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Application of Polymer Materials in Shear Thickening Gel-based Impact Protective Knee Pads for Martial Arts

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Martial arts exercise causes significant wear and tear on the knee joint. The existing anti-collision knee pads are insufficient to meet the requirements of wearing comfort and mechanical performance. Therefore, a composite material based on shear thickening gel (STG) is proposed. The preparation process of this material is doped with polyester short fibers and multi-walled carbon nanotubes (MWNT). The composite is filled into naturally structured Kevlar flat weave fabric (Kevlar) to enhance the mechanical properties of the pure fabric. The results indicated that the MWNT/STG/Kevlar composite material prepared by the proposed method effectively enhanced the dynamic properties of the shear thickening agent. The worst fracture strength and displacement were 600 N and 38 mm, respectively, both of which complied with national standards. The bending performance was 10.2 % and 14.2 % higher than the other two composite materials. The average air permeability was 190 mm/s, which was 60 % and 78 % higher than the other two materials, respectively. The impact resistance performance decreased by 42 %, 54 %, 57 %, and 68 % compared with the other three knee pads, respectively. Therefore, the MWNT/STG/Kevlar composite material prepared by the proposed method can be applied in the knee pad preparation process, effectively increasing the mechanical properties of the knee pad, preventing impact during martial arts exercise, and improving the wear comfort.

Keywords: anti-collision knee pads, polyester short fibers, MWNT, STG, mechanical property.

1. INTRODUCTION

With the continuous development of the social economy, the number of sub healthy people is increasing and gradually moving towards younger age groups [1]. As the benefits of exercise for physical and mental health continue to be proven, people of all ages are beginning to integrate exercise into their daily lives. Martial arts not only benefit physical health, but also have a significant effect on soothing the mood [2]. However, martial arts involve various knee joint movements. If one does not pay attention to controlling the impact force on the knee joint, it can cause irreversible injuries [3]. Therefore, designing a collision resistant knee brace as a knee joint protection device is of great significance for the widespread promotion of martial arts [4]. Considering that anti-collision knee pads not only have resistance to low-speed impact, but also require a comfortable wearing experience [5]. Therefore, choosing fabrics with natural structural advantages as raw materials for knee pads and filling them with cushioning materials can further improve the protective performance and wear comfort requirements [6]. Many existing studies focus on composite and modified materials with various functions, and combining them with natural fabrics to obtain stronger performance composite materials to meet various protection needs [7].

At present, the research on functional materials is aimed at increasing the mechanical properties and wearing comfort of fabric materials [8]. Chandran et al. proposed the composite functional filler based on ethylene vinyl acetate (EVA), which enhanced the functional properties of EVA. It was applied in the knee pad preparation process. Through material testing, this method effectively increased the elasticity and cushioning performance of knee pads [9]. Yue et al. proposed a polyurethane-based composite material. The addition amount of polyether polyols and the pH value of the dispersed phase were explored to obtain the optimal material ratio. The results indicated that this method could be effectively used in the actual production of knee protection equipment, ensuring the flexibility of knee protection activities and protective effect [10]. Shrivastava et al. proposed a protective knee pad based on built-in silicone. The breathability and weight of knee pads were improved, resulting in a composite material with a simple preparation process and low cost. The results indicated that this method improved the breathability and portability of knee pads, effectively enhancing comfort while retaining the sports protection function [11]. Cheng et al. proposed a composite material that combined corn starch with polystyrene. The stirring method was used to increase the shear consistency of the material, allowing it to disperse and reduce the impact force. The results indicated that the composite material provides certain restraint on knee movement without loss of activity, which had excellent impact resistance [12]. Liu et al. proposed a shear thickener based on calcium carbonate filled in fabrics, aiming to solve the impact resistance of fabrics. The results indicated that this method effectively improved the impact resistance of materials, which was applied in wearable devices to avoid puncture injuries to the human body.

In summary, existing research has combined materials with various properties to obtain stronger protective materials. However, the existing materials are not yet

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simple and economical in their preparation process, and do not have long-term storage stability. There is still room for improvement in the mechanical properties and wearing comfort of composite materials. Therefore, a shear thickening adhesive based on shear thickening gel (STG) is proposed to enhance the protective performance and wearing comfort of anti-collision knee pads. The research innovation is to use doped polyester short fibers and multi-walled carbon nanotubes (MWNT) to increase the surface area of the dispersed phase and increase the connection between the media to enhance its mechanical properties. In addition, STG has strong adhesion and impact resistance, which can be filled into Kevlar flat weave fabric (Kevlar) to enhance the shock absorption effect.

2. MATERIALS AND METHODS

2.1. Experimental materials and equipment

Three materials need to be prepared for research, namely, doped short fibers STG, MWNT/STG, and MWNT/STG/Kevlar composite. The required test reagents for the preparation of the three materials are shown in Table 1 [13]. The experimental instruments and equipment required are shown in Table 2.

2.2. Preparation process of doped short fibers MWNT/STC

STG is a viscous functional material that adds particle concentration, matrix liquid, and crosslinking agent based on STF, connected by chemical bonds. It can quickly counteract impact energy under strong external forces [14]. Therefore, based on the impact resistance performance of STG, a new type of material is developed by combining it with other materials to increase its shear and tensile strength performance. The performance of STG can be improved to some extent from the preparation process by doping flexible material short fibers into STG and taking polymethyl methacrylate (PMMA) and mold silicone (MS) as dispersed phases.

