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UNIVERSITY OF CALIFORNIA, SAN DIEGO

Polymer nanofiber reinforced double network gel composites: strong, tough and
transparent

A thesis submitted in partial satisfaction of the requirements for the degree Master of
Science

in

Engineering Science (Mechanical Engineering)

by

Qiguang He

Committee in charge:

Professor Shengqiang Cai, Chair
Professor Renkun Chen
Professor Michael T. Tolley

2016

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2016

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ACKNOWLEDGEMENTS

This work was completed and supported by Professor Shengqiang Cai. I would like to thank him for giving me this precious opportunity to do research with his careful supervision. Also, Professor Cai always gives me brilliant ideas and inspirations during my research career.

Dr. Zhijian Wang, Yumin Yan and Jianlin Zheng, I would also thank for providing me suggestion during my thesis project. Thank for your hardworking which make this project goes well.

Lastly, I would thank my parents who give me great support and always take good care of me during my master career.

Chapter 1, in full, is a reprint of the material as it appears in *Extreme Mechanics Letters* 2016. Qiguang He; Zhijian Wang; Yumin Yan; Jianlin Zheng; Shengqiang Cai. The thesis author was the primary investigator and author of this paper.

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ABSTRACT OF THE THESIS

Polymer nanofiber reinforced double network gel composites: strong, tough and
transparent

by

Qiguang He

Master of Science in Engineering Science (Mechanical Engineering)

University of California, San Diego, 2016

Professor Shengqiang Cai, Chair

Double network gel is well known for its extraordinarily high toughness and stretchability. However, compared to natural rubber and many soft biological tissues such as articular cartilage and tendon, both strength and stiffness of double network gel are significantly lower, which greatly limits its further applications. In this article, to improve mechanical properties of double network gel, we embed a small percentage of aligned electrospun polymer nanofibers into double network gel matrix to make a sandwich-like double network gel composite. Mechanical tests conducted by us show that polymer nanofiber reinforced double network gel composite have

much higher strength and stiffness, while maintaining its good transparency.

1. Introduction

A combination of two different polymer chains can lead to a double network gel (DN gel) with high toughness and high stretchability [1-3]. Thanks to excellent mechanical properties, DN gels have drawn intensive attention for their potential applications in diverse areas such as tissue replacement [4-6], microfluidic devices [7] and soft robotics [8]. Recently, tremendous efforts have been made by different researchers to synthesize various DN gels, including temperature-sensitive DN gels [9, 10] pH-sensitive gels [11] and supramolecular DN hydrogels [12].

However, compared to many soft biological tissues such as articular cartilage and tendons, the strength of DN gels is significantly smaller. For example, tensile strength of articular cartilage is around 1-48MPa [13], while the typical strength of DN gel is usually one order of magnitude smaller [1, 14-16]. To make DN gel stronger, different strategies have been recently adopted. For example, fracture toughness and mechanical strength of DN gel can be enhanced through introducing microvoids or microparticles into it [17, 18]. In addition, through embedding reinforced fibers into DN gel matrix, one can also obtain DN gel composite with high strength and stiffness [19]. For instance, Liao et al. integrate a three-dimensional woven fibrous films into a DN gel and obtain a DN gel composite with greatly improved strength [16]. Illueperuma et al. fabricate steel fiber reinforced DN gel composite with high strength [19]. However, in most of these studies on the fiber reinforced DN gel composite, to have significant strengthening effect, the weight percentage of the reinforced fibers is typically high

(over 5%) [19, 20], which may significantly alter the properties of DN gel such as optical transparency, mobility of different species in the gel and their biocompatibilities.

Since the first fabrication of electrospun polymer nanofibers, they have been used as reinforcement for composites by different researchers [21, 22]. Electrospun polymer nanofibers have many superior mechanical properties, compared to their bulk counterparts. For example, both strength and toughness of electrospun polymer nanofibers can be dramatically higher than their bulk counterparts [23-25]. Many bioengineering studies have also shown that electrospun polymer nanofibers have better biocompatibility and can facilitate the formation of different tissues [26]. Therefore, electrospun polymer nanofibers have been widely used as medical prostheses [27, 28], tissue template [28, 29], wound dressing [26] and drug delivery carriers [30, 31].

