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Enhancement of a Novel Sizing Agent in Mechanical Properties and Stab/Puncture Resistance of Kevlar Fabrics

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Abstract: In the work, a kind of composite material with excellent stab/puncture resistance was prepared by resin bonded Kevlar fabric. Water-borne epoxy resin (PAEK), polyacrylamide (APAM), fatty alcohol polyoxyethylene phosphate potassium salt (TFPK) are formulated to form a novel sizing agent that can be used for the sizing Kevlar fabrics. The effects of the sizing agent on the mechanical and stab/puncture resistance are examined. A field emission scanning electron microscopy (SEM), an ultra-depth of field 3d microscope, and a universal testing machine were used to observe and evaluate the morphology of sizing fabrics, the stab/puncture morphology, mechanical properties, and quasi-static stabbing properties, respectively. The test results show that the puncture resistance of the sizing Kevlar fabrics increases first and then decreases with the increase of sizing agent concentration. Compared with non-sizing fabrics, the Kevlar fabrics that are treated with a sizing agent at a concentration of 10 wt% have 524 % higher puncture resistance, 301 % higher stab resistance, and a 6.9-fold increase in the burst strength. Because the fiber bundles in the sizing fabrics are confined due to the resin saturation, the friction among fibers is enhanced and thus better resists an external force and contributes a greater resistance against sharp objects.

Keywords: Kevlar fabrics, Sizing agent, Puncture/stab morphology, Mechanical properties, Quasi-static stab resistance

Introduction

Diverse protective equipment such as stab resistant gloves, protective gear, bulletproof vests, biological and physical protective clothes have been rapidly developed because of the advanced economy, aggravating social conflicts, and cumulative self-protective awareness [1,2]. Blades, knives, spikes, and other sharp and pointed objects have become the major threats to hurt people because of strict rules on the use of guns, which subsequently makes the research and development on puncture resistant equipments imperatively meaningful [3].

High performance Kevlar fibers have intrinsic high tensile strength. Besides they also have a high crystallinity, but the smooth surface and low surface energy adversely affect the interaction between Kevlar fibers and other materials. Therefore, the resulting fabrics commonly unable to resist sharp and pointed objects [4]. The majority of studies on the enhancement in the stab/puncture resistance of fabrics commonly employ the modification by shear thickening fluid (STF) and reinforcement by resin. Qin *et al*. [5] combined Kevlar fabrics with STF to form soft bulletproof composites. They found that an increase in the STF concentration actually improved the dynamic puncture resistance by 36.23-65.21 %. STF modification is usually based on a monodisperse silica system in studies, but the practical use of STF shows that STF exhibits a relatively low initial viscosity, which results in a low adhesion of STF to fibers. Furthermore, STF would lose its rheological property because of aging or a humid environment, which in turn interferes with the stab resistance after STF being adhered to the fabrics [6]. Ahmad *et al*. [7] coated natural rubber latex (NRL) over polyethylene fabrics. The test results indicated that comparing to the control group without NRL coating, the experimental groups exhibited 39 % and 47 % greater puncture resistance for a single and double NRL-coating layers, separately. Resin impregnation treatment can make up for this disadvantage. Lin *et al*. [8] coated resin over aramid fabrics. The experiment results show that the epoxy group in the resin is firmly bonded with the oxygen-containing active group in the aramid fiber and the bond strength of the complex is better. Mayo *et al*. [9] studied how the three types of thermoplastic resins affected the puncture resistance of Kevlar fabrics. A combination of surlyn resin and Kevlar fabrics yielded the maximal stab/puncture resistance.

In order to enhance the stab/puncture resistance of Kevlar fibers and the adhesion between resin and fibers, this study formulates water-borne epoxy resin, polyacrylamide, and fatty alcohol polyoxyethylene phosphate potassium salt to

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form a novel sizing agent. Kevlar fabrics undergo the sizing process, after which the effects of the sizing agent on the mechanical properties and puncture/stab resistance of the sizing fabrics are evaluated.