Table 1. Raw materials and test reagents information

Material and reagent name	Standard	Chemical formula, abbreviation	Manufacturer
Polymethyl methacrylate	500 nm	PMMA	Dongguan Zhangmutou Jinyunlai Plastic Raw Material Business Department
Polyester short velvet	5 %	PSV	Jiaxing Qida Textile / Textile Co., Ltd
	1 mm		
	3D		
Mold silicone	825 type	MS	Shenzhen Changdashun Trading Co., Ltd
Anhydrous ethanol	Surface density of 200 g/mol	C_2H_5OH	Chengdu Cologne Co. Ltd
Polyethylene glycol	Surface density of 200 g/mol	$C_6H_{14}O_6$	German Degussa Company
Silicon dioxide powder	Particle size 12, 50, 70, 100 nm Specific Surface area of 200 g/m^2	SiO_2	Tianjin Kemio Chemical Reagent Co., Ltd.
Kevlar plain fabric	Surface area of 200 g/m^2	–	DuPont (China) Co., Ltd
Ethylene glycol	Analyze pure AR	$C_2H_5O_2$	Tianjin Kemio Chemical Reagent Co., Ltd.
Polyethylene glycol	Analyze pure AR	HO-(CH-CH-O)$_n$-H	Tianjin Fengchuan Chemical Reagent Technology Co., Ltd.
1,3-Propanediol	Analyze pure AR	$C_3H_8O_2$	Tianjin Guangfu Fine Chemical Research Institute
Multi-walled carbon nanotubes	Diameter 20 ~ 30 µm	MWNT	Nanjing Pioneer Nanomaterial Technology Co., Ltd
	Length 5 ~ 30 µm		
Propylene glycol	Analyze pure AR	$C_3H_8O_3$	Tianjin Fengchuan Chemical Reagent Technology Co.

Table 2. Instrument and equipment information

Instrument name	Model	Manufacturer
Electronic balance	PMQW type	Nanjing Nanda Co., Ltd
Ultrasonic cleaning machine	VGT-2013 model	GuTe Ultrasound Co., Ltd
Vacuum drying oven	DZF type	Beijing Yongguangming Medical Instrument Co., Ltd
Rheometer	MCR302 type	Anton Paar, Austria
Tube furnace	OTL1200	OTL1200
Scanning electron microscope	ZEISS Gemini 300	CarlZeiss GmbH, Germany
Thermogravimetric analyzer	TGA 550	American TA Instrument
Fourier transform infrared spectroscopy malvern particle size analyzer universal testing machine	Thermo Scientific Nicolet 6700	Thermo Fisher Scientific Molecular Spectroscopy, Brookhaven Instruments, USA
Malvern particle size analyzer	NanoBrook Omni	Shimadzu Manufacturing Co., Ltd., Japan
Universal testing machine	AG-X plus	Shimadzu Manufacturing Co., Ltd., Japan
Drop hammer impact testing machine	Self-control	Self-control
DMA dynamic thermomechanical analyzer	TA Q800	U.S.A / TA Instrument Company
Electric sub fabric strength tester	HD026N	–
Martindale flat grinder	LLY01	–
Fully automatic air permeability meter	YG461GQ	–
Hopkinson compression rod	SHPB	–
Double line guide rail collision testing machine	–	Cadex Defence Canada
Thermostatic water bath	HN-6	Bonsi Instruments (Shanghai) Technology Co.

The preparation steps of doped with short fibers STG are as follows: (1) add 7 g of MMA particle dispersed phase to a beaker, then add 2 g of SiO_2, 0.5 g of MWNT, and 1.01 g of polyester short fibers while stirring; (2) after adding the mixture, place the beaker in a constant temperature water bath at 35 ℃ and stir with a mechanical stirrer at 150 rpm/min for 5 minutes. After initial stirring into a ball, place the beaker in a high-speed disperser and stir at 7,000 rpm/min for 7 minutes; (3) to make the STG system more stable, transfer the prepared STG system to a vacuum drying oven and react at 55 ℃ for 36 hours to eliminate bubbles [15].

2.3. Preparation process of MWNT/STG/Kevlar composite materials

The prepared MWNT/STG has a high viscosity, and placing it directly on the surface of Kevlar results in significant fluidity and uneven distribution [16]. Therefore, the MWNT/STG/Kevlar composite material is prepared by soaking and drying [17]. The main steps are divided into 4 steps: (1) dilute MWNT/STG with C_2H_5OH, and take a high-speed disperser to evenly distribute the diluted mixture; (2) soak the Kevlar fabric in a uniformly dispersed diluent for 3 minutes, then apply a certain pressure while rotating it at high speed to fully immerse the diluent into the Kevlar fabric; (3) transfer the prepared MWNT/STG/Kevlar composite material to a blast oven and maintain it at 55 ℃ for 7 hours to remove C_2H_5OH; (4) after air drying, remove the MWNT/STG/Kevlar composite material, seal it, and place it in a cool and dry place for testing.

2.4. Performance testing and characterization methods

2.4.1. Dynamic mechanics testing and characterization

The dynamic mechanical properties can be used as a testing method for shear thickening response. The response is positively correlated with shear thickening [18]. Therefore, dynamic performance tests are conducted on the prepared doped short fibers MWNT/STG shear thickening. Firstly, place 0.5 g of doped short fibers MWNT/STC in a vacuum drying oven, let it stand, and eliminate bubbles for 6 hours. Then, transfer the MWNT/STC colloid to the testing tool, use a DAM dynamic mechanical analyzer, maintain a constant temperature of 22 ℃, and perform dynamic modulus testing at a frequency that continuously changes from 1 – 150 Hz.

The characterization index of dynamic mechanical performance is the loss energy consumption factor, which represents the viscosity of the material. The loss factor of a material is determined by two factors, namely the loss modulus and the storage modulus. The ratio of the two determines the loss factor. Therefore, the smaller the loss factor, the better the thickening performance of the material. The shear thickening performance is shown in Eq. 1 [19].

$$\tan\delta = G''/G', \tag{1}$$

where $\tan\delta$ is the loss factor; G'' is the loss modulus; G' is the storage modulus.

The temperature and stirring rate conditions during the material preparation process are optimized to obtain the optimal dynamic mechanical properties, thereby optimizing the preparation process to obtain MWNT/STG materials with better performance.

2.4.2. Basic wearability testing and characterization

The prepared MWNT/STG/Kevlar composite material is ultimately intended for use in knee sports products. Therefore, there is a high demand for wearing comfort [20]. It must meet the standards of tensile fracture, breathability, flexibility, and wear resistance to satisfy basic wearability. The basic environmental conditions for performance testing are set to 22 ℃ and a relative humidity of 70 %.

