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Investigate Polyacrylonitrile Nanotube Carbon Properties Fibers

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ABSTRACT: Spinning slurry was prepared by surface modification of carbon nanotubes with polyacrylonitrile solution. Polyacrylonitrile / multiwall carbon nanotube (PAN/MWNT) Nanotube fibers were prepared by wet spinning technology. The effects of carbon nanotubes on the dynamic rheological properties of Nanotube solutions were studied, and the physical and mechanical properties and crystallization characteristics of Nanotube fibers were discussed. The PAN primary fibers observation and analysis of the morphology of fiber samples using TEM, X-ray diffraction (XRD), TEM and other testing and analysis techniques to characterize the structure of the fiber. The results show that the addition of MWNTs reduces the viscosity of the spinning dope, significantly improves the mechanical properties of the Nanotube fibers, reduces the elongation, and has a certain effect on the crystallinity of the fibers.

KEYWORDS: carbon nanotubes, polyacrylonitrile, wet spinning, Nanotube fibers

INTRODUCTION

With the progress of society and the development of science and technology, rapid changes have taken place in the field of materials [1-3]. High-quality polyacrylonitrile (PAN) is a prerequisite for the production of high-performance carbon fibers, and the compactness of the primary fiber is the key to determining the quality of the PAN. Polyacrylonitrile (PAN) fiber has good heat resistance, light resistance and weather resistance. It has many applications in the fields of clothing and industry. It is one of the early synthetic fibers to achieve industrial production [4, 5]. As a precursor of carbon fiber, the production and modification of polyacrylonitrile precursors have also received great attention at home and abroad. It has the advantages of light weight and high strength, corrosion resistance, fatigue resistance, electrical conductivity, and heat transfer [6-11].

In recent years, no matter whether it is military or civilian materials, on the premise of meeting its application functions, people have paid more and more attention to the requirements for lightweight products [12, 13]. Therefore, some lightweight and high-strength materials are required to replace heavy metal materials. Carbon fiber has higher strength than steel and lighter density than aluminum. Under the conditions of strength and stiffness, carbon fiber composite materials can reduce weight by more than 50% compared to steel. Magnesium-aluminum alloy can reduce weight by about 30%, and has a unique lightweight effect, so it is often used in reinforcements of various composite materials. At present, carbon fiber composite materials are widely used in aerospace, military, and civilian fields, and have become one of the hot spots in the field of new materials [8, 9].

Recently carbon nanotubes (CNTs) -reinforced polymers attracts a lot of attention. The polymer matrix and processing technology involved are also diverse. People expect to obtain excellent mechanical properties, good thermal properties, or excellent electrical conductivity. Composites. At present, the research of carbon nanotubes in polymers such as polymethyl methacrylate, polystyrene, epoxy resin, nylon 6, polyvinyl alcohol has been quite in-depth [14]. Sreekumar et al. [15], Prepared single-walled carbon nanotubes (SWNTs)/polyacrylonitrile fibers using a dry-wet method. Compared to pure PAN fibers, the Nanotube fibers with a SWNT content of 10% increased 100% at room temperature. Hailong Zhang et al. [16], Prepared carbon nanotube/polyacrylonitrile conductive fibers, and found that when the carbon nanotube content is 5%, the fiber conductivity can reach 10-3S / cm. We try to prepare polyacrylonitrile/multiwall carbon nanotube (MWNTs) fibers by wet spinning.

Studying the structure of PAN primary fibers, and understanding their internal relations, has important theoretical guiding significance for improving the density of PAN primary fibers and the quality of filaments. The effects of carbon nanotubes on the rheological properties of spinning dope and the mechanical and crystalline properties of Nanotube fibers were studied.