Although fiber reinforced gel composites have been studied previously, according to our knowledge, no report can be found in the literature about using electrospun polymer nanofiber to reinforce DN gels. In this article, we are going to demonstrate that with including a small percentage of electrospun polymer nanofibers, both stiffness and strength of DN gel composites can be dramatically enhanced. We hope that our studies in the article can further broaden engineering applications of DN gels.

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2. Experiment

2.1 Fabrication of aligned polyacrylonitrile (PAN) nanofibers

0.75g powder of PAN ($M_n=150,000$ g/mol; Sigma Aldrich, USA) and 0.03g calcium chloride (Fisher Scientific, USA) were dissolved in 9.25g dimethylformamide (Fisher Scientific, USA). Another concentration of PAN polymer solution was made by dissolving 0.50g powder of PAN and 0.03g calcium chloride in 9.5g dimethylformamide. Both solutions were stirred for 2 h to obtain homogeneous ones at 45 °C. A dissolved polymer solution was then placed into 10 mL plastic syringe with 18-gauge needle.

Schematic of electrospinning setup is shown in Figure. 2.1. Positive electrode of high voltage power supply was attached to the 18-gauge needle by alligator clip and its negative electrode was connected to drum collector. 20 kV was applied by the power supply. A syringe pump (Cole-Parmer, USA) was used to precisely control the flow rate of polymer solution from the needle, which was set at 0.02 mL/min. Aluminum foil was wrapped around the surface of drum to collect electrospun polymer nanofibers. The rotating speed of the drum was set to be 750 round/min. The distance between tip of needle and drum was 15 cm.

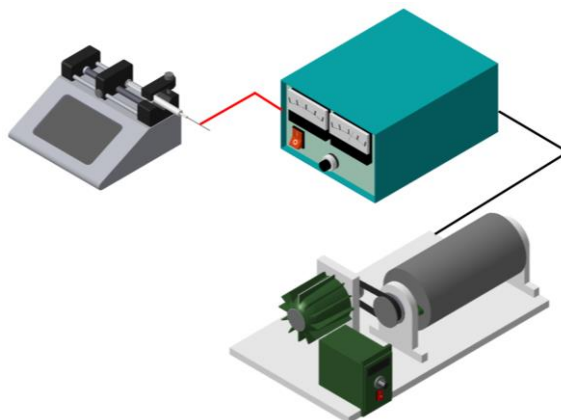


Figure 2.1: Schematic of electrospinning setup in our experiment.

Time for electrospinning was set as 30 min, 1 h, 2 h and 3 h to obtain the fibers with different amount. After electrospinning, electrospun polymer nanofiber film was cut into 50 mm×30 mm pieces and kept in chamber for 24 h for complete solvent evaporation.

2.2 Morphology of aligned PAN fibrous film

The morphology of PAN fibrous film and single PAN fiber were characterized by optical microscope (ZESIS) and scanning electron microscope (SEM) (FEI XL30).

2.3 Preparation of PAN nanofiber reinforced hydrogel

Double network hydrogel was prepared by following the previous article [3]. Briefly, 8 g acrylamide (99+%; Arcos, USA), 1g alginate (FMC Biopolymer, LF10/60, USA), 0.0048 g N, N'-methylenebis(acrylamide) (MBAA) (Sigma Aldrich, USA) as crosslinker for acrylamide, 0.02 g ammonium persulfate (>98%; Sigma Aldrich, USA) as thermal initiator for acrylamide are dissolved in 51g deionized water. Mixture was stirred for 2 h to be homogenous. Then, the solution was degassed in the vacuum

chamber and denoted as solution 1. 0.02 g N,N,N',N'-tetramethyl-ethylenediamine (TEMED) (>99%; Sigma Aldrich, USA) as initiator accelerator and 0.1328 g calcium sulfate dihydrate (98%; Sigma Aldrich, USA) as ionic crosslinker for alginate were dissolved in 5 g deionized water. The mixture was sonicated for 2 min and was denoted as solution 2.