Firstly, the tensile fracture performance test is conducted using an electronic strength tester as the testing instrument for the two types of doped short fibers materials, MWNT/STC and MWNT/STG/Kevlar. Two material samples with a total testing length of 2,000 mm are prepared. Radial and axial tensile forces are applied at fixed intervals along the length of each sample. The tensile test is conducted at a speed of 200 mm/min, with a pre-tension of 25 cN/dtex. The fracture location (in mm) and the fracture strength (in N) are recorded as key indicators to evaluate the tensile failure performance of the materials.

The abrasion resistance test is conducted using a Martindale abrasion tester to simulate the wear process of two types of materials: short-fiber-doped MWNT/STC and MWNT/STG/Kevlar composites. The wear resistance characterization index is the number of visible wear occurrences such as fuzz or other visible wear. Using the Lissajou trajectory for polishing, the speed and total distance are 100 min and 30 mm, respectively. The bending performance test uses an electronic stiffness tester to observe the bending length and bending resistance of the material as characterization indicators. The initial bending angle is set to 31°, and 1 g and 1.5 g of doped short fibers MWNT/STC and MWNT/STG/Kevlar materials are used, respectively. The weight values of the materials are input into the instrument. Five materials of the same size are taken as comparative experimental samples for each material, and the samples are cut into length, width, and thickness of 20 mm, 55 mm, and 2 mm, respectively. Each sample's front, back, and ends are tested 5 times under the same conditions, for a total of 20 times.

An air permeability meter is used to test the breathability performance, with air permeability as the characterization index. The conditions are set to a pressure gauge of 120 Pa, a nozzle aperture of 3, and a sample area of 22 cm^2. Five materials of the same size are taken as comparative experimental samples for each material, and 10 test points are uniformly selected for each sample. Each test point is tested 15 times, for a total of 150 times.

2.4.3. Testing and characterization of low-speed impact resistance performance

The movement speed in martial arts is usually below 30 mm/s. Therefore, low-speed impact tests are conducted on the prepared materials to verify their protective effect during low-speed impact movements. The experiment uses a collision testing machine to conduct a drop hammer impact test on the prepared material, with impact energy, heavy hammer mass, impact velocity, and drop height as characterization parameters. The correlation between the characterization parameters is shown in Eq. 2 [21].

$$E = (1/2)mv^2 = mgh, \tag{2}$$

where E is the impact energy; m is the mass of the heavy hammer; v is the impact velocity; g represents the acceleration due to gravity; h represents the height at which the heavy hammer falls.

The testing process is as follows. CAD software controls the collision testing machine to impact 10 types of specimens with impact energies of 2 J, 5 J, and 8 J, respectively, for a total of 30 impacts. 10 samples are doped with short fibers MWNT/STC and MWNT/STG/Kevlar, with 5 samples each. The force magnitude generated by the impact on the sample is a characteristic indicator of its impact resistance performance.

3. RESULTS

3.1. Performance testing and characterization of doped short fibers MWNT/STC

3.1.1. Characterization analysis of doped short fibers MWNT/STC materials

When preparing MWNT/STC materials, adding SiO_2 with different particle sizes to the dispersion system can affect the stability of the material. Therefore, different composite materials are prepared using SiO_2 with particle sizes of 90 nm, 110 nm, 130 nm, and 150 nm, and stability tests are conducted. Firstly, TEM is used to characterize the morphology of SiO_2 with different particle sizes. The results are shown in Fig. 1.

Fig. 2 shows the viscosity and shear stress curves of composite materials prepared with SiO_2 of different particle sizes. In Fig. 2 a, the viscosity of the composite material decreased first and then increased with the increase of shear stress. When the particle size of SiO_2 was 90 nm, the viscosity was the highest. In Fig. 2 b, the shear stress of the composite material gradually increases with increasing shear rate. When the particle size of SiO_2 was 90 nm, the shear stress was the highest. From TEM analysis, the small particle size of SiO_2 indicates a larger surface area, which promotes contact between the media. Therefore, it has a higher viscosity. The smaller SiO_2 particle size indicates more particles, which increases its viscosity and leads to higher shear stress.

3.1.2. MWNT/STG dynamic mechanical performance testing

The preparation process of doped short fibers MWNT/STG shows that its dynamic mechanical properties are determined by stirring speed, temperature, and time. Therefore, different preparation conditions are set to obtain different dynamic mechanical properties of MWNT/STG materials to optimize their preparation process. The stirring rates are set to 510 rpm/min, 710 rpm/min, 910 rpm/min, and 1100 rpm/min, respectively. The temperatures of the mechanical stirrer, electric constant temperature bathtub, and ultrasonic cleaner are kept consistent at 22 °C, 35 °C, 50 °C, and 90 °C, corresponding to temperature and stirring rate one by one.

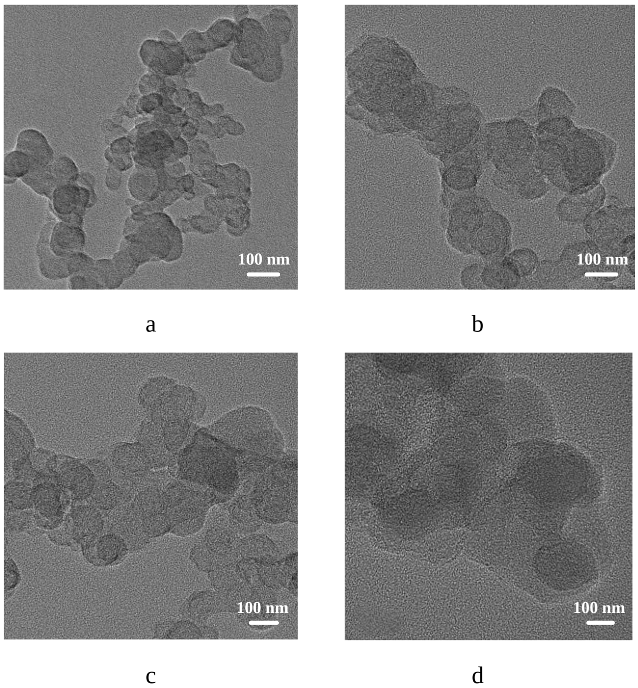


Fig. 1. TEM images of SiO_2 with different particle sizes: a – 90 nm; b – 110 nm; c – 130 nm; d – 150 nm