Based on the People's Republic of China GA 68-2008 Stab-proof Clothing standard [10] and the American NIJ [11] stab-proof performance test standard, a specified knife head is custom-made. The puncture and stab resistant performances of sizing Kevlar fabrics are tested using a universal tester equipped with a spike and a knife head, respectively. The influences of the sizing treatment on the puncture and stab resistant performances, bursting strength, and mechanical properties of the sizing Kevlar fabrics are studied. In the meanwhile, the morphology of sizing Kevlar fabrics and the stab/puncture morphology are characterized using an ultra-depth of field 3D microscope, thereby examining the stab/puncture resistant mechanisms. The use of novel sizing agents over Kevlar fabrics is proved to have a great application prospect in terms of the stab/puncture resistance.

Experimental

Materials

Kevlar plain weave fabrics (Dongguan Tekelon New Materials Co., Ltd., China) have specifications as Table 1. Water-borne epoxy resin (PAEK, Tianjin University of Technology Textile Auxiliaries Co., Ltd., China) has an epoxy value of 0.04 mol/100 g and the content of 50 %. Polyacrylamide (APAM, PA6558, Tianjin University of Technology Textile Auxiliaries Co., Ltd., China) has a molecular weight of 15 million. Fatty alcohol polyoxyethylene phosphate potassium salt (TFPK) is purchased from Tianjin University of Technology Textile Auxiliaries Co., Ltd., China.

Table 1. Performance parameters of Kevlar fabric

Specifications	Parameters
Weave pattern	Plain weave
Quality (g/m^2)	200
Thickness (mm)	0.262
Wale density (waves cm^{-1})	9
Course density (courses cm^{-1})	9

Preparation of Sizing Agent

The content ratio of PAEK, APAM, and TFPK is 1:0.0003:0.1, which is yielded from the previous study [12]. APAM is made into a solution beforehand in order to enable a better mixing level with APAM and PAEK, during which the ingredients are added in several batches instead of one batch, and mixed well for better dissolution. The solution was stirred at room temperature for 30 minutes.

Sizing Process of Kevlar Fabrics

Figure 1 shows that the Kevlar fabrics are trimmed into a size of 15 cm×15 cm and immersed in the 10 wt.% sizing agents for thirty minutes. By extruding excess resin solution from plastic sheet to control sizing weight, sizing fabrics with sizing rate of 6 %, 8 %, 10 % and 12 % were prepared respectively. The sizing fabric is dried in an oven at 75 °C for two hours and then sealed for storage.

Stab-resistance Mechanism

Piercing fabrics with sharp objects is a kind of low-speed continuous mechanical process, whose damage range is narrow, but strong penetration and mainly shear action. Therefore, anti-piercing materials must have dense structure and better strength to resist cutting and dispersing energy at the beginning of the tool [12,13].

The anti-prong mechanism of resin treatment of kevlar fiber is shown in Figure 2. Resin slurry impregnation coating method is used to fill the inner part of kevlar fiber with resin, and a film is formed on the outer layer of kevlar fiber, which acts as the bridge of adhesion between resin and fiber, so as to increase the bunching property and improve the mechanical properties of kevlar fiber bundle. The effect of slurry on the product performance of kevlar fiber is mainly shown in the following two aspects: (1) enhance the fiber cluster, and then improve the fiber post-processing performance; (2) The slurry can fill the micro-defects on the surface of the fiber, improve the breaking strength of the fiber, play a role of reinforcement.

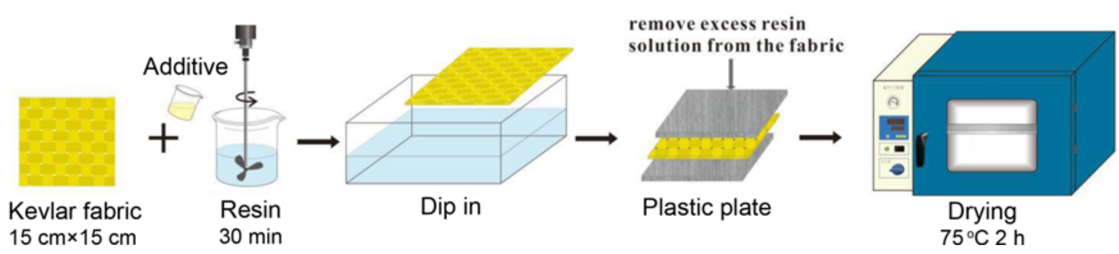

Figure 1. Sizing process of Kevlar fabrics.