In the experiment, in order to make DN gel-PAN fiber laminate, solution 1 and solution 2 were firstly mixed and form homogeneous solution which contain AAm monomer, alginate and CaSO₄. Then, the solution was poured into a homemade mode with the dimension of 50mm×30mm×20mm. Immediately after that, aligned PAN fibrous film collected by drum collector was put on the top of the solution. After fibrous film was fully wetted, same amount of solution was poured on the top of the thin film to make another gel layer. Finally, the “sandwiched-like” specimen was put into the oven under 53 °C for 100 minutes to initiate polymerization of AAm and form a DN gel matrix.

2.4 Tensile test

Tensile test of DN gel composite was performed using Instron Machine (5965 Dual Column Testing systems, Instron) with a 1000 N loading cell. Samples were cut into dumbbell-shape. The ends of sample were glued onto acrylic plates that were clipped by the clamp of Instron machine. The engineering strain rate of our tensile testing was fixed at 0.05 s⁻¹. For each condition, 3 measurements were conducted.

2.5 Transmittance test

Transmittance test of DN gel was conducted using UV-Vis spectroscopy (UNICO 4802 UV/Vis double beam spectrophotometer).

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The thesis author was the primary investigator and author of this paper.

3. Results and discussion

In the experiments, we prepared electrospun PAN nanofibers by following the method described in the literature [32]. It has been shown in many previous studies that mechanical properties of electrospun PAN nanofibers strongly depend on their diameters, which can be well controlled by tuning the electrospinning voltage. In our experiment, the electrospinning voltage is set to be 20 kV and the diameters of the electrospun polymer fibers from two different PAN solutions were around 300nm and 150nm as shown in Figure 3.1 (b) and Figure 3.1 (c). A rotating drum collector was used to continuously collect electrospun PAN fibers. Figure 3.1 (a) shows a well-aligned electrospun PAN fibrous film under optical microscope.

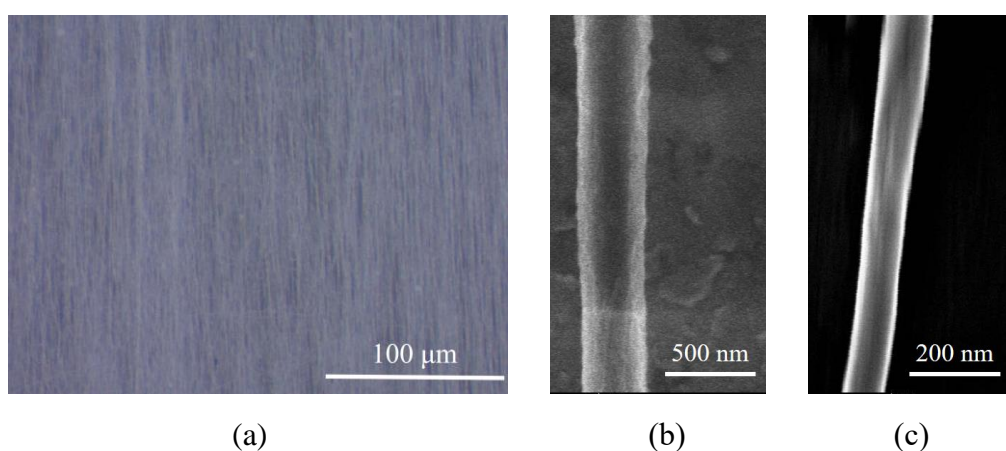


Figure 3.1: Images of PAN fibrous film. (a) Dark-field optical micrographs of aligned PAN fibrous film. (b) SEM image of single PAN nanofiber, the diameter of PAN fiber is 300nm. (c) SEM image of single PAN nanofiber, the diameter of PAN fiber is 150nm.