MATERIAL AND METHODS

Materials

Polyacrylonitrile powder: containing 6% of methyl acrylate, produced by Shanghai Jinshan Petrochemical; MWNTs: outer diameter of 10-20nm, length of 5-15μm, purity greater than 95%, produced by Shenzhen Nanoport Co., Ltd [17]. Chemical modification of 1.2MWNTs Put quantitative MWNTs into a three-necked flask, slowly add 70% concentrated nitric acid and 95% concentrated sulfuric acid mixture (volume ratio of 1: 3), sonicate for 2 hours, and then magnetically stir at 60 ° C under reflux for 6 hours. Centrifuge at high speed several times until the pH value of the mixed solution is about neutral. The product was centrifuged and dried. 1.3 Preparation of PAN/MWNT spinning solution and wet spinning process Quantitatively, PAN was added to N,N-dimethylacetamide (DMAc) solvent, swelled at 0-15°C for 4 hours, and the water bath was slowly heated to 70 ° C, and stirring was continued for 2 hours. To obtain a PAN solution. The chemically modified MWNTs were dispersed into a certain amount of DMAc by an ultrasonic cell pulverizer, and then added to the PAN solution, and stirred at room temperature for 4 hours to prepare MWNTs with a mass percentage of 0%, 1%, 3%, and 7%, respectively. Solution (16% solids). The Nanotube fibers were obtained through wet spinning. The coagulation bath was a 40% DMAc aqueous solution, and the draw ratio was 7 times.

Preparation

The dynamic rheological properties of the PAN / MWNT solution were tested on an ARES-RFS type rotary rheometer produced by American TA company. The dynamic scanning frequency was 0.01 ~ 100rad / s, and the test temperatures were 30 ℃. The Nanotube fibers were embedded in epoxy resin, made into ultra-thin sections, placed on a copper mesh, and the dispersibility of carbon nanotubes in the PAN matrix was observed using a Hitachi-800 transmission electron microscope. Japanese Rigaku D / max-2550PCX-light diffractometer was used to determine the crystallinity of the Nanotube fibers.

Fiber mechanical properties were measured by XQ-1 monofilament tensiometer (developed by Donghua University). The same sample was tested 15 times and the average value was taken. The storage modulus (E ') and loss factor (tanδ) of the fiber were measured by Q800 DMA dynamic mechanical analyzer of American TA company, the frequency was 10Hz, the temperature range was from room temperature to 200 ℃, and the heating rate was 2 ℃ / min.

RESULTS AND DISCUSSION

Dynamic rheological properties of spinning dope

In dynamic rheological tests, the rheological behavior at high frequencies is often used to study the effect of fillers on processability, while the rheological behavior at low frequencies is very sensitive to the structure of composites and can be used to study the incorporation of fillers in composites. And structure can provide more information for subsequent processing and forming.

The relationship between the absolute value of the complex viscosity of the PAN / MWNT solution η * and the applied frequency ω is shown in Figure 1. It can be seen from the figure that in the entire test range, η * decreases with the increase of ω, and the spinning dope behaves as a shear-thinning fluid. When the carbon nanotube content is low (1%), the relationship between η * and ω is very similar to the frequency dependence of pure PAN solution. The complex viscosity is slightly higher than pure PAN at low frequencies, and decreases with frequency at higher frequencies. Fast, indicating that the addition of a small amount of carbon nanotubes enhances the frequency dependence of the viscosity of the solution, but generally has little effect on the complex viscosity of the PAN system. However, when the content of carbon nanotubes is increased to 3% or more, the sensitivity of η* to frequency decreases, and at the same alternating frequency, the addition of carbon nanotubes significantly reduces the complex viscosity of the solution. The possible reason is that MWNTs act as a lubricant between PAN macromolecules, increasing the distance between PAN molecules, thereby reducing the intermolecular force and reducing the instantaneous entanglement point. These effects promote the orientation of the PAN molecular chain and the diffusion of MWNTs, the solution is uniformly dispersed, and the viscosity decreases. Similar results are also obtained in other polymer / carbon nanotube mixed solutions. For example, in the ultra-high molecular weight polyethylene / paraffin oil gel system, when the carbon nanotubes are added less than or equal to 3%, the apparent viscosity of the system is also Both are lower than the blank sample, the reason is that the orientation of the carbon tube has played a role as a plasticizer [18, 19].

