Dry Spinning of Continuous Graphene Oxide/TPU Composite Fibers with Excellent Strength and Toughness

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Abstract. Graphene fiber has broad application prospects in aerospace, biomedical and other fields because of its excellent mechanical properties. In this paper, graphene oxide (GO) and thermoplastic polyurethane (TPU) composite fibers have been prepared by two comparable methods including wet spinning and dry spinning. The fibers obtained by dry spinning show better strength and toughness compared with wet spinning. Further research results show that the dry spinning process can effectively control the internal microstructure of the fiber, improve the internal stress distribution and load transfer efficiency, then realize the optimization of its macro mechanical properties. This study will provide useful guidance for the optimization strategy of internal microstructure and the improvement of preparation process of graphene fiber.

1. Introduction
Graphene is a new type of high-performance nanomaterials with excellent elastic modulus, tensile strength and flexibility [1-3]. At present, researchers have prepared a variety of macro graphene derivatives, such as one-dimensional fiber [4,5,10], two-dimensional film [6,7] and three-dimensional block [8]. Compared with bulk and thin film materials, graphene fiber [4,5,9] has attracted great attention due to its light weight, high strength and flexibility, since it was created by the wet spinning by Gao and Xu in 2011 [10].

Some methods have been developed for the preparation of graphene-based fiber composites in recent years. Among them, wet spinning [11-13] is the most commonly used method. During the wet spinning process, the continuous unidirectional flow of the GO liquid crystals solution, makes the free powder crystal phase change into uniform orientational order of GO sheets, which are immobilized by gelation in coagulation baths. The dry spinning approach [14] is another industrially viable strategy and can be used to fabricate continuous graphene fiber. Different from the wet spinning, GO liquid crystals are extruded from a dry-spun spinneret and directly shaped into fibers without a coagulation bath. To ensure the successful fabrication of continuous GO fibers by the dry spinning method, the concentration of the spinning original solution is high enough to form viscoelastic liquid crystals gels and the solvent of the GO spinning dope need to have the characteristics of low surface tension and high saturated vapor pressure. Due to avoid the trouble of using a coagulation bath, dry spinning has higher spinning efficiency, energy saving and environmental protection compared with wet spinning, and is a potential ideal green preparation technology of GO fiber. It is worth noting that the dry-spun GO fiber has good flexibility and toughness, but generally shows poor tensile strength due to the existence of many micropores [15,16]. It has been assumed that some polymers are introduced
between GO sheets, which would regulate the internal microstructure and reduce the interlayer defects, as so to optimize the internal stress distribution and load transfer, thus effectively improving the overall mechanical properties of the GO fiber. As a result, the dry spinning fiber would show superior properties.

In this paper, two kinds of GO-TPU composite fibers have been obtained by dry spinning and wet spinning. It is found from the results of the microstructure characterized that the internal defects in dry-spun GO fibers are effectively inhibited compared with the wet one. The mechanical test results show that the mechanical properties of the composite fiber prepared by dry spinning are better than those by wet spinning. In order to further analyze the enhancement mechanisms of the strengthening and toughening of dry spinning fiber, the effect of internal defects in the fiber on the macro mechanical properties of the material is studied by finite element numerical simulation, combined with the microstructure characteristics. The results show that, compared with wet spinning, the internal defects of dry spinning fiber are more minor, which would be beneficial to alleviate the local stress concentration in the staggered laminated structure [17-19] and delay the ultimate failure of the material, as so to effectively improve the macro mechanical properties of nacre-like structure materials. The work in this paper will provide useful guidance for the optimization strategy of internal microstructure and the improvement of preparation process of fiber composites.

2. Experiment and characterization
Firstly, the improved Hummers’ method was used to prepare the ethanol solution of GO. The DMF mixture of GO-TPU was obtained by adding TPU-DMF solution into GO solution. Then, GO fibers were prepared by wet spinning and dry spinning methods. On the self-made wet spinning device, the GO-TPU dopes were loaded in the plastic syringe and injected into the CTAB coagulation bath of 5 mg/ml with the injection pump (diameter: 0.51 mm) at a stable spinning speed. The obtained GO-TPU fibers were dried at 45 ℃ for 48 h after taking out from the coagulation bath. The main preparation process is shown in figure 1 (A). Compared with the above wet spinning process, the GO-TPU mixed solution with relatively high concentration was also loaded into the injection pump (diameter: 0.51mm) by using the self-made dry spinning device, and it was directly spun into the fiber at a stable speed without coagulation bath. After drying at 45 ℃ for 48 h, the dry-spun GO-TPU fiber was obtained. The main preparation process is shown in figure 1 (B).

