Shear Thickening and Impact Resistance Properties of STG in Flexible Protection Application

Hao Zong¹, Zhipeng Liu², Rubin Wei¹, Bin Dong¹, Xingjuan Yang¹ and Wen Zhai*¹

¹ Shandong Institute of Nonmetallic Materials, Jinan 250031, China
² Army Equipment Department Equipment Bidding Center, Beijing 100072, China

Abstract. The rheological properties of shear thickening gel (STG) and its application as protective composite were studied in the paper. Upon applying a shear stress with excitation frequency from 1 Hz to 100 Hz, the storage modulus (G') of the STG increases from 10¹ Pa to 10⁵ Pa, demonstrating an excellent shear thickening effect. The reduction of temperature increases the G'min of STG, but when the temperature reaches at 50°C, the G' curve shows a moderate slope and a gradual transition to the constant plateau value. By introducing STG into polyurethane foam and kevlar fiber with dip and dry method, successfully fabricate a new safeguarding polymer composite. The protective performance of composite protective materials was studied by static compression experiment and drop hammer impact experiment. The addition of STG increases the impact resistance and puncture resistance of PU and kevlar by at least two times. The materials shows excellent shear stiffening effect, creep resisting and impact resistant properties.

1. Introduction

The research field of terrorism and international conflicts are rising all over the world. Traditional personal body armors are made of rigid materials such as metals¹ and ceramics². However, its rigidity, inflexibility, heavy and other shortcomings limit its wide application in modern times. Therefore, developing flexible and lightweight body armors is urgent, and so far a series of safeguards based on novel materials have been developed to resist attacks and absorb impact energy³⁻⁵. One of the most applied flexible materials in energy absorption was polyurethane foam (PU), which had the advantages of low density, structural robustness, high porosity, and flexibility⁶⁻⁸. Meanwhile, kevlar fiber has the characteristics of high strength and high modulus, and is also suitable for application in the field of human protection⁹⁻¹⁰.

Shear thickening (ST) is a very common physical phenomenon in many concentrated colloidal suspensions, whose viscosity could be steeply increased once the externally applied shear stress is
beyond a critical shear rate and so far much works have been reported by N. Wagner on its rheological properties and mechanisms of shear thickening fluid (STF)\textsuperscript{[11-13]}. Owing to the reversible shearing rate activated ST characteristic, STF is promising to be applied in energy adsorption and body protection to impede severe damages\textsuperscript{[14]}. For example, Wagner et al. developed a novel safeguarding composite by embedding SiO\textsubscript{2}-based STF into kevlar fabric and fragment simulation projectile ballistic penetration measurements at 244 m/s have been conducted to demonstrate the excellent ballistic penetration performance of the composite material\textsuperscript{[15]}. However, shear thickening suspensions are liquid and their unique rheological properties exist within a narrow range of concentration, they are difficult to be used in practical applications. Therefore, several groups introduced the STF into foam composites with hierarchical macro porous network structures to overcome these disadvantages. Afeshejani et al. studied the energy absorption of neat shear-thickening fluid and the flexible PU soaked in STF\textsuperscript{[16]}. Under impact conditions, the energy absorption of the STF impregnated foam scaffold increased by 85\%. Similarly, a smart structure based on commercial foam and STF has been developed and the tunable stiffness characteristics enabled it had potential application in damping\textsuperscript{[17]}. Additionally, Dawson et al. reported the dynamic compressive response of STF-based foam composite and a mechanical model was proposed\textsuperscript{[18]}. Since the shear thickening effect occurs in specific condition and the fluid can flow out easily once the STF-based foam composite is destroyed, its practical application is still limited. To this end, large numbers of attention has been paid to shear thickening gel (STG) which is a derivative of boron siloxane materials and its modulus can increase with the increasing of external shear force\textsuperscript{[19]}. Tian fabricated a novel shear-stiffened elastomer by mixing silicone rubber with silicone oil and investigated the mechanical and rheological properties under both steady-state and dynamic loading conditions\textsuperscript{[20]}. Recently, a novel multifunctional polymer composite with excellent shear stiffening performance and magneto rheological effect was reported and the shear thickening properties can be precisely controlled by external triggers\textsuperscript{[21]}. Due to the rate dependent mechanical property and plasticity, STG has potential application in safeguarding area with PU and kevlar fabric to resist shock, blast impact, and high strain rate loadings. To this end, STG composite might provide a protective pad with flexibility and high mechanical strength. In this paper, a novel plastic composite with ST functionalities was synthesized, and the effect of temperature on STG modulus was investigated. The rheological testing indicated that this hybrid polymer composite exhibits excel lent shear stiffening performance. A stretchable PU embedded shear stiffening polymer composite(STP) and a soft shear stiffening kevlar fabric(STK) was developed by “dip and dry” method. The storage modulus and stress–strain curves of this polymer composite are rate dependent, exhibiting a typical shear stiffening property. The plastic composite is flexible and presents excellent creep resistance. More importantly, this material can dissipate energy efficiently and the impact force is remarkably declined by orders of magnitude. Additionally, the higher specific strength ensures the composite can withstand consecutive dynamic impact loadings with no degradation. Due to the high performance shear-stiffening property, this smart polymer composite is promising to be applied in wearable body armor, vibration controlling, and damping.