Figure 3.2 (a) shows the structure of the sandwich-like DN gel composite fabricated in our experiments. An aligned PAN fibrous film is placed in the middle of two layers of DN gels as shown in Figure 3.2 (b), the DN gel composite is semi-transparent with the PAN fibrous film of 0.3 wt% and 0.45 wt%. The transmittance

spectra of DN gel composites with 0.3 wt% fiber is shown in Figure 3.2 (c). As pointed out in the literature [33], one advantage of using electrospun polymer nanofibers as reinforcement for composite is that the composite can be made transparent to visible light, because the diameter of electrospun polymer nanofibers can be much smaller than the wavelength of visible light. In our experiment, although the DN gel composite is semi-transparent as shown in Figure 3.2 (b) due to the large fiber diameters, it is still much more transparent than most fiber reinforced gel composite made by others [16, 19]. We believe the transparency of the DN gel composite can be further improved by further reducing the diameter of the nanofibers [34]. In many applications, transparency of hydrogels is regarded as one of highly desired features. Examples include responsive hydrogel lens [35], transparent ionic conductors [36], and stretchable electroluminescent devices [37].

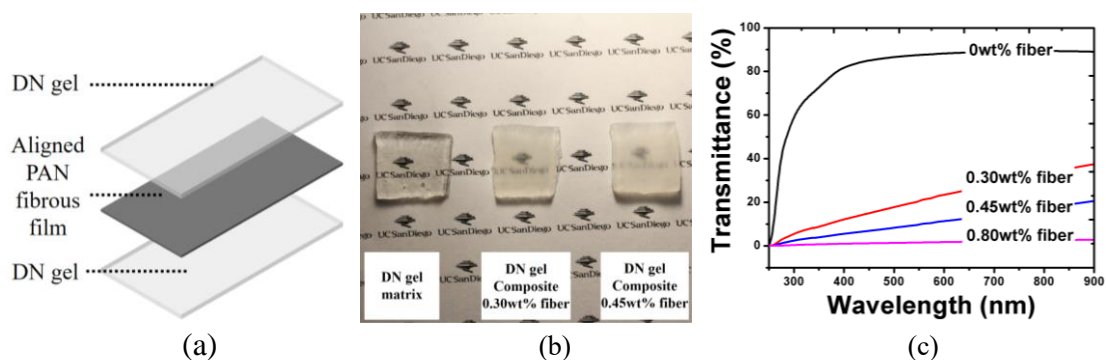


Figure 3.2: (a) Schematic of sandwich structure of DN gel composite. (b) Photos of DN gel matrix (Left) and DN gel composite (Middle and Right). (c) The transmittance spectra of DN gel composites for different weight percentage of fibers.

To measure the mechanical properties of DN gel composite, we next conduct uniaxial tensile tests. The direction of the tensile force was along the fiber direction as shown in the inset of Figure 3.3 (a). The fiber diameters in Figure 3.3 (a) and (b) are

300nm and 150nm, respectively. It can be clearly seen from the stress-strain curve of DN gel composite, with adding a small weight percentage of PAN nanofibers, both strength and initial stiffness of the composite are dramatically higher than DN gel matrix. For example, with including 1.04 wt% of PAN nanofibers, the tensile strength of DN gel composite increases from 95KPa for DN gel matrix to 420KPa, and the initial stiffness of DN gel composite increases from 20KPa for DN gel matrix to 3.4MPa. This is simply because both strength and stiffness of PAN nanofibers are dramatically higher than DN gel matrix. As reported in the literature [32], Young's modulus and strength of PAN nanofibers are 815MPa and 21.5MPa respectively, as compared to 20KPa and 77.8KPa for DN gel matrix used in our experiments.