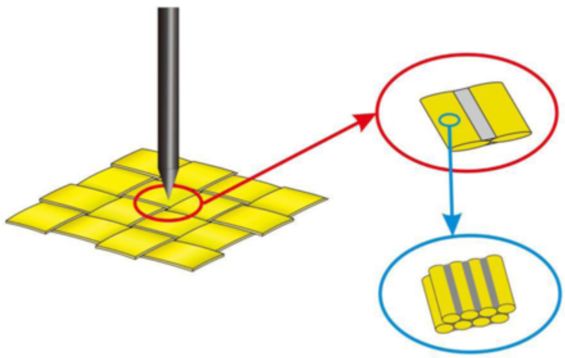

Figure 2. Prick - proof mechanism of Kevlar fabric treated with resin.

Testing and Characterizations

Scanning Electron Microscope (SEM)

The morphology of Kevlar fabrics before and after the sizing treatment is observed at an accelerating voltage of 10 kV using a field emission scanning electron microscope (SEM, S4800, HITACHI, Japan). Samples need to be coated with a thin layer of gold for fifteen minutes before the observation.

Static Stabbing Test

The burst strength of sizing fabrics is measured at a rate of 100 mm/min using a universal material testing machine (HT-2402, Hung Ta Instrument, Taiwan) as specified in ASTM D3787. Figure 3(a) shows a schematic diagram of a quasi-static stabbing tester while Figure 3(b) shows the specification of the impact head. Samples have a size of 150 mm×150 mm. Five samples for each specification are used.

The static stabbing performance of sizing fabrics is measured at a rate of 508 mm/min using a universal material testing machine (HT-2402, Hung Ta Instrument, Taiwan) as specified in ASTM F1342-05. Samples are fastened with bolts and custom-made cylindrical clamps. There are two types of impact heads, including a spike and a knife as Figure 3(c, d). Samples are a size of 150 mm×150 mm. Six samples for each specification are used.

Stab/Puncture Morphology Analyses of Sizing Fabrics

The stabs and punctures of sizing fabrics are observed and analyzed using an ultra-depth of field 3D microscope (Z16 APO, Lecia, China) that has ×22.8 magnification.

Results and Discussion

Effects of Sizing Treatment on Protective Performance of Kevlar Fabrics

Puncture Resistance

Figure 4 shows the quasi-static stabbing results of conical spines. Figure 4(a) shows the average tapering strength of the fabric treated with different sizing rates, and Figure 4(b) shows the curve of tool displacement and load during tapering.

Figure 4(a) show the static puncture results where the control group exhibits an average puncture resistance of 19.66 N while the experimental groups have mean puncture resistance strength of 79.32 N, 84.53 N, 103.03 N and 91.78 N when the sizing rate is 6 %, 8 %, 10 % and 12 %,

