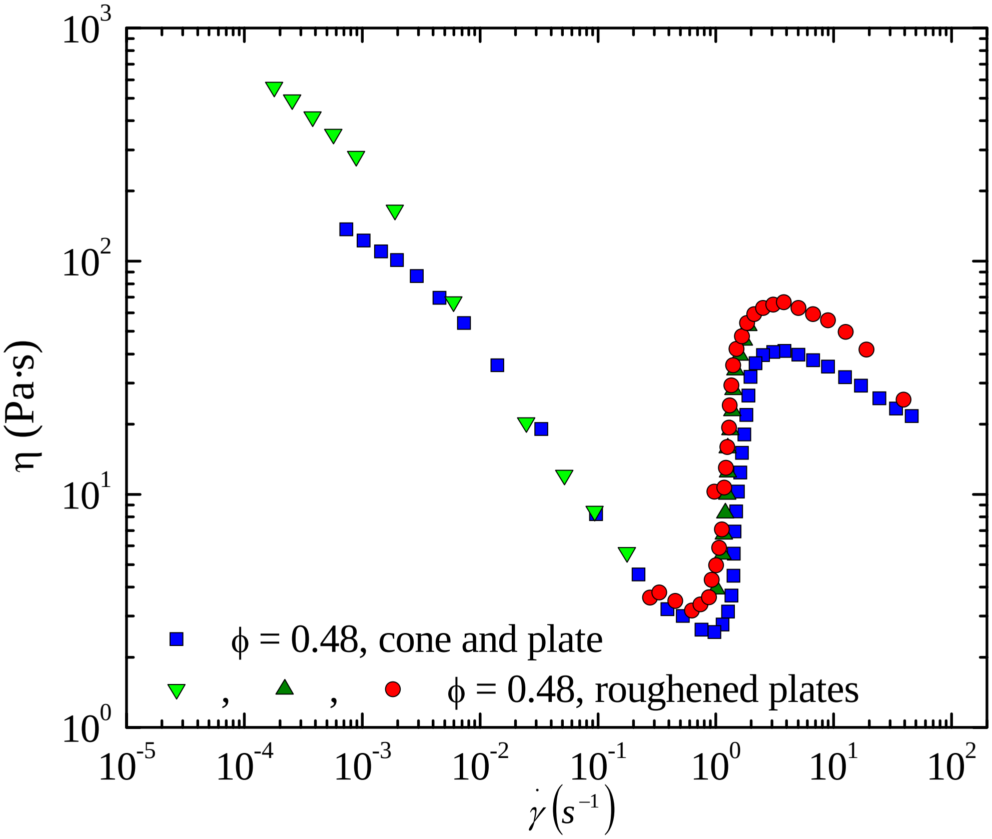


Figure 5: Comparison of roughened parallel plate results with cone and plate results for PMMA-STF at ϕ=0.48 to test for wall slip.

2.2 Quasi-static Spike Performance Load versus displacement data for the quasi-static spike testing of the PMMA-STF-Kevlar can be seen in Figure 6, in comparison to the neat Kevlar, NIJ backing, and S-STF-Kevlar. The PMMA-STF imparts a significant improvement over the neat Kevlar, comparable to the S-STF. The load increases to about 150 N at a maximum displacement of 20 mm for both samples, although the S-STF Kevlar supports a larger load at all displacements. This difference is probably due to the increased loading of the STF in the S-STF samples, but may also be due to the differences in the ultimate particle strength.

Figure 7 shows SEM micrographs of the S-STF-Kevlar and PMMA-STF-Kevlar fabrics in the damage zone after quasi-static testing. Particle “tracking” of the Kevlar is evident in the S-STF but not in the PMMA-STF. The hardness of the aramid fibers lies between that of the PMMA and the silica. Notice that there is little evidence of particle damage. Further, both composites have good efficacy in resisting spike penetration, as shown in Figure 6.