The mechanical properties of the fibers were tested on an Instron 3343 dynamometer with a loading speed of 1 mm/ min. The microstructure of the specimens was characterized by a scanning electron microscopy (SEM) system (Type: JEOL 7100F, accelerating voltage: 10 kV).

Figure 1. (A) Schematic diagram of wet spinning process (B) Schematic diagram of dry spinning process.
3. Results and discussion

The test results of mechanical properties of fibers prepared by wet spinning with different mass ratios of TPU and GO are shown in figure 2 (A). It can be found that when the mass ratio of TPU to GO is 10:100, the fiber shows better mechanical properties (strength: 105.28 MPa, toughness: 2.09 MJ/m³). On this basis, the spinning dope with this mass ratio of 10:100 (TPU and GO) has been selected for the preparation of dry-spun fibers. The mechanical properties test results of GO-TPU composite fibers obtained by the wet spinning and the dry spinning with the same composition are compared in figure 2 (B) and (C).

Figure 2. (A) Tensile test results of GO-TPU fibers obtained by the wet spinning with different mass ratio of TPU to GO , (B) and (C) Tensile test results of GO-TPU fibers obtained by different preparation processes with the mass ratio of 10:100.

It has been shown in our previous research [20] that GO-TPU composite with nacre-like structure contains the hard sheets and the soft rubber layer. Their respective mechanical properties, the mass ratio between them, their interface bonding characteristics, the formed microstructure and so on, have an important impact on the stress distribution and load transfer inside the composite material, and then affect the macro-mechanical properties of the material. It can be seen from figure 2 (B) that different spinning processes have significant effects on the mechanical properties of GO-TPU fiber materials. When wet spinning is used, the tensile strength and toughness are 105.28 MPa and 2.09 MJ/m³, respectively. However, when the dry spinning process is adopted, its strength and toughness reach 176.78 MPa and 2.81 MJ/m³, which are 67.91% and 34.45% higher than those prepared by wet spinning, respectively. The reason may be that the GO-TPU solution in the unidirectional flow microtubule during injection spinning is controlled by the shear flow field, and the GO sheets in the microtubule have the preferred orientation. In the dry spinning process, the high concentration of the GO-TPU spinning dope leads to poor fluidity of GO sheets. Therefore, the orderly arrangement of GO sheets can be better maintained after spinning. In addition, the interlayer structure is denser because of the higher concentration, which results in fewer internal defects. The internal micro morphology of these two kinds of fibers prepared by the dry spinning and the wet spinning is characterized by the SEM system. The results have been shown in figure 3. It is found that the micro morphology of composite fibers prepared by different processes is entirely different. In figure 3 (B) and (E), the cross sections of the fibers prepared by the two processes have been characterized to observe their differences. It can be found that the cross section of dry-spun fiber is denser than that of wet-spun fiber. The SEM images with higher resolution in figure 3 (C) and (F) show that the inner GO sheets of wet-spun fiber have more obvious wrinkles compared with dry spinning. What's more, there are some large pores (the dotted area in figure 3 (F)) in the lamellar of the wet-spun fiber, but only some tiny pores (the dotted area in figure 3 (C)) in the cross section of the dry-spun fiber. In addition, it can also be found from figure 3 (C) and (F) that both types of the GO-TPU composite fibers prepared by different methods have regular layered structure in which TPU is embedded between the GO sheets. This structure is similar to the alternate laminated structure of "brick-mortar" arrangement in nacre. In this structure, the hard material lamella as the brick mainly bears the normal stress, while the soft material as the mortar mainly transfers the load through shear deformation. Relatively fewer defects in
the dry-spun fiber than that in the wet-spun fiber have an important impact on the internal stress distribution and load transfer efficiency, then affect the strength and toughness of the material. This aspect will be further analyzed below.