2. Experimental
2.1. Materials
SiO$_2$ and benzoyl peroxide (BPO) were all purchased from Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. Dimethylsiloxane and boric acid were used to prepare shear stiffening polymer, and they were also provided by Sinopharm Chemical Reagent Co. Ltd., Shanghai, China. The above reagents are of analytical purity before use. The 3D-interconnected polyurethane foam with an apparent core density of 15.88kg/m$^3$ in this work is commercially available. Kevlar fabric were purchased from Japan Teijin Limited.

2.2. Preparing the polymer matrix
In the experiment, an oil bath was selected as the heating source to prepare STG. Dimethyl silicone oil and BA were weighed according to the mass ratio of 100 : 15 and poured into a beaker. Start stirring and heat up, react to 250℃ for 5 h, then stop heating, and take out the STG in the beaker after 30 min cooling after the reaction.

2.3. Fabrication of polymer composite
The polymer matrix, different contents of fillers, and BPO were homogeneously mixed by a two-roll mill at room temperature. Then, all the samples were collected in beakers and the vulcanization process was performed in ovens at about 100℃ for 1 h. In our experiment, the total contents of fillers were kept at 60%.

A “dip and dry” process is developed to fabricate the polymer composite. First, 100 g of polymer matrix were homogeneously dispersed in 400 mL of acetone solvent in a round bottomed flask by continuously stirring for 30 min. Second, the suspension was poured into beakers to sonicate for 20 min. Then, the slurry was dropped into the PU/kevlar and dried under vacuum to remove the acetone. The immersion and drying processes have been repeated for several times until the PU/kevlar tended to saturation. Finally, the composite and BPO were vulcanized in an oven at 50℃ for 2 h. The as-prepared composite were named as shear stiffening polyurethane foam (STP) and shear stiffening kevlar fabric (STK). For simplicity, STP and STK filled by STG with different mass fractions are defined as STP-X% and STK-Y%, where X and Y are the contents of STG.

3. Results and discussion

Figure 1. The FTIR spectrum of polymer matrix in the range of 4000–500 cm$^{-1}$. Figure 1 shows the FTIR spectrum of polymer matrix in the range of 4000–500 cm$^{-1}$. The absorption peak at 2970 cm$^{-1}$ is ascribed to methyl asymmetric stretching. The characteristic band of 1339 cm$^{-1}$
derives from B–O vibration. The strong absorption band at 1261 cm$^{-1}$ demonstrates the presence of the Si–CH$_3$ group. The peak at 1024 cm$^{-1}$ relates to the Si–O bond. A strong absorption band located at 889 cm$^{-1}$ and 678 cm$^{-1}$ indicates the formation of an Si–O–B bond.

![Figure 2. Modulus of STG at different shear frequencies.](image)

As can be seen from Figure 2, with the increase of shear frequency, both STG's energy storage modulus($G'$) and loss modulus($G''$) increase with the increase of shear frequency, but $G'$ increases more rapidly. $G'$ represents the material's ability to store elastic deformation energy, and represents the elastic size of the material; $G''$ represents the material's ability to dissipate deformation energy, and represents the viscosity of the material. The intersection point of $G'$ and $G''$ occurs at about 20 Hz. When the frequency is less than 20 Hz, $G' < G''$, STG is more viscous, showing the properties of a fluid. When the frequency is greater than 20 Hz, $G' > G''$, STG is more elastic, showing high elastic solid characteristics. Within the frequency test range, the $G'$ of STG was increased from 30 Pa to 0.36 MPa, which increased by four orders of magnitude. The rigidity of STG was enhanced and the shear thickening effect was obvious.