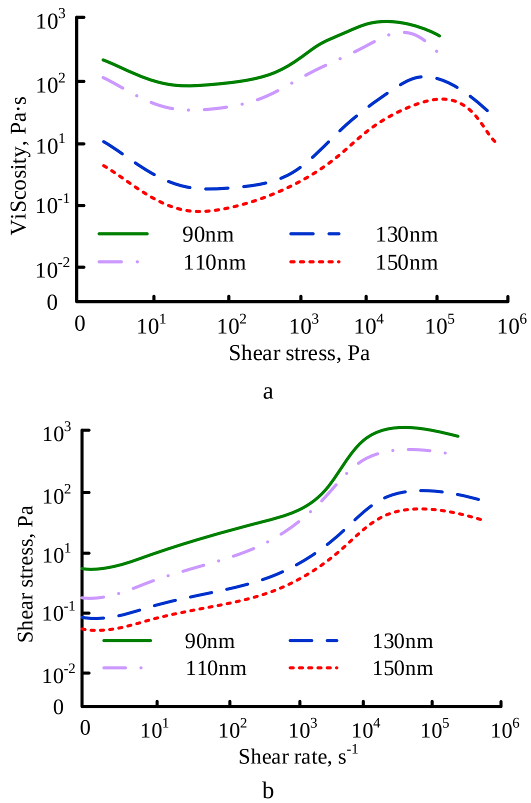
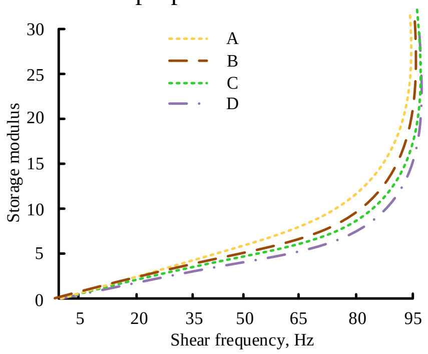


Fig. 2. The effect of SiO_2 with different particle sizes on the properties of composite materials: a – viscosity; b – shear stress

There are a total of 4 experimental groups, namely Group A: 510 rpm/min, 22 °C; Group B: 710 rpm/min, 35 °C; Group C: 910 rpm/min, 50 °C; Group D: 110 rpm/min, 90 °C.

The characterization results of MWNT/STG material properties are shown in Fig. 3. As shown in Fig. 3 a, the storage modulus of MWNT/STG gradually increased with the increase of shear frequency. The increase trend of storage modulus was relatively gentle at low shear frequencies, while the increase trend of storage modulus was faster at high shear frequencies. In Fig. 3 b, at the low shear frequency, the loss factor was less than 1, indicating that the state was viscous. When the shear frequency was high, the loss factor was less than 1, indicating that it exhibited elastic characteristics at this time. The results indicate that the prepared MWNT/STG material exhibits shear thickening characteristics, which are consistent with the actual material properties.



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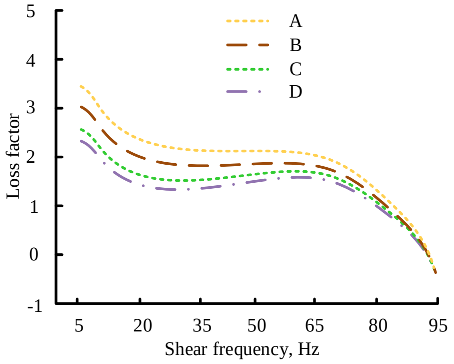
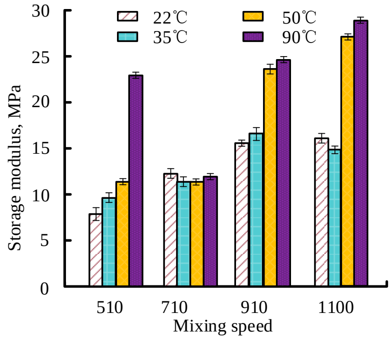


b

Fig. 3. Dynamic mechanical performance testing: a – storage mosulus; b – loss factor

During the material preparation process, excessively fast or slow mechanical stirring rates, as well as high or low temperatures, may lead to uneven distribution and dispersion of doped short fibers and PMMA particles during the material preparation stage. Therefore, exploring the appropriate stirring rate is of great significance for the preparation process of materials. The effect of mechanical stirrer stirring rate on the dynamic mechanical properties of MWNT/STG materials is analyzed. The results are shown in Fig. 4, which represents the variation of material storage modulus under different stirring speeds and preparation temperatures. In Fig. 4 a, when the stirring speed was 710 MPa, the difference in storage modulus between the materials prepared at four different temperatures was the smallest, and the storage modulus was as the highest at a temperature of 22 ℃.

When the stirring speed was 1100 MPa, the difference in storage modulus between the materials prepared at four different temperatures was the smallest. When the stirring speed was 510 MPa and 910 MPa, there were significant fluctuations in the storage modulus of materials at certain temperatures.



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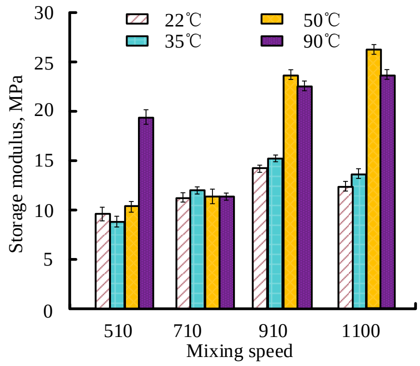

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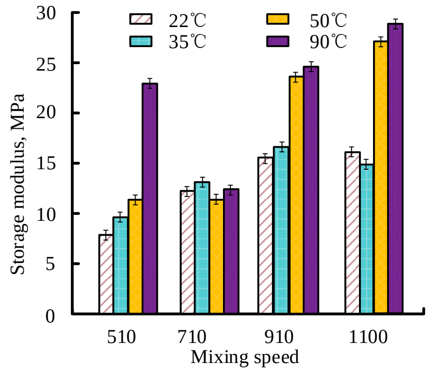