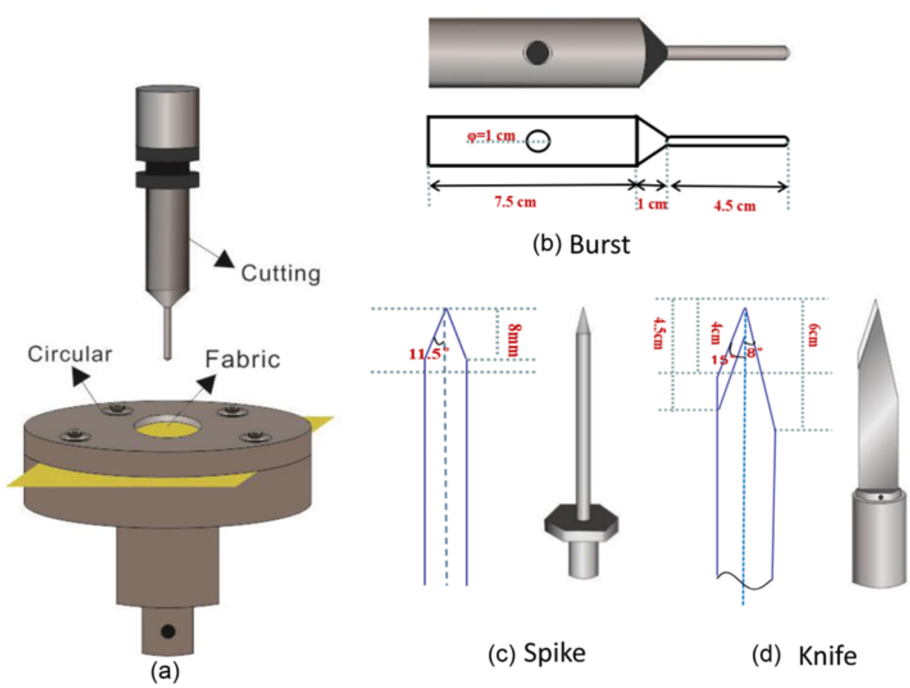

Figure 3. Schematic diagrams of (a) quasi-static stab tester and (b-d) the quasi-static impact head for burst, puncture and stab.

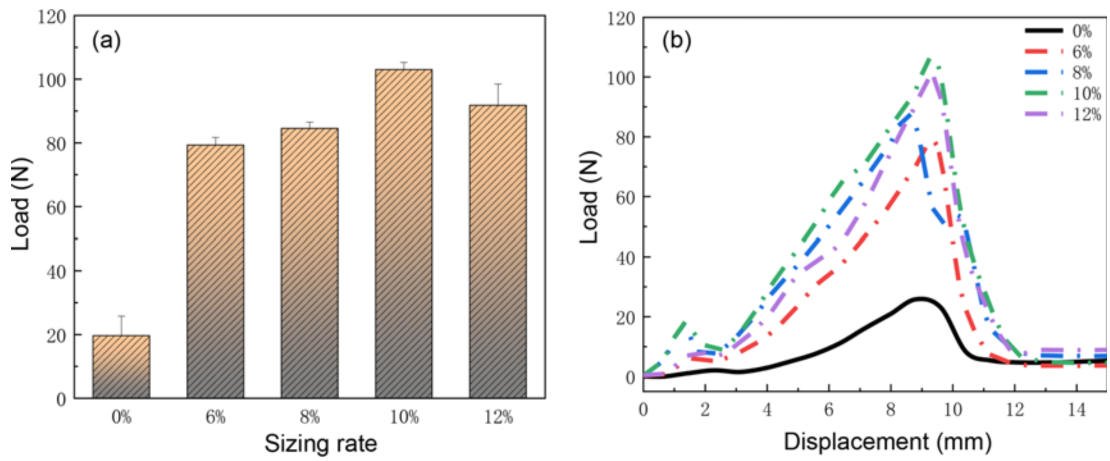

Figure 4. (a) Average puncture strength of fabrics treated with different sizing concentrations and (b) the tool displacement-load curve for the puncture process.

respectively. Comparatively, the sizing Kevlar fabrics demonstrate better puncture resistance. With an increase in the sizing rate, the puncture resistance first increases and then decreases. In particular, a sizing rate of 10 wt.% provides the Kevlar fabrics with the maximal puncture resistance, which is 524 % greater than that of the control group. An appropriate concentration of the sizing agent makes the fabric structure denser and the friction among fibers is thus improved. Conversely, an excessive concentration of the sizing agent makes the sizing Kevlar fabrics brittle, which in turn mitigates the friction and deformation between the spike and sizing Kevlar fabrics, and the puncture resistance of the sizing Kevlar fabrics is compromised [9].

Based on the Figure 4(b) load-displacement curves, as the spike approaches the fabrics, the spike is given a force that increases with a greater tool displacement. When the tip of the spike moves at a constant speed to damage some of the fibers in the proximity, the pressure from the spike surface constantly pushes the fibers. Subsequently, the fibers are accumulated, which strengthens the friction between the fibers and the spike surface, resulting in sudden stress. With the continuity of the puncture process, the puncture strength spikes to the maximum and then drastically drops, during which the spike total goes through the fabrics. Due to the presence of the friction between fibers and the spike, the load is not equal to zero [14,15].

Stab Resistance

Figure 5 shows the static stab resistance of Kevlar fabrics by a single-bladed knife head. Figure 5(a) is the average stab resistance of sizing Kevlar fabrics as related to the sizing rate. Figure 5(b) shows the tool displacement-load curves.