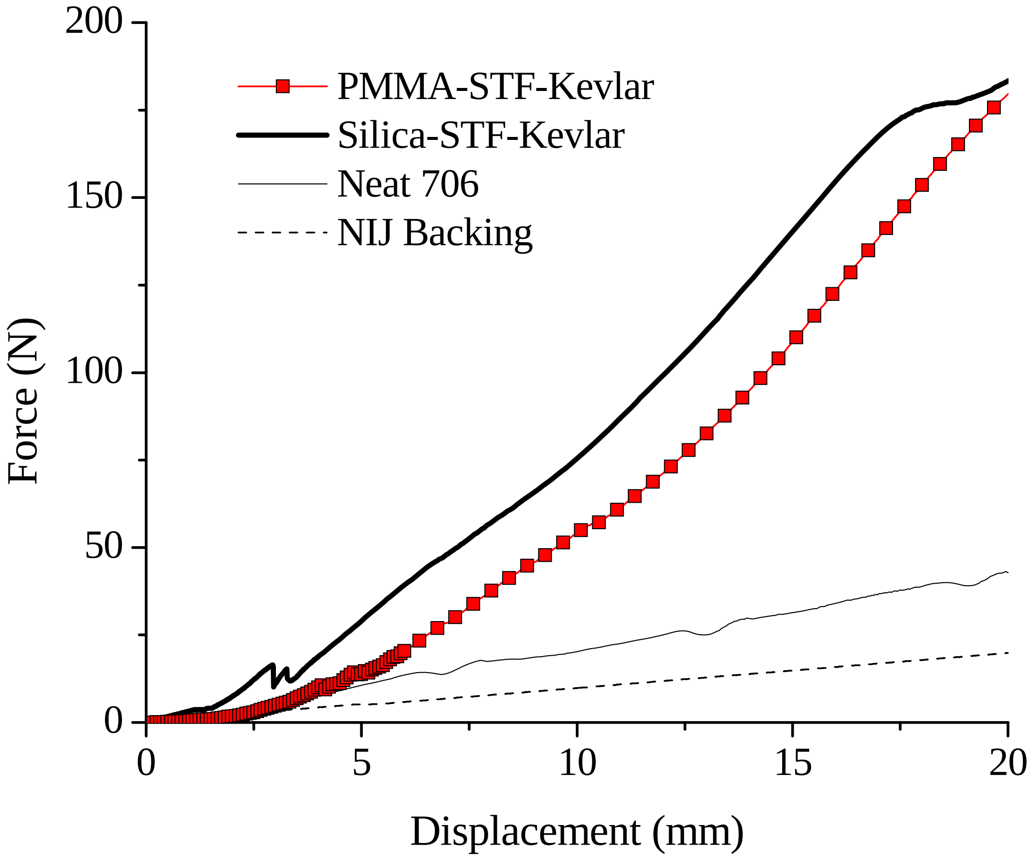
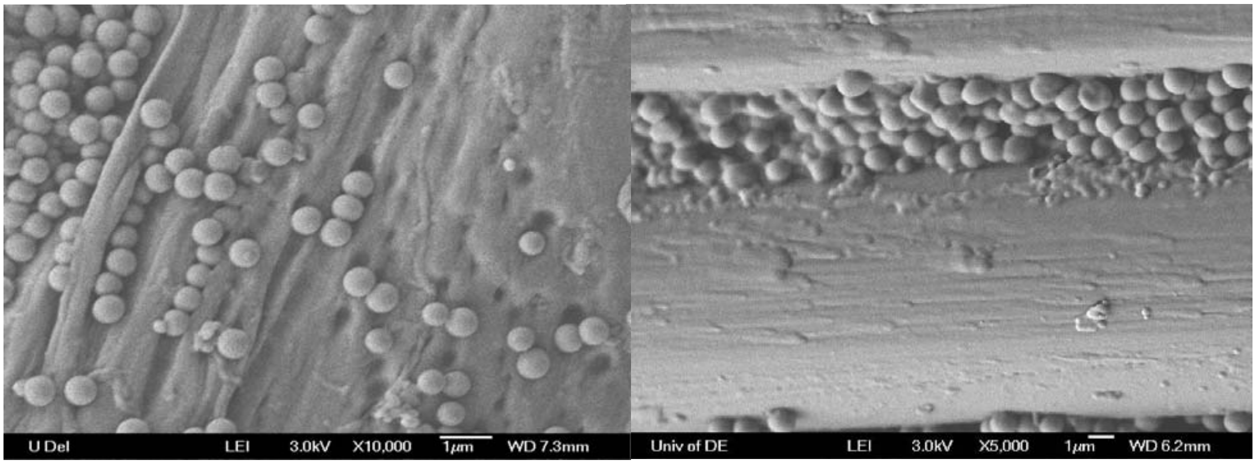


Figure 6: Quasi-static spike data of 4-layer fabric targets on NIJ backing.



(a) **(b)**

Figure 7: SEM micrographs of STF-Kevlar after QS spike testing: (a) S-STF-Kevlar. (b) PMMA-STF-Kevlar.