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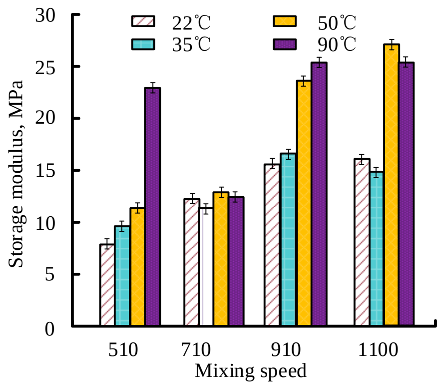


d

Fig. 4. Comparison of storage modulus under different mixing conditions: a – experimental group; b, c, d – parallel experiments

Four parallel experiments were conducted, and the differences in results between each experimental group were within 5 %. Therefore, when the stirring speed is set to 710 MPa, the shear thickening effect of the material is the best, with neither excessive adhesion nor high fluidity. This result has high repeatability.

3.2. Performance testing and characterization of doped with short fibers MWNT/STC

3.2.1. Characterization analysis of MWNT/STG/Kevlar composite materials

The cross-section morphology of MWNT/STG/Kevlar composite material is characterized. The Scanning Electron Microscope (SEM) image is shown in Fig. 5. Among them, Fig. 5 a, b, and c represent pure Kevlar fibers with particle sizes of 90 μm, 20 μm, and 90 μm, respectively. Fig. 5 a and b show the surface of pure Kevlar fibers, indicating a smooth surface. Fig. 5 c shows a pure Kevlar cross-section, indicating that the fiber gaps are unfilled. Fig. 5 d, e, and f represent MWNT/STG/Kevlar composite fibers with particle sizes of 90 μm, 20 μm, and 90 μm, respectively. Fig. 5 d and e show the surface of the composite fibers, indicating that the filled MWNT/STG material makes the fiber surface rough. Fig. 5 f shows the fiber cross-section. After filling with MWNT/STG material, the interior of the fiber is denser.

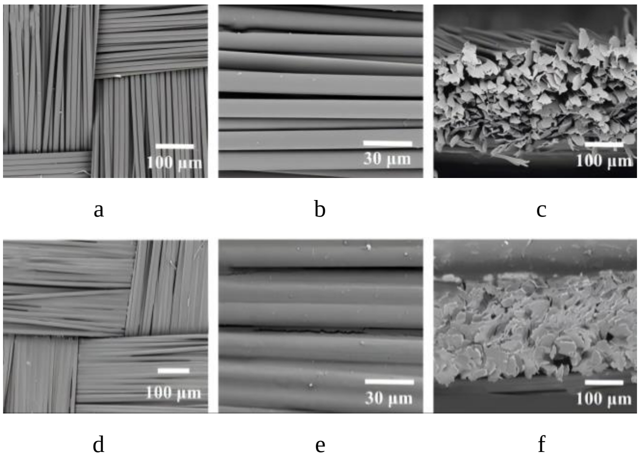


Fig. 5. SEM images of surfaces and cross-sections of Kevlar and MWNT/STG/Kevlar materials: a – the surface of pure Kevlar fibers with particle size of 90 μm; b – the surface of pure Kevlar fibers with particle size of 20 μm; c – the cross-section of pure Kevlar fibers with particle size of 90 μm; d – the surface of MWNT/STG/Kevlar composite fibers with particle size of 90 μm; e – the surface of MWNT/STG/Kevlar composite fibers with particle size of 20 μm; f – the cross-section of MWNT/STG/Kevlar composite fibers with particle size of 90 μm

3.2.2. Tensile fracture performance testing of MWNT/STG/Kevlar composite materials

To verify the tensile fracture properties of MWNT/STC materials doped with short fibers, radial and axial tensile tests are conducted. The fracture strength and displacement are used as evaluation indicators. Three different sample parameters are selected and the experiment is repeated four times for each sample. The results are shown in Fig. 6. MSK1 represents sample 1, with a length, width, and thickness of 13 mm, 6 mm, and 9 mm, respectively.

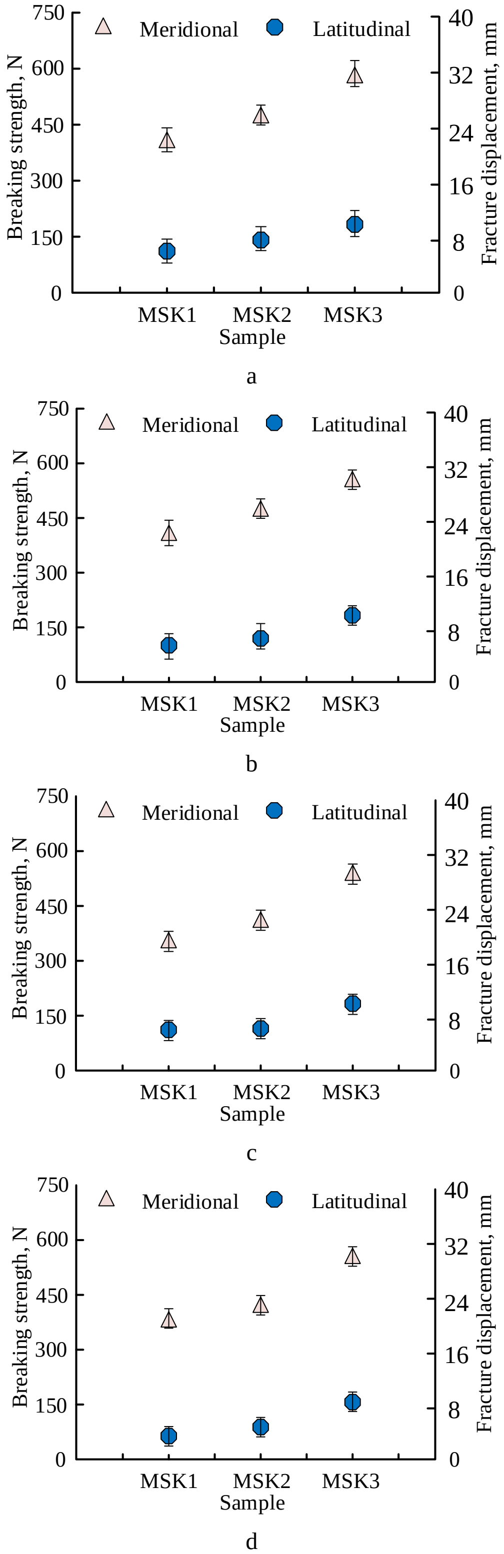


Fig. 6. Tensile fracture performance test results: a – experimental group; b, c, d – parallel experiments