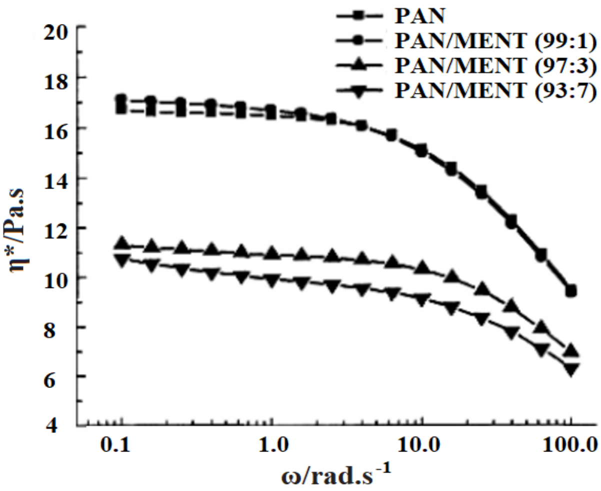

Figure 1. Effect of different carbon nanotube content on complex viscosity of PAN/MWNT solution.

Morphological analysis of Nanotube fibers

The dispersion and compatibility of carbon nanotubes in the matrix will affect the structure and properties of the composite. Figure 2 is a TEM photograph of a PAN / MWNT (93:7) Nanotube fiber at 20,000 and 50,000 times magnification. Because the PAN matrix and MWNTs in the sample have different electron densities, they have different transmittances to the electrons. It can be seen from the photos that the dark area is the PAN matrix, and the brighter ones are the carbon tubes, and some of the carbon tubes are well dispersed in the matrix. Due to the stretching effect during spinning, part of the carbon tube is oriented along the fiber axis. Achieving good dispersion of carbon tubes may play a role in strengthening the matrix, which is conducive to improving the mechanical properties of the Nanotube fibers.

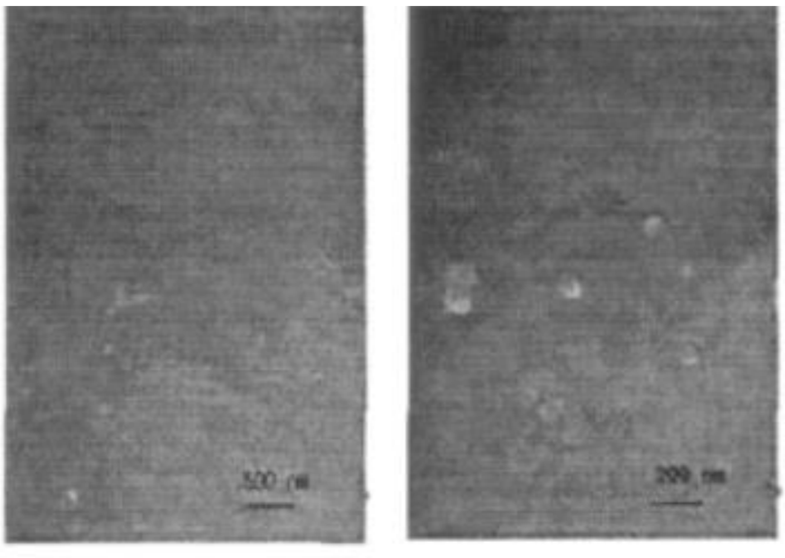

Figure 2. TEM Nanotube fibre PAN/MWNT (93:7)

Mechanical properties of Nanotube fibers

The mechanical properties of Nanotube fibers changed significantly with the addition of carbon nanotubes. It can be seen from Figure 3 that with the increase of the content of carbon nanotubes, the tensile strength of the Nanotube fibers increases under the same processing conditions, and the elongation at break is also reduced.

Compared with pure PAN fibers, the tensile strength of Nanotube fibers with 7% carbon nanotubes increased by 24%. When the carbon tube content reaches or when it exceeds 3%, the increase in tensile strength decreases. This may be related to the degree of dispersion of the carbon tube in the PAN matrix. When the content is relatively low, the dispersion of the carbon tube is relatively easy; when the content of the carbon tube is relatively high, the carbon tube is easy to aggregate, which affects the enhancement of the enhancement effect [20].