![Figure 3. SEM characterization results of GO-TPU fibers prepared by different spinning processes with the mass ratio of 10:100, (A-C) dry spinning, (D-F) wet spinning. (A) and (D) profile morphology, (B) and (E) Cross-sectional morphology, (C) and (F) the enlargement of cross-section morphology.](image)

For the GO-TPU composite fiber with nacre-like structure, the internal defects would cause a high concentration of shear stress, further induce the debonding of the lamellar interface, and finally lead to the macroscopic failure of the material. In this paper, the ABAQUS analysis software has been used to analyze the influence of the internal hole defects of this nacre-like material on the full-field stress distribution. An ideal centrosymmetric alternating laminated structure is used as the geometric model of the material. In the model, the aspect ratio of the GO sheet is 200:1. One end of the model is fixed and the other is pulled. The external equivalent stress of the fiber is set as 100MPa. The elastic modulus and Poisson's ratio of GO are 77 GPa and 0.175 respectively. The elastic modulus and Poisson's ratio of TPU are 60 MPa and 0.47. The type of meshing unit is CPS4R. Several typical pores are designed in the model to represent the defects inside the fiber. The simulation results are shown in figure 4.

![Figure 4.](image)

It can be seen from figure 4 that the pores in the composite fiber can affect the shear stress distribution and further influence the macro mechanical properties. When the model is in the ideal state without pores, shown in figure 4 (A) and (B), the peak value of internal normal stress is 217.6 MPa, and the interfacial shear stress is mainly concentrated at the end of GO sheets. In addition, the closer to the end of GO sheets, the more obvious the shear stress concentration will be. The peak value of shear stress is 6.23 MPa. When there is a small pore (like the micro pores in figure 3 (C)) close to the end of the sheet, the peak value of interfacial shear stress increases to 8.86 MPa, and the stress concentration intensifies at the pore tip (figure 4 (D)). Therefore, the interface debonding is easy to spread from here to the whole sample. As shown in figure 4 (E) and (F), if there are multiple pores (like the dotted area in figure 3 (F)) inside the material, the peak interfacial shear stress increases sharply from 6.23MPa to 20.80MPa. At this time, the material is easy to be damaged by the increased shear stress from the lamella near the pores, which will eventually lead to global failure. For the GO sheet, its ultimate strength far exceeds that of TPU. So, it’s hard to be broken, which will lead to that the material failure is mainly caused by the interfacial debonding and the GO sheets pulling out due to shear fracture. It can also be seen from figure 3 (C) and (F) that the cross sections of the fibers are
uneven due to the pulling out of the GO sheets, and the existence of pores will cause shear stress concentration. This result indicates that the more the pore defects are, the more obvious the stress concentration is. In comparison, as for the fiber prepared by dry spinning, the inner defects (like the case as shown in figure 4 (C) and (D)) are more minor and fewer than that prepared by wet spinning (like the case as shown in figure 4 (E) and (F)). So, the stress concentration inside the dry-spun fiber is less significant compared with the wet one, then the mechanical properties of dry-spun fiber increase as a result.

Figure 4. Full-field stress analysis results including the distribution of normal stress (left) and shear stress (right), where (A) and (B) no pores, (C) and (D) a small pore (The pore size is 1/3 of the length of GO sheet, (E) and (F) multiple holes (From top to bottom, the hole size is 1/5, 2/3 and 1/3 of the length of GO sheet).

4. Conclusion
In this paper, GO-TPU composite fibers have been prepared by wet spinning and dry spinning. The fiber obtained by dry spinning shows better strength and toughness. Then the internal microstructure of these two kinds of fiber is characterized by SEM and the mechanical behavior of them is analyzed by finite element analysis. The results show that the internal defects of the composite fiber prepared by the dry spinning process are more minor than those by wet spinning, which can effectively control the microstructure of the fiber, improve the internal stress distribution and load transfer efficiency, thereby optimizing its macro mechanical properties. This study will provide useful guidance for the optimization strategy of internal microstructure and the improvement of the preparation process of GO composite fiber.

Acknowledgement
This work was supported by the National Natural Science Foundation of China [No.12041202] and the “1331 project” Key Innovation Team Building Plan of Shanxi Province.

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