![Figure 3. Storage modulus versus shear frequency at different temperature.](image)

The temperature will also affect the mechanical properties of the SP besides shear rate. Figure 3 shows the plots of the storage modulus($G'$) versus the frequency at temperatures of -40°C, -10°C, 0°C, and 55°C. For all temperatures, the $G'$ is showing a gradual slope upwards with increasing frequencies until the constant plateau value is reached, and the $G'$ rises to a maximum.
When the temperature reaches -40°C, the shear thickening performance of the material begins to weaken, and G’ can only increase very little. This is because the molecular chain of the material has tended to be fixed under the action of low temperature, and it is difficult to slip and move, which is close to the solid. When the temperature rises to -10°C, the fixation of molecular chains slows down, and the difference between $G'_\text{min}$ and $G'_\text{max}$ is nearly 10 times. In addition, G’ tends to be stable after 10 Hz, but it is still limited to some extent. The material reaches the maximum change value of G’ at 25°C, and G’ increases by nearly three orders of magnitude.

When the temperature rises to 55°C, the increase amplitude is still relatively large, but there is also a plateau in the case of low frequency. This is because at high temperature the molecular chains of the material are not entangled and the movement is very convenient, resulting in the properties of liquid at high temperature and different curves from other cases. It can be seen that the $G'_\text{min}$ of STG increases with the decrease of temperature below room temperature, and the shear frequency when G’ reaches a stable level increases, and the value of $G'_\text{max}$ is not affected by the temperature change. This is because it is difficult to have strong entanglement force between molecular chains at high temperature, and the crosslinking bond is easy to break, so that $G'_\text{max}$ decreases. Therefore, STG can be regarded as a widely cross-linked polymer. These plots show that G’ approach asymptotes at low and high angular frequencies, respectively. And with temperature increasing, the elasticity appears to enter a plateau region at a higher shear rate.

Figure 4 shows the change of loss factor with shear frequency. The loss factor is the ratio of $G''$ and G’. The higher the ratio is, the better the viscoelasticity of the material is. Under 25°C, the loss factor decreases with the increase of shear frequency, and the initial loss modulus of 25°C is the largest, reaching 10, indicating that it has excellent viscoelasticity. At -40°C, the loss factor is less than 1 at the beginning. The frequency at which the loss factor is equal to 1 is the critical frequency of solid-liquid transition of STG. After passing the critical shear frequency, STG begins to change from quasi-liquid to quasi-solid state, and the energy absorption effect is enhanced. This indicates that at this time, STG is always in a solid-like state with poor elasticity and weak energy absorption effect. When the temperature increases to 55°C, the loss factor increases first and then decreases with the increase of shear frequency, which is consistent with Figure 3.
The above phenomenon occurs in part because the molecular chain concentration in STG is high, and they can entangle with each other. Here, the only occurring forces are friction forces between the STG chains, which act as virtual crosslinks. On the other hand, the boron mediated cross-linked chains show a network of bridges between the STG chains which are fixed by chemical bonds. However, this is a dynamic linkage. As the frequency increases, thermal motion in the molecule can break the linkage, allowing it to slide to a new position along the chain where it reattaches. A pair of chains can move past each other when the cross-linking bonds are temporarily broken. And the internal structure of the STG is broken and rebuilt. When loss factors is greater than 1, the temporary network behaves like a closely cross-linked polymer, which induces the $G'$ to be almost frequency-independent, and it is high in relation to $G''$. The network can give a stable and solid-like structure to the STG above a certain temperature. In the shear process, at the same time, more molecules are oriented in the shear direction, and the molecules gradually disentangle, which lowers their flow resistance.

**Figure 5.** Photographs of the cold flow property of STG and STP sample.
Creep behavior or cold flow property is a common phenomenon in polymer materials which is defined as polymer materials can deform slowly under the excitation of a given constant stress. This phenomenon is time dependent, and the deformation is commonly irreversible. The flow deformation of STP is so severe that they have to be sealed so as to keep a definite shape in practical application. As shown in Figures 5a-(c), the polymer matrix collapses easily and the height decreases apparently with the increase of time, exhibiting remarkable cold flow characteristic, which will severely restrict its application. Here, the PU foam can act as a skeleton and the sizes and dimensions of STG are kept constant with the increase of time. In summary, PU foam is an ideal supporting material for STP and the creep resistance and mechanical property of polymer composite are significantly enhanced.

**Figure 6.** The SEM images of STP.
Figures 6a and b show the microstructures of PU foam and STP sample, respectively. As shown in SEM images, PU foam has a three-dimensional and cellular-like porous network. The dimension of cellular-like pores is about 500–600 μm which can provide a mechanically stable sponge backbone for STG. In
Figure 6b, the sponge networks are filled with STG and little sponge skeleton can be observed in the surface. Clearly, the polymer is uniformly impregnated into the PU scaffold. It is proved that our dip and dry process is effective to prepare a mechanically robust polymer composite with homogeneous dispersion of STG in 3D PU sponge.