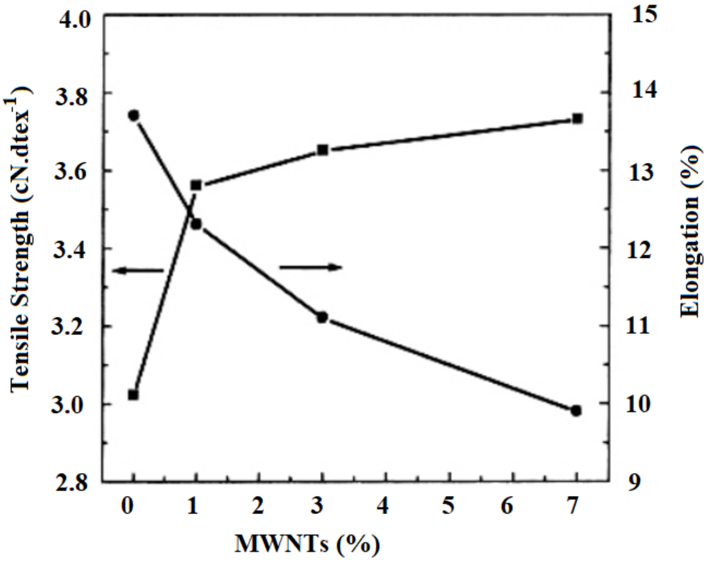

Figure 3. Mechanical properties of PAN / MWNT fibers

The mechanical properties of polymer materials are greatly affected by time, frequency and temperature. Dynamic mechanical behavior analysis has become one of the most important methods to study the properties of polymer materials. As can be seen from Figure 4 (a), compared to pure PAN fibers, the storage modulus of PAN / MWNT fibers has been improved to varying degrees, indicating that the addition of carbon nanotubes has improved the mechanical properties of the fibers; when the content of MWNTs is 7% At this time, the storage modulus of the Nanotube fibers is 1 to 2 times higher than that of pure PAN fibers. Figure 4 (b) shows similar results with the change of the loss factor *tanδ* of the fiber with temperature. The loss factor *tanδ* is the ratio of the loss modulus E '' to the storage modulus E '. The greater the value of *tanδ*, the greater the value of E' 'relative to E', the greater the viscosity of the material; the smaller the *tanδ*, the value of E ' The greater the relative E '', the greater the elasticity of the material. It can be seen from Fig. 4 (b) that the maximum value of *tanδ* appears at 112 °C. Around this maximum value, the addition of carbon nanotubes reduces the loss factor of the Nanotube fibers, indicating that the fiber's elasticity has improved. Due to the good rigidity of carbon nanotubes, the elasticity of carbon nanotubes / polymer composites has been significantly improved. This phenomenon is also reflected in the PAN/MWNT Nanotube fiber system in this study.

Properties of Nanotube fibers

It can be seen from Figure 5 that PAN fibers have two crystalline peaks near 17° and 29°, which correspond to the (200,110), (310,020) crystal planes of PAN, and a large and diffuse amorphous diffuse peak near 25°. After purification treatment, the diffraction pattern of multiwall carbon nanotubes showed a strong diffraction peak and a weak diffraction peak around 26 ° and 43 °, corresponding to the (002) and (100) planes of graphite, respectively. With the increase of the content of carbon nanotubes, the intensity of the crystalline and amorphous peaks of the samples decreased, and when the content of carbon nanotubes increased to 3% or more, the characteristic peaks corresponding to the (002) plane of the carbon nanotubes gradually appeared. From Fig. 5, no new PAN crystal diffraction peak was generated due to the addition of carbon nanotubes, and the position of the original PAN crystal diffraction peak did not change, indicating that the addition of MWNT did not change the crystal type of PAN. Matsuo et al. [21, 22] used WXRD to study the crystallization properties of PAN / MWNT films. Even with the addition of 10% carbon tubes, the crystallization peak of the PAN matrix can still be clearly displayed, indicating that the addition of MWNT did not change the crystal type of polyacrylonitrile molecules. Our experiments also verified this result.