The control group has an average stab resistance of 25.90 N and the experimental groups have an average stab resistance of 47.06 N, 54.92 N, 77.91 N and 62.24 N when the sizing rate is 6 %, 8 %, 10 % and 12 %, respectively. The

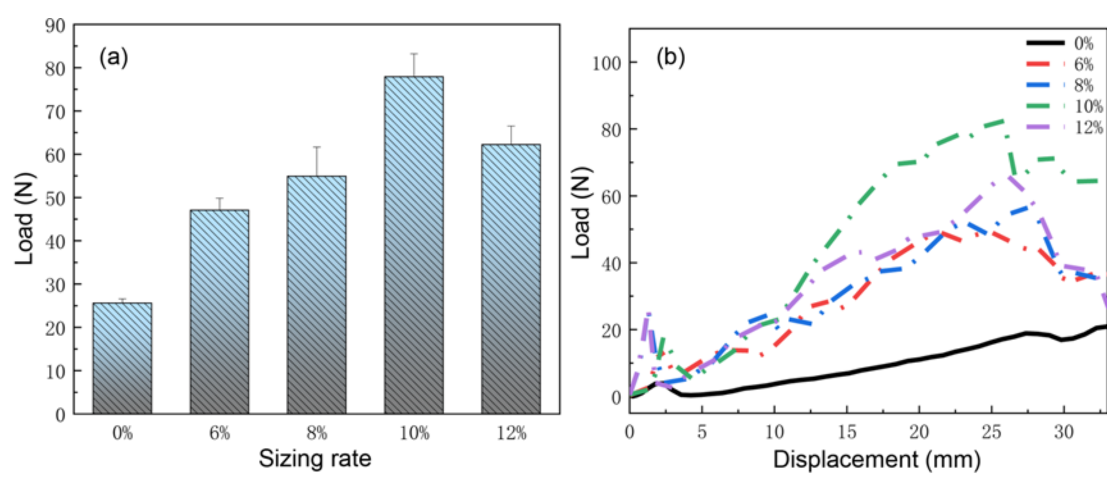

Figure 5. (a) Average knife strength of fabrics treated with different sizing concentrations and (b) tool displacement-load curve for stab process.

maximal stab resistance of sizing Kevlar fabrics occurs when the sizing rate is 10 wt.%, and it is 301 % greater than that of the control group. Hence, an increase in the sizing rate first increases and then decreases the stab resistance. Figure 5(a) shows that the sizing Kevlar fabrics demonstrate higher stab resistance than the control group. Comparing to the control groups, the experimental groups have a significantly greater displacement between that the knife head contacts the fabrics and that it cuts through the fabrics. Because in the control group, fibers without sizing treatment can be moved and pulled easily, the non-sizing Kevlar fabrics show lower stab resistance. Contrarily, the sizing Kevlar fabrics have greater friction among fibers and between fibers and the knife head that causes the friction self - locking phenomenon, which in turn reduces the slippage of fibers and strengthens the expelling and shearing effects of the tool on the fabrics [16]. When the sizing rate increases to 12 %, the thick sizing agent makes fabrics fragile and brittle, which has a negative influence on the stab resistance of the sizing Kevlar fabrics.

According to the displacement-load curve in Figure 5(b), as the knife head first contacts the fabrics, the fabrics exhibit bending deformation due to the compression. With the knife going deeper, it expands and shears the fibers of the Kevlar fabrics lengthwise, and meanwhile, the shear resistance of the fabrics strengthens the force exerted on the tool as a result of a rise in the displacement [17]. When the tool cuts through the sizing layer and enters between the sizing agent and the fabrics, fabrics lose the sizing protection, and the stab force diminishes concurrently. With the tool cuts further, fibers are continuously being cut and accumulated in the stab site until the stab strength reaches the peak. Then, there are no more fibers stop the tool so the stab force descends until the fabrics are totally cut through. Namely, the stab size allows the passage of the tool, which is the very moment that the load drops drastically [18].

Burst Strength

Figure 6 is the quasi-static stab-proof result of jacking. Figure 6(a) shows the average bursting strength of Kevlar fabrics treated with different coating sizing rate, and Figure 6(b) shows the curve of top displacement and load in the bursting process.