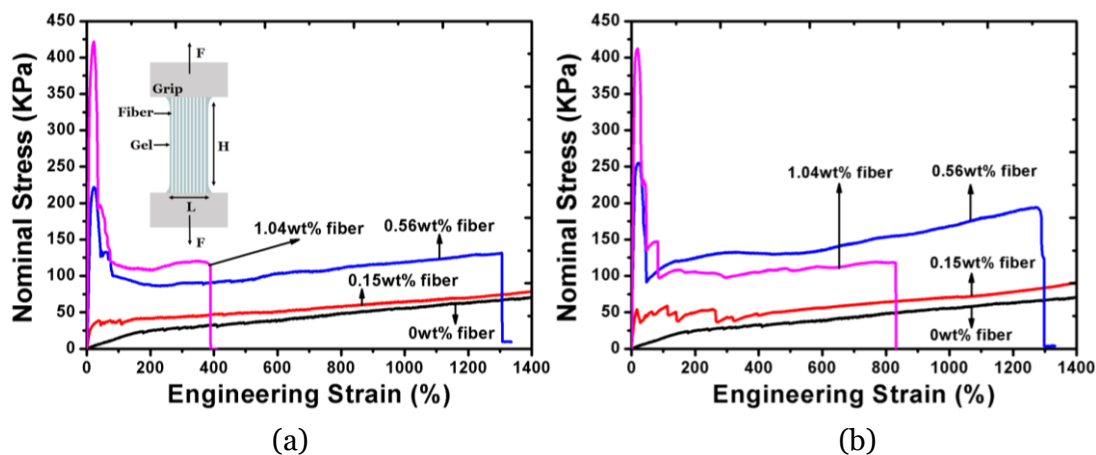


Figure 3.3: Stress-strain curves of fiber reinforced DN gel composite with different weight percentage of electrospun PAN nanofibers. (a) The diameter of single PAN fiber is around 300nm. (b) The diameter of single PAN fiber is around 150nm.

As illustrated in Figure 3.3 (a) and (b), the shapes of stress-strain curves of DN gel composite are also dramatically different from DN gel matrix. For DN gel matrix or the DN gel composite with ultralow weight percentage of PAN nanofibers (0.15 wt%), the

stress-strain curve is monotonic. However, for DN gel composite, except for the one with the lowest weight percentage of polymer nanofibers, there is a peak stress in the stress-strain curve, which corresponds to its mechanical strength. After the peak stress is reached in the tensile test, the stress drops to a much lower value. The stress maintains the lower level with further deformation till the sample breakage. We believe the drop of the peak stress in DN gel composite in the tensile tests is mainly due to the breakage of the embedded PAN nanofibers. The corresponding strain for the peak stress in all the DN gel composite are around 21%, which is close to the rupture strain of aligned PAN nanofiber network [32]. As shown in Illeperuma's paper [19], in steel fiber reinforced DN gel composite, the sliding between the reinforced of fibers and gel matrix is one of the damage mechanisms. In our DN gel composite, after the first breakage of PAN nanofibers, further deformation of DN gel composite may involve the sliding between PAN nanofibers and DN gel matrix and fragmentation of PAN nanofibers as shown in Figure 3.4 (a-c).

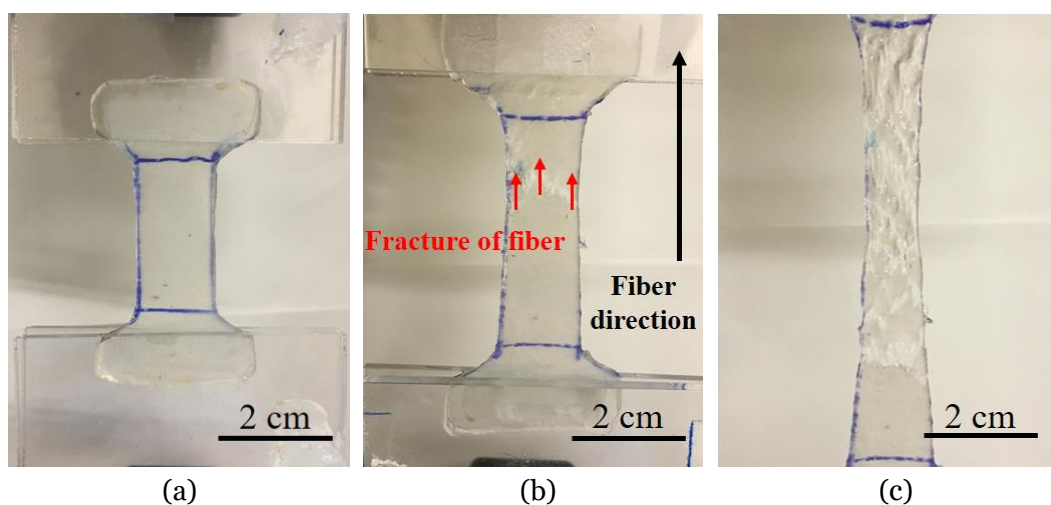


Figure 3.4: A group of representative photos of DN gel composites under tensile test. When the stretch is large, PAN fibrous film breaks into pieces. The engineering strain for (a), (b) and (c) are 0%, 30% and 145% respectively.