MSK2 represents sample 2, with a length, width, and thickness of 16 mm, 9 mm, and 12 mm, respectively. MSK3 represents sample 3, with a length, width, and thickness of 19 mm, 12 mm, and 15 mm, respectively. In Fig. 6 a, in the first test, MSK3 showed the best fracture strength and displacement under radial tension, with values of 600 N and 38 mm, respectively. The other two tests performed slightly worse, but both exceeded 200 N and

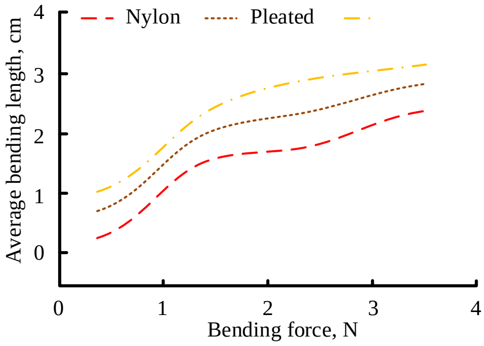
10 mm, which comply with the national standard GB/T21295-2014. When subjected to axial tension, MSK3 showed the best performance in terms of fracture strength and displacement. The other two tests performed slightly worse, but both exceeded 300 N and 8 mm, and also met national standards. The difference between the experimental results in Fig. 6 b, c, and d and Fig. 6 a was within 5 %. The results indicate that the proposed method has high tensile fracture performance and repeatability.

3.2.3. Bending performance testing of MWNT/STG/Kevlar composite materials

To verify the bending performance of the prepared MWNT/STG/Kevlar composite material, the method proposed for nylon fabric and pleated fabric are used to fill MWNT/STG shear thickening adhesive with the same process as experimental comparison. The bending length is used as the evaluation index. Four identical samples are selected for repeated testing, and each sample is cut into sizes of 22 mm in length, 55 mm in width, and 2 mm in thickness. The results are shown in Fig. 7. Fig. 7 shows the bending length and flexural strength of each composite material as the applied bending force gradually increases. The composite material prepared by the proposed method had the best bending performance, and the average bending curve was always above the other two composite materials. The average maximum bending length of the proposed composite material in four repeated tests was 3.14 cm, which was 10.2 % and 14.2 % higher than the composite materials prepared from nylon fabric and pleated fabric, respectively. In the four repeated experiments, there was no significant change in the test results of the three composite materials, with a difference within 5 %. Therefore, the MWNT/STG/Kevlar composite material prepared by the proposed method has high bending performance. When applied to knee pads, it can maintain the flexibility of the wearer's movement.

3.2.4. Breathability testing of MWNT/STG/Kevlar composite materials

The breathability of materials before and after composite is verified, using national standards as the baseline. The shell knee pads are used for comparison. The change in air permeability of the two materials with increasing material weight is shown in Fig. 8. From Fig. 8, in the two experiments using material thicknesses of 2 mm and 3 mm, the proposed composite material showed the best breathability, while the shell knee pads performed the worst. The breathability of pure Kevlar material before the composite was at an intermediate level. In two experiments, the average air permeability of the proposed composite material was 190 mm/s, meeting the national standard, which was 60 % and 78 % higher than that of shell knee pads and pure Kevlar, respectively. In the experiment with a material thickness of 3 mm, the air permeability decreased by 4 % compared with a thickness of 2 mm, and the difference was relatively small. Therefore, the composite material prepared by the proposed method has high air permeability and reliability, which meets the national standard when applied in practical knee protection equipment.



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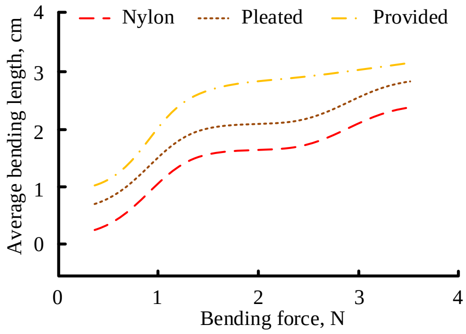

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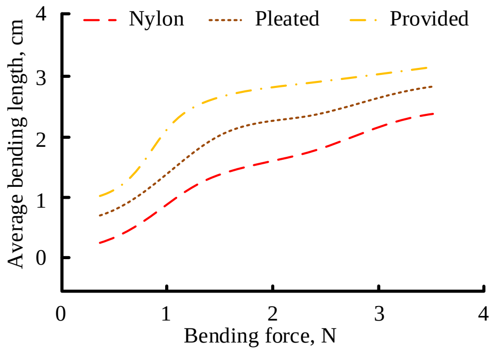

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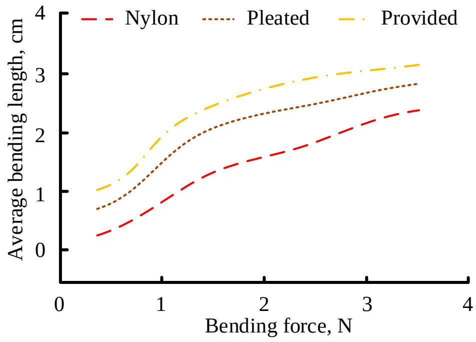

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Fig. 7. Comparison of bending properties of different composite materials: a – experimental group; b, c, d – parallel experiments