Figure 6 shows the static burst strength. Figure 6(a) shows that the control group has an average burst strength of 95.68 N while the experimental groups have an average burst strength of 451.48 N, 530.53 N, 657.98 N and 629.39 N when the sizing rate is 6 %, 8 %, 10 % and 12 %, respectively. It is clear that the sizing Kevlar fabrics have comparatively higher burst strength than the control group. In particular, a sizing rate of 10 wt.% provides the Kevlar fabrics with the maximal burst strength that is 6.9-fold greater than that of the control group. Figure 6(b) shows that both of the control group and the experimental groups have a comparable trend in the burst strength, but the burst strength of the experimental groups is much higher. With the increase of sizing rate, the bursting strength of the sizing fabric increases, which is mainly due to the reduces of fiber pull-out in the sizing process. The sizing can make the load of top crack distributed all over the fabric and increase the stressed area. The resin penetrates into the fabric, and both the fiber and the resin coating bear the burden when subjected to the external force of the top [19]. When sizing rate is 10 %, the average bursting strength of the fabric is the highest. When the sizing rate reaches 12 %, the fabric becomes brittle due to sizing accumulation, thus reducing the resistance to top breakage.

Figure 6(b) shows the burst load-displacement curves. The burst failure mechanism of a single sizing layer of Kevlar fabrics involves three stages as follows [20,21]. In the first stage, the burst head just approaches and touches the fabrics. The contact area is small, so is the exerted burst force. The concentrated load rendered by the burst head is distributed

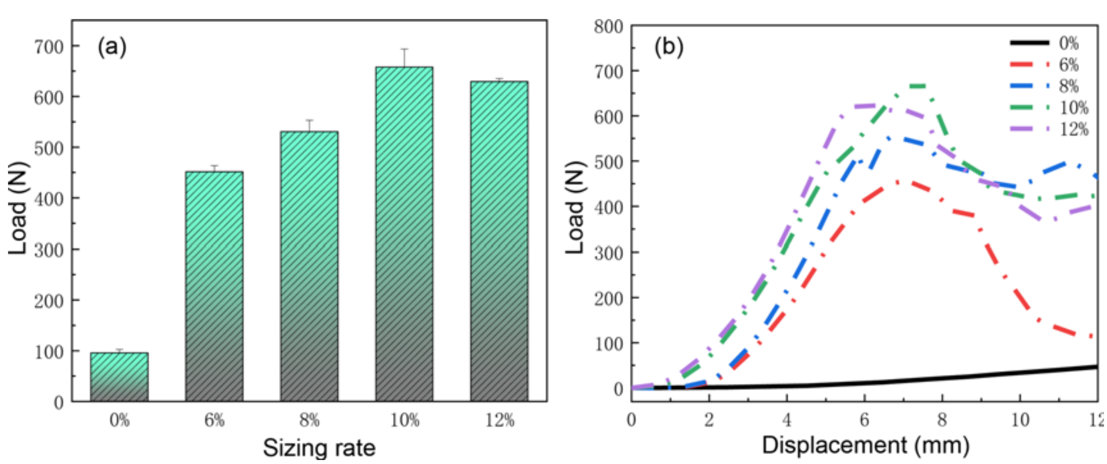

Figure 6. (a) Average burst strength of fabrics treated with different sizing concentrations and (b) head displacement-load curve of the bursting process.

over the fabrics. In the second stage, the burst stress is radiated while gradually forming a protrusion on the fabrics with the burst head as the central point. The burst force shows an ascending trend. In the third stage, the burst head damages the sizing layer and penetrates the sizing Kevlar fabrics. As a result, the burst load of the sizing Kevlar fabrics drops.