Comparing the stress-strain diagram of Figure 3.3 (a) and (b), we find that fiber diameter has little effect on the overall performance of the DN gel composite. It is mainly because mechanical properties of PAN fiber has weak size dependence between when its diameter is larger than 100 nm [38].

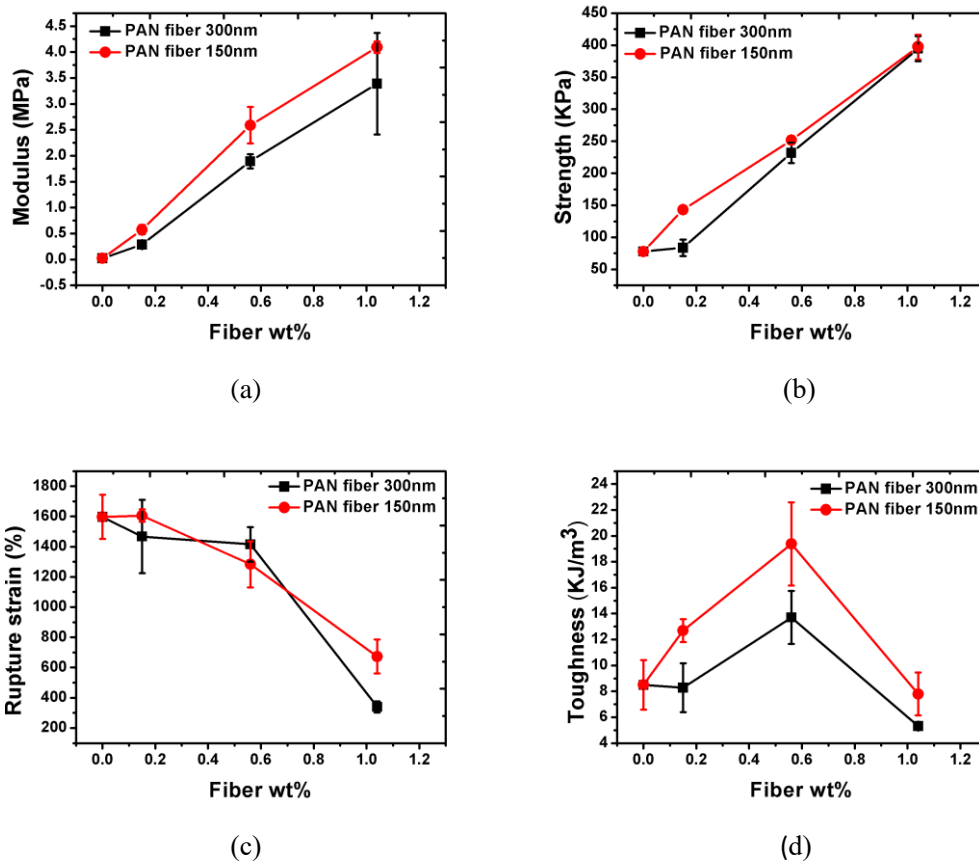


Figure 3.5: Effects of the weight percentage of polymer nanofibers with two different diameters on the overall mechanical properties of DN gel composite. (a) Elastic modulus (b) tensile strength (c) Rupture strain (d) Toughness.

Figure 3.5 illustrates the quantitative effects of weight percentage of PAN nanofibers on the mechanical properties of polymer nanofiber reinforced DN gel composite. For instance, for the DN gel composite with 300nm diameter fibers, the