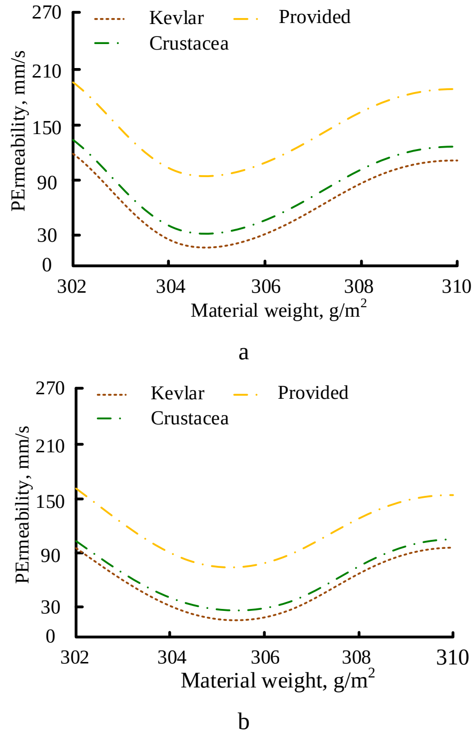

Fig. 8. Breathability testing of different material thicknesses: a – thickness of 2 mm; b – thickness of 3 mm

3.2.5. Low speed impact resistance testing of MWNT/STG/Kevlar composite materials

To verify the low-speed impact resistance of the prepared composite material, different impact energies are applied to the material to test the impact resistance. The maximum peak force of the material is used as the evaluation index. Three other DE, MC, and RI knee pads are also compared. The results are shown in Fig. 9. In Fig. 9 a, as the impact energy gradually increased, the force curve of the proposed composite material was below the Kevlar material before the composite. The maximum peak force of the proposed composite material was 4,000 N on average, which was 42 % lower than the pre-composite material. In Fig. 9 b, when gradually increasing impact energy was applied to four different knee pad materials, the proposed method exhibited the best impact resistance performance, with a maximum peak force of 3,405 N, which was 54 %, 57 %, and 68 % lower than DE, MC, and RI knee pad products, respectively. The results indicate that the impact resistance of the proposed composite material is better than before composite and superior to other knee pads.

3.2.6. Dynamic stab resistance performance testing of MWNT/STG/Kevlar composite materials

Due to the fact that martial arts anti-collision knee pads are commonly used in sports scenarios, dynamic anti-stab performance verification is conducted on the composite materials prepared in the research. Cutting tools weighing 400 g, 450 g, 500 g, and 550 g are dropped from the same height to pierce through composite materials. The time load curve is used as the evaluation index. Three types of DE, MC, and RI knee pads are compared. The results are shown in Fig. 10.

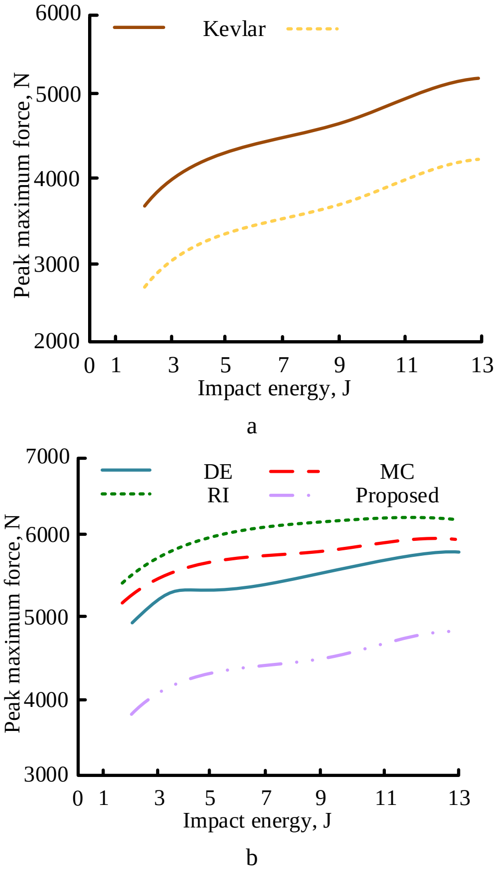

Fig. 9. Comparison of impact resistance performance of different materials: a – composite front and rear materials; b – different materials for knee pads

In Fig. 10 a, when using a 400 g knife for puncture testing, the average peak knife puncture load of the proposed material was 700 N, which was 39 %, 40 %, and 55 % higher than DE, MC, and RI knee pads, respectively. In Fig. 10 b, c, and d, the time-load curve remained consistent, with the difference of less than 2 % in the peak average knife piercing load of each material. Therefore, the proposed method has the best dynamic anti-stab performance and high reliability.

3.3. Discussion

In recent years, to mitigate chronic wear and acute impact injuries to the knee joint caused by high-intensity activities such as martial arts, researchers have explored various material designs for knee pads focused on impact absorption and comfort enhancement. Ding et al. explored natural weft yarn materials with excellent anti-collision performance, which had special arrangement and connection structures. Based on this structure, a longitudinal folding method was proposed to prepare a new weaving process to enhance the shear stress of fabrics [22]. Sun et al. proposed a shear thickening adhesive based on the optimal ratio of SiO_2 and $CaCO_3$. Its production process was optimized using the "impregnation drying method" to obtain the best performance sports anti-collision knee pads [23]. Balasooriya et al. proposed a shear thickening adhesive based on graphene, which effectively improved the tensile properties of fabric yarns to prevent displacement of knee pads during movement and enhance the impact resistance [24].