Morphology of Puncture and Stab on Sizing Kevlar Fabrics

Figure 7 shows the morphology of the Kevlar fabrics before and after the sizing process in terms of the puncture (a, b, c, d) and stab (e, f, g, h). The punctures appear circular while the stabs appear rectangular, which is ascribed to the different damage mechanisms of the tools. The damage of a spike head is dependent on the friction between the spike and the fibers whereas the damage of a stab head is dependent on the shear effect [22]. Figure 7(a, e, and i) shows the control group where a few amounts of broken fibers are presented in the punctures and the stabs, while the majority of the fibers are expelled along the punctures and the stabs without being broken. Figure 7(b, c, and d) show the punctures of sizing Kevlar fabrics where the amount of slippage of fibers is decreased when the fabrics are punctured. Treated with a sizing rate of 10 %, the sizing Kevlar fabrics exhibit broken fibers, suggesting that the fabric has a more compact structure. Furthermore, Figure 7 (f, g, and h) show the stabs of sizing Kevlar fabrics. It is obvious that the fabrics display a lower level of yarn slippage as the sizing treatment renders the fabrics with a compact structure while strengthening the friction among yarns. It is difficult for fibers to slip and deform, and the knife head exerts damage by shearing fibers, instead of pulling out them. Comparing to 6 %, 10 % provides the Kevlar fabrics with a more regular cutting section of yarns as well as a more tidy stab morphology as Figure 7(j, k, and l). By comparing (c, g, and k) and (d, h, and l) in Figure 7, we find that when sizing rate is 12 %, the effect of cutter head on fabric is mainly cutting. However, the fabric becomes brittle due to excessive sizing, so compared with the sizing rate of 10 %, the sizing rate of 12 % shows a poor stab-proof performance.

Surface Morphology of Fabric before and after Sizing

Figure 8 shows the SEM images at different magnifications of non-sizing and sizing Kevlar fabrics, the latter of which being treated with a sizing rate being 10 %. The images show that the sizing agent completely saturates Kevlar fabrics and is present among yarns. Figure 8(a) shows the control group without sizing treatment where the Kevlar fabrics have a sleek surface and fibers are aligned with the presence of voids. Figure 8(b) shows the sizing Kevlar fabrics are covered with resin while the voids in fabrics are filled with resin due to the sizing treatment. There is a dense protective layer over the Kevlar fabrics enhancing the entire properties of the sizing Kevlar fabrics. Figure 8(c, d) show that with a sizing rate of 10 %, the SEM images have a ×900 and ×3000 magnification. It is clearly shown that samples