small deformation Young's modulus of the DN gel composite can increase from 20KPa to 3.4MPa with 0 wt% to 1.04 wt% PAN fibers. Similarly, the tensile strength of the DN gel composite increase from 94.9KPa to 421.5KPa. Figure 3.5 (c) shows the relationship between rupture strain of DN gel composite and weight percentage of PAN nanofibers. When the weight percentage is 0.15%, the rupture strain is around 1500%, which is similar to DN gel matrix. As the weight percentage gradually increase, the rupture strain decreases. When the weight percentage of polymer nanofiber is 1.04%, the rupture strain decreases to 400%. By integrating the area enclosed by the stress-strain curve of DN gel composite in Figure 3.3, we can obtain toughness of DN gel composites. Figure 3.5 (d) illustrates how the toughness of DN gel composite varies with fiber weight percentage. The toughness of the composite first increases and then decreases with increasing the weight percentage of PAN nanofibers. The maximum toughness of the DN gel composites with 300 nm diameter fiber can reach 12 kJ/m^3 with 0.56wt% fibers. It demonstrates that in addition to significant enhancement of stiffness and strength, toughness of DN gel can also be improved by including certain amount of electrospun polymer nanofibers. The toughness enhancement in DN gels may attribute to the rupture/fragmentation of nanofibers and the sliding between the fiber and gel matrix.

Since the PAN nanofibers are aligned in the gel composite, mechanical properties of the DN gel composite are expected to be anisotropic. We next conduct tensile tests on the DN gel composite with the loading direction perpendicular to the direction of

PAN fibers. The stress-strain curves of the DN gel composite with 0.41 wt% PAN nanofibers for two perpendicular loading directions are shown in Figure 3.6 (a). The stiffness of the DN gel composite in two perpendicular directions are both significantly higher than DN gel matrix. Images of DN gel composite with loading direction perpendicular to fiber direction are shown in Figure 3.6 (b) and (c). In the process of tensile deformation, as shown in Figure 3.6 (c), PAN nanofibers reorient toward the loading direction to stiffen the DN gel composite.

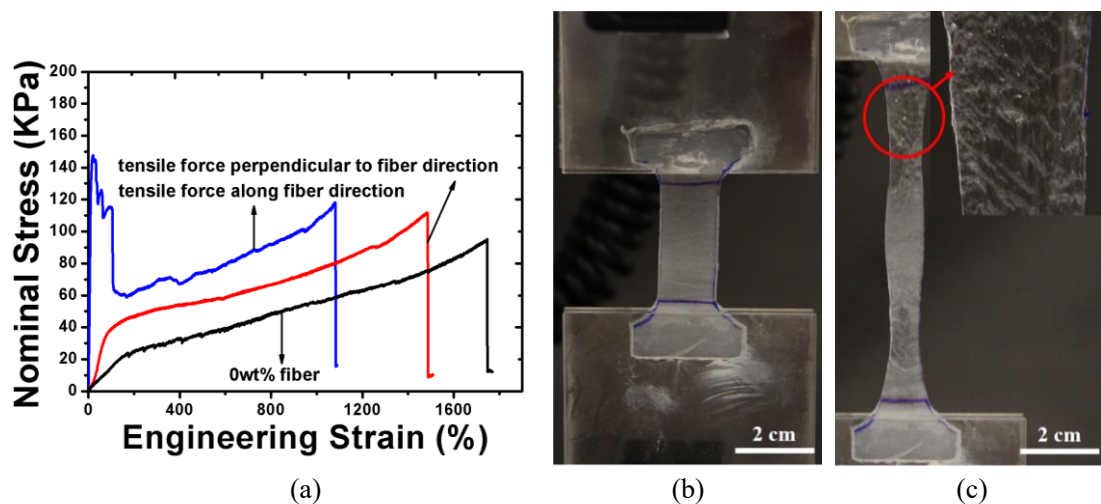


Figure 3.6: (a) Stress-strain curves of DN gel composites with 0.41wt% PAN nanofibers for two orthogonal loading directions. (b) and (c) are the photos of the DN gel composite during tensile test with loading direction perpendicular to the fiber.

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4. Conclusion

In the article, we fabricate PAN nanofiber reinforced DN gel composites. Our experiments have demonstrated that through embedding a small weight percentage of PAN nanofibers into DN gel matrix, both stiffness and strength of the material can be dramatically enhanced. For a certain range of weight percentage of PAN nanofibers, toughness of DN gel composite can be also higher than DN gel matrix. In addition, since the amount of PAN nanofibers in the DN gel composite is so small, the gel composite maintains transparent.

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