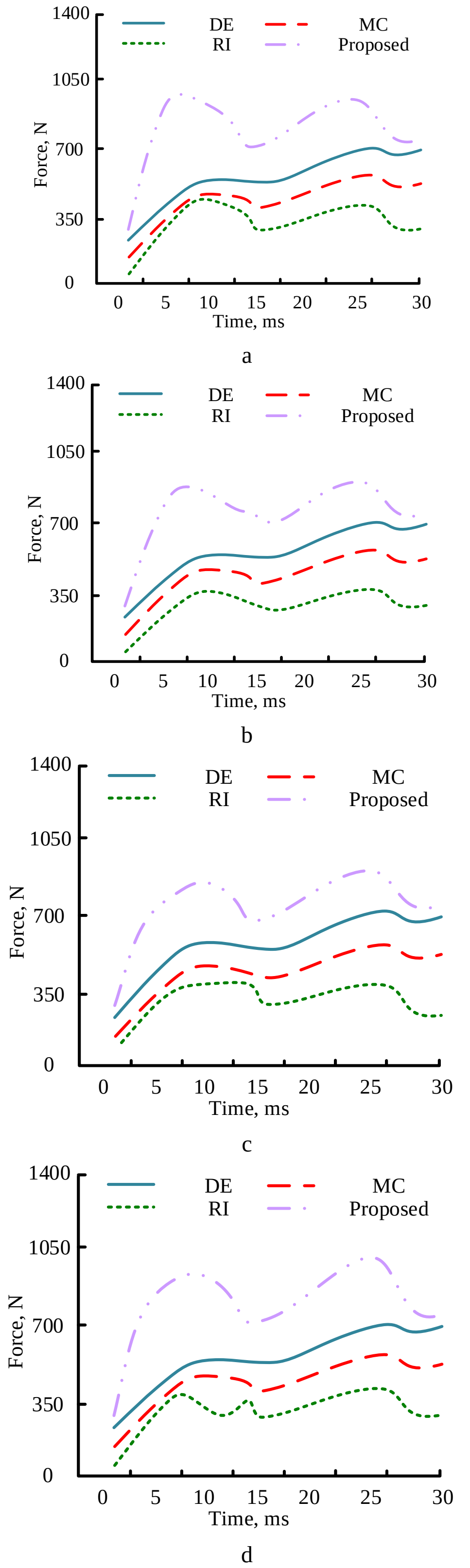

Fig. 10. Comparison of time load curves for different specimens: a – bayonet weight of 400 g; b – bayonet weight of 450 g; c – bayonet weight of 500 g; d – bayonet weight of 550 g

However, these approaches often face trade-offs between mechanical performance enhancement and wearability, with limited advancement in multi-functional synergy.

On the basis of previous work, this study proposes a MWNT/STG/Kevlar composite system that integrates shear-thickening mechanisms with multi-scale structural design, achieving coordinated improvements in mechanical stability, wearability, and impact resistance. Experimental results show that under 2-8 J impact energy, the maximum peak force of the proposed material is reduced by 42 %, 54 %, 57 %, and 68 %, respectively, compared with pure Kevlar and commercial DE, MC, and RI knee pad products. This demonstrates superior impact resistance within the typical force ranges encountered in actual movement. The enhanced performance can be attributed to the phase transition behavior of the STG component, which rapidly increases viscosity under stress, forming temporary “force chain networks” that convert the material into a quasi-solid state. Meanwhile, MWNTs contribute high rigidity and thermal conductivity, reinforcing the overall structural response and improving energy dispersion efficiency.

Dynamic mechanical analysis further confirms that the MWNT/STG composite exhibits increasing storage modulus and decreasing loss factor with higher shear frequency, indicating its ability to rapidly absorb energy and maintain structural stability under frequent impacts. The optimized process parameters indicate that a stirring speed of 710 rpm and a preparation temperature of 22 °C result in the most uniform dispersion of particles, thereby achieving the best shear thickening performance and reproducibility. This suggests that controlled interface interactions between dispersed phases play a key role in ensuring material performance stability.

In terms of wearability, the MWNT/STG/Kevlar composite also performs well. The bending test shows that the average maximum bending length is 3.14 cm, which increases by 10.2 % and 14.2 %, respectively compared with nylon and curly fabric composite materials. This allows better adaptation to joint movement. In breathability tests, the composite exhibits an average air permeability of 190 mm/s, substantially higher than that of traditional knee pad fabrics, alleviating local heat and moisture accumulation during extended wear. In tensile tests, the maximum fracture strength reaches 600 N, with a maximum displacement of 38 mm, exceeding the GB/T21295-2014 national standard and outperforming most EVA- and PU-based knee pad composites reported in the literature. Notably, in dynamic anti-puncture experiments, the material withstands higher puncture loads under various knife weights, indicating strong resistance to sharp dynamic impacts and reliable emergency protection.

In summary, the proposed MWNT/STG/Kevlar composite material successfully builds a micro-scale shear-induced adhesive network and a macro-scale rigid support architecture through structural and process-level synergy. Under repeated use, it can simultaneously optimize impact resistance, comfort, and durability. Compared with existing knee pad materials, this composite demonstrates clear advantages in performance integration, balanced functional properties, and practical applicability. The findings expand the application scope of shear-thickening materials in protective sports gear, providing a feasible design path for future wearable impact protection solutions.

4. CONCLUSIONS

The results indicate that the polymer material prepared in the study has been effectively applied in the anti-impact knee pads of martial arts STG. The main conclusions drawn from the research are as follows:

1. In terms of preparation process, during the preparation of MWNT/STC, as the shear frequency increased, the loss factor gradually decreased from greater than 1 to below 1, and the storage modulus gradually increased, which was consistent with the dynamic properties. When the stirring speed was 710 MPa and the temperature was 22 °C, the shear thickening effect was better. After filling MWNT/STC shear thickening adhesive into Kevlar smooth fabric, the fibers of the fabric were tight.
2. In the tensile fracture performance test, after cutting the composite material into different sizes, the worst fracture strength and displacement were 600 N and 38 mm, respectively, both of which met national standards.
3. In the bending resistance performance test, the average maximum bending length was 3.14 cm, which was 10.2 % and 14.2 % higher than the composite materials prepared from nylon fabric and pleated fabric, respectively, indicating high flexibility.
4. In terms of breathability, the material had an average breathability of 190 mm/s at 2 mm and 3 mm, which met national standards. It was 60 % and 78 % higher than shell knee pads and pure Kevlar, respectively.
5. In the low impact resistance test, the maximum force peak of pure Kevlar and the other three knee pad products was reduced by 42 %, 54 %, 57 %, and 68 %, respectively. Therefore, the composite MWNT/STG/Kevlar composite material has excellent performance and wearing comfort in protecting the knee joint compared with single pure Kevlar and other knee protection products.

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