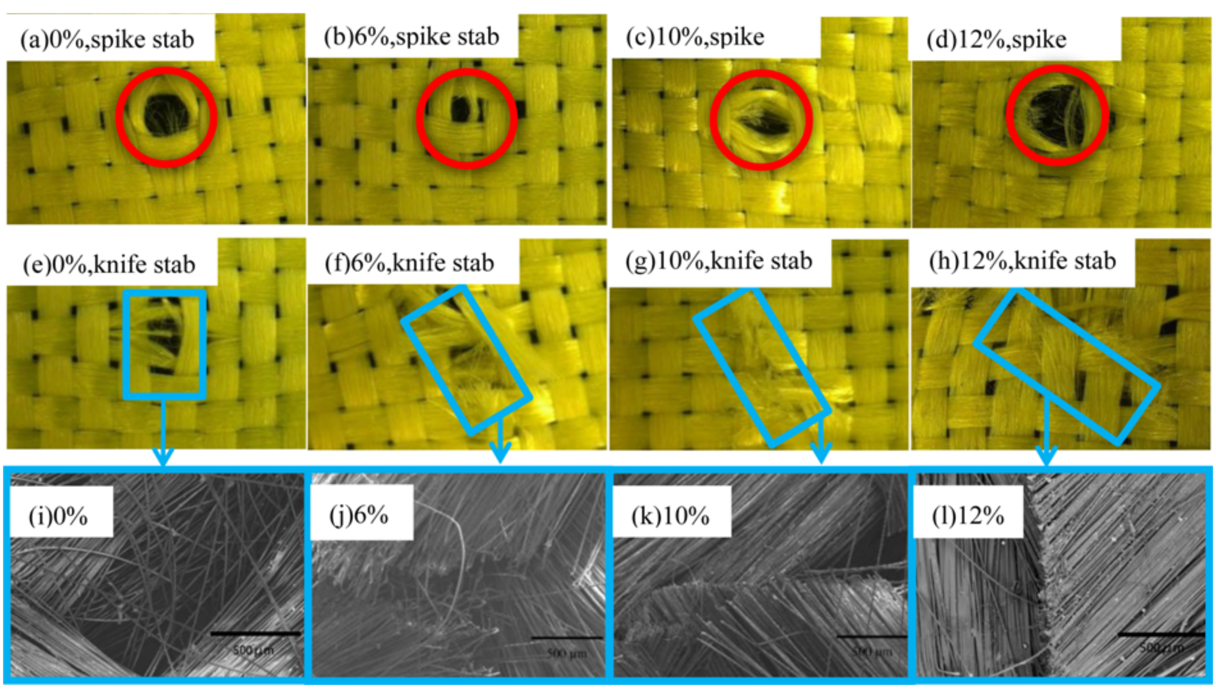

Figure 7. Images of (a, b, c, d) the punctures and (e, f, g, h) the stabs of Kevlar fabrics before and after the sizing treatment as well as (i, j, k, l) the microscopic images of the stabs.

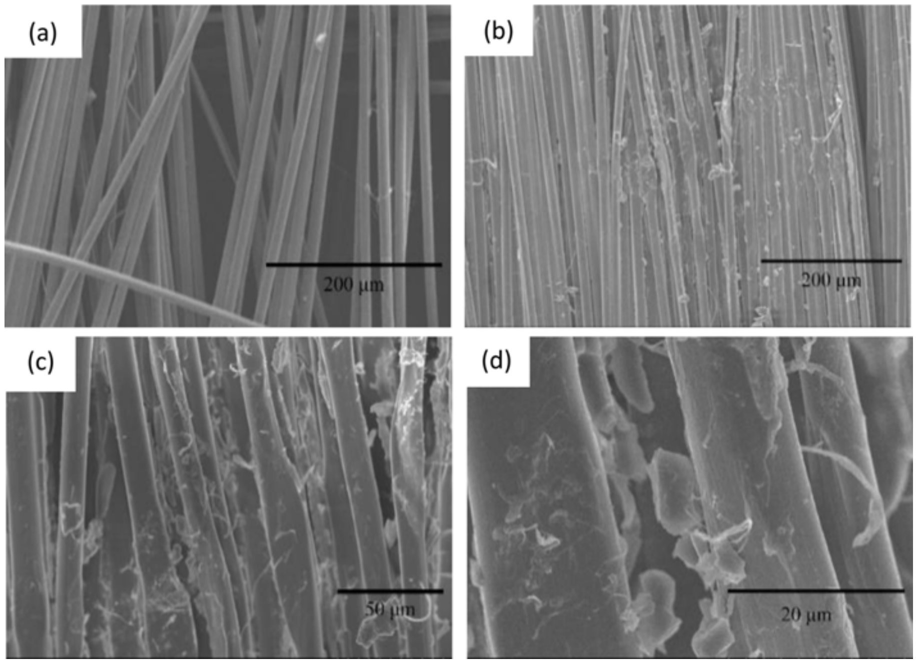

Figure 8. SEM images of Kevlar fabrics (a) before and (b, c, and d) after sizing treatment at a sizing rate of 10 %.

are saturated with resin and the voids in Kevlar fabrics are filled with resin. There are also resin lumps over the fibers, which can serve as enhancement points, confining the fiber bundles and strengthening the stab/puncture resistance of sizing Kevlar fabrics.

Conclusion

In this study, water-borne epoxy resin, polyacrylamide, and fatty alcohol polyoxyethylene phosphate potassium salt are formulated into the sizing agent that is used in the sizing treatment of Kevlar plain weave fabrics with an aim to enhance the puncture/stab resistance of the fabrics. The test results of morphology, tensile strength, and static puncture/stab/burst resistance are as follows. The sizing treatment is proven to provide the fabrics with a dense protective layer and a compact fabric structure. Comparing with the control group, the sizing Kevlar fabrics have 524 % higher puncture resistance, 301 % greater stab resistance, and 6.9-fold greater burst strength. The non-treated Kevlar fabrics tend to be softer so the fiber bundles glide and fibers are pulled out easily. In this case, they fail to resist an external force and are compromised by a sharp tool. By contrast, the sizing Kevlar fabrics have immobilized fiber bundles due to resin saturation, and therefore exhibit greater resistance against any external impact. Therefore, the performance of Kevlar fabric can be improved by increasing the friction effect by adding resin paste. And the resin coating method has also brought broad application prospects for the anti-thorn materials.

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