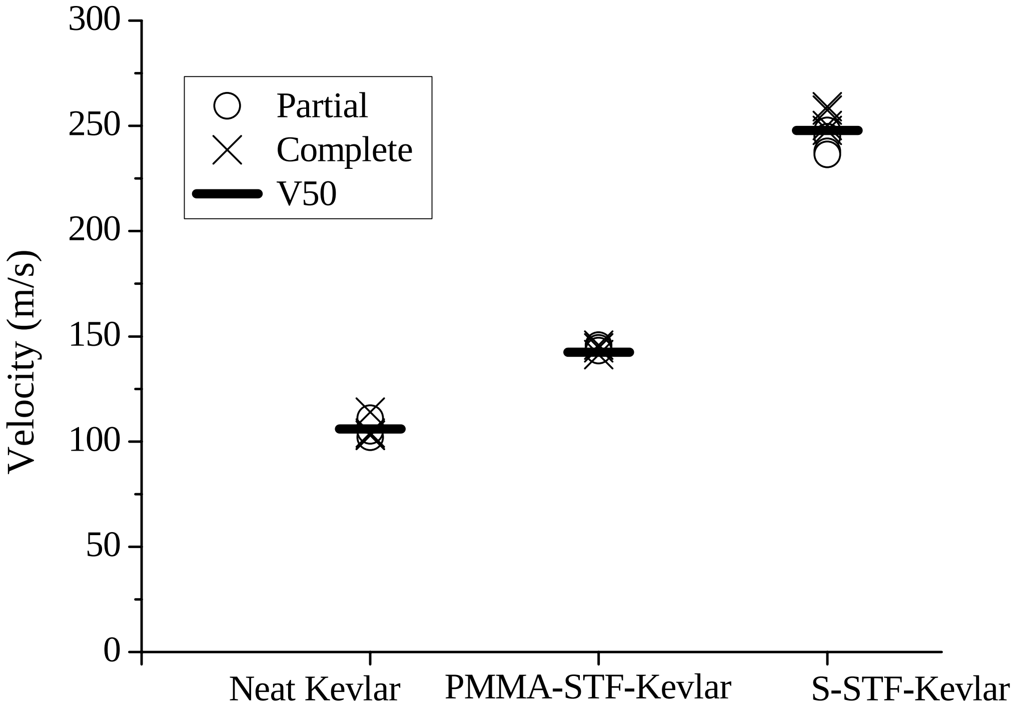


Figure 8: Single-layer ballistic V_{50} results of fabric samples. The neat Kevlar and S-STF-Kevlar are 10-shot V_{50}, while the PMMA-STF-Kevlar is a 6-shot V_{50}.

2.3 V_{50} Ballistic Performance The ballistic performance of the PMMA-STF Kevlar is compared to the neat Kevlar and S-STF-Kevlar in Figure 8. The V_{50} for PMMA-STF-Kevlar at a loading of 14.1% STF was 145 3m/s; this should be compared to neat Kevlar at 106.0 m/s and S-STF-Kevlar, with a loading of 20% STF, at 248 m/s. The difference between the PMMA-STF and S-STF can only be partly attributed to the lower mass loading of the PMMA-STF as previous work shows the S-STF having a V_{50} of 223 4m/s at a loading of only 8%[1]. Thus, the PMMA-STF-Kevlar fabric has lower efficacy than the S-STF in providing ballistic resistance in this test.

The difference in ballistic penetration resistance between the silica and PMMA STFs could be due to a number of factors. One possibility is that the hardness of the silica particles enables them to abrade the Kevlar filaments, providing mechanical interlocking for STF-fiber and fiber-fiber load transfer. Another hypothesis is that the difference in ballistic penetration resistance is associated with the rheological properties of the STF phase. The PMMA-STF shows a less extreme shear thickening followed by shear thinning at higher shear rates. This rheological behavior stands in contrast to the S-STF, which shows a much more significant rise in viscosity and a limiting shear rate beyond which the sample does not flow in laboratory rheological experiments. These differences in STF behavior could cause differences in STF-fabric performance, perhaps due to STF-coupled fiber-fiber and yarn-yarn interactions. Note that the rheometry shear rates are much lower than the characteristic shear rates of the ballistic tests. Further work is ongoing using split Hopkinson pressure bar (SHPB) methods to measure the rheological differences at shear rates relevant for these ballistic measurements.

4. CONCLUSIONS

The effect of particle hardness on STF-fabric performance is explored by synthesizing a model dispersion of PMMA particles, which are softer than the silica particles and the Kevlar fibers used in previous STF-fabric tests. The PMMA-STF exhibited a post-thickening behavior different from the hard, S-STF in that a second shear thinning regime was observed at high shear rates. This behavior is thought to be a manifestation of the softness of the particles under high shear stresses. The PMMA-STF was successfully intercalated into 706 Kevlar. Comparable quasi-static spike performance was observed for the PMMA-STF-Kevlar as compared to the S-STF-Kevlar given the differences in particle loading; this result shows that the PMMA-STF-Kevlar is effective against spike penetration. SEM micrographs of the damage zone showed that, unlike the S-STF, the softer PMMA particles did not abrade the Kevlar. The ballistic V_{50} results, however, showed the softer PMMA particles led to reduced performance in comparison to the harder silica dispersions. This result may indicate that particle hardness plays a more significant role in resisting the higher energy ballistic impact than the quasi-static stab penetration. This work shows the importance of particle hardness in STF-fabric performance.

5. ACKNOWLEDGEMENTS

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