Figure 7. Storage modulus of STP versus shear frequency at different STG content.
Figure 7 shows the variation of STP's $G'$ with shear frequency. The more STG content in STP, the greater $G'$ is. When the STG content is less than 40%, $G'$ will not change significantly with the shear frequency and there is no shear thickening effect. However, the addition of STG increases the modulus of PU by at least one order of magnitude. When the STG amount reaches 40%, $G'$ starts to increase with the increase of shear frequency. $G'_{\text{min}}$ and $G'_{\text{max}}$ are $7.6 \times 10^4 \text{Pa}$ and $2.9 \times 10^5 \text{Pa}$, respectively, increasing by 3.81 times. When the STG content reached 50%, the shear thickening of STP became more obvious, and $G'_{\text{max}}$ increased by 76 times compared with $G'_{\text{min}}$. This indicates that in STP-30%, STG is not fully filled into PU bubble holes, and STG can only enhance part of the modulus, and the shear thickening performance is not obvious. When the STG content increases to 40%, STG can be evenly dispersed on the PU skeleton, the supporting role of PU and the shearing thickening role of STG can be fully played.

Figure 8. Surface morphology of the sample before and after puncture: (a) pure kevlar (b) STK(c) kevlar after puncture(d) STK after puncture.
The apparent morphology of pure kevlar fibers was characterized by magnifying camera. The fiber bundles are interwoven in a cross shape, but the bond was not tight, and there were gaps between the fiber bundles (Figure 8a). After impregnation with STG, the STG is evenly distributed in Kevlar and fills the void that would have existed between the fiber bundles to bind them more tightly (Figure 8b). After the knife puncture, the fiber bundles were distributed disorderly and the fibers at the fracture were loosely interwoven (Figure 8c), while the STK section was cleaner and the destruction effect of the knife on the fiber bundles was less (Figure 8d).
Figure 9. The static compression experiment curve of STK.
Figure 9 shows the relationship between displacement and load of STK in puncture experiment. It can be seen that the maximum load of the Kevlar fiber impregnated with STG is much greater than that of the pure Kevlar fiber. The more STG is impregnated, the better puncture resistance of STK will be. The STK-50% has a maximum load of 70 N, which is twice as high as pure Kevlar and 21.4% higher than the STK-20%. This indicated that the addition of STG effectively increased the puncture resistance of Kevlar fiber. At the same time, it was also found that the more STG was added, the larger the curve fluctuation amplitude of the composite obtained during puncture. Since the fiber is broken root by root when subjected to the cutting action of the cutter, the load increases with each cutting, and decreases rapidly when the fiber is just cut off. The increase in fluctuation also means that each fiber can withstand more force, which means that STG has an excellent effect on the performance of Kevlar fibers.

Figure 10. Interweave resistance curve of STK.
In order to further characterize the influence of STG on the fiber, an interweave resistance experiment was conducted (Figure 10). During the stretching process, the fiber is gradually straightened by bending, at the same time, the tensile force increases continuously until it reaches the maximum value. Finally, the filament is completely pulled out. In this process, the tension decreases with the increase of displacement.

The resistance of all STK composites is greater than that of pure fibers. The maximum strength of the sample increases with the increase of the content of shear hardened adhesive. Due to the effect of binding
force, the maximum interweaving resistance of STK-50% reaches 12 N, which is 12 times higher than that of pure kevlar fiber 1 N. This indicates that STG has a significant enhancement effect on the interweaving resistance of fibers. The maximum interweaving resistance of STK-35%/STK-20% is 10 N and 7 N, respectively, which is also significantly increased compared with pure Kevlar. Therefore, the high mass fraction of shear hardening adhesive can significantly improve the friction force of the fiber and effectively improve the protective performance of the composite.

4. Conclusion
In this work, the dynamic properties of STG in different angular frequency were tested by using a rheometer at different temperatures. once the frequency exceeds a critical value, the G' will exceed the G'' under the condition of all temperatures, and the G' shows a moderate slope and a gradual transition to the constant plateau value. From the point of view of G', the STG is more like a dilatant material. Besides, the heat will enhance the critical value of the frequency.

A flexible protective composite with shear stiffening effect, adhesive, and property was prepared by integrating STG with commercial polyurethane sponge. Rheological tests suggested the mechanical properties, including the storage modulus and stress, were rate-dependent and could response to the environment stimuli automatically. More importantly, the presence of STG increases the interleaving resistance of STK, which makes the STK could absorb and dissipate much impact energy and decline the impact force by more than two times. The plastic, flexible, and adhesive characteristics ensured the excellent reliability of the composite under cyclic loading impacts. Additionally, in the presence of STG, STP had a stronger protective effect in wearable body armor, vibration control, damping, and so forth. Finally, the B-O cross bond and the entanglement of polymer chains are believed to be the reason for shear stiffening properties.

5. References
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