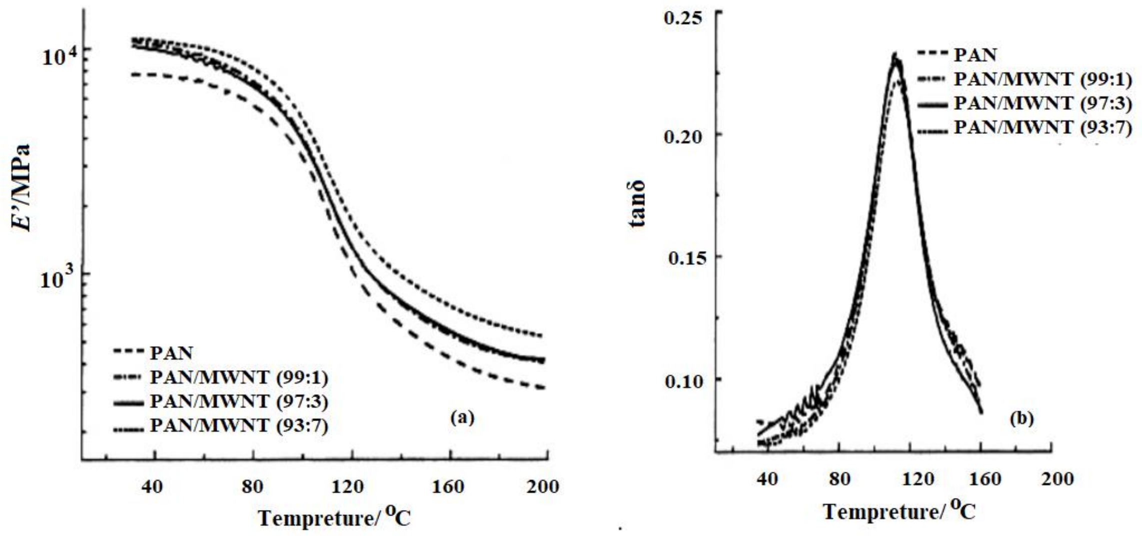

Figure 4. Curves of storage modulus and loss factor versus temperature for PAN / MWNT fibers

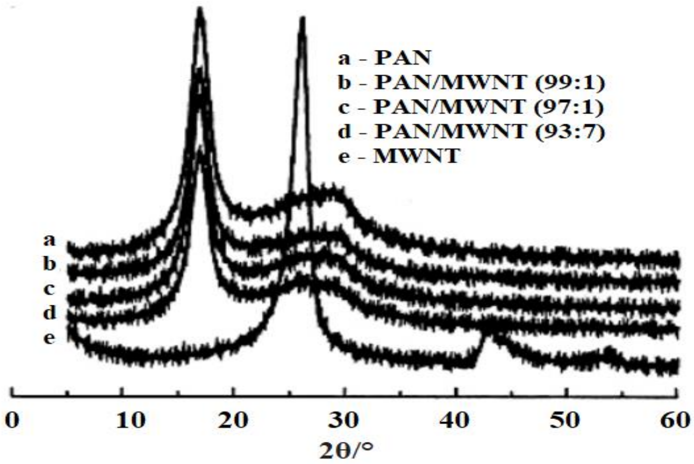

Figure 5. X-ray diffraction curves of fibers with different carbon tube contents and control samples

From Table 1 it can be seen that under the same spinning conditions and draw ratio, the crystallinity of PAN/MWNT fiber has improved. When the carbon tube content reached 7%, the fiber crystallinity increased by about 11%. It is speculated that MWNTs may play two roles in the fiber forming process. On the one hand, the addition of carbon tubes hinders the orderly arrangement of PAN molecular chains along the stretching direction, which increases the disorder of the PAN molecules in the axial alignment. The crystalline peak strength of the fibers decreases; on the other hand, due to the stretching effect during the fiber forming process, carbon nanotubes may be oriented in the polymer matrix, forming partially ordered regions with PAN molecules close to them, so blending the fibers Crystallinity increases. In this study, the effect of carbon tubes on the crystallization properties of PAN was the result of the interaction of the above two factors, that is, the addition of MWNTs increased the crystallinity of PAN.

Table 1. Crystallinity of different fiber samples

PAN:MWNT	100:0	99:1	97:3	93:7
Crystallinity %	59.98	64.08	64.07	66.66

Mechanical Properties

The tensile strength of carbon fiber changes with tensile modulus as shown in the figure 6 below. As the tensile modulus increases, the tensile strength of the carbon fiber gradually decreases. When the tensile modulus is lower than 350GPa, the tensile strength remains constant around 4.9GPa. As the tensile modulus increases to 460GPa, the tensile strength drops rapidly to 4.2GPa. There is a transition period when the tensile modulus changes from 460GPa to 540 GPa, and then the tensile strength decreases again. Comparing, the tensile strength decreased by 26% from 5.0GPa to 3.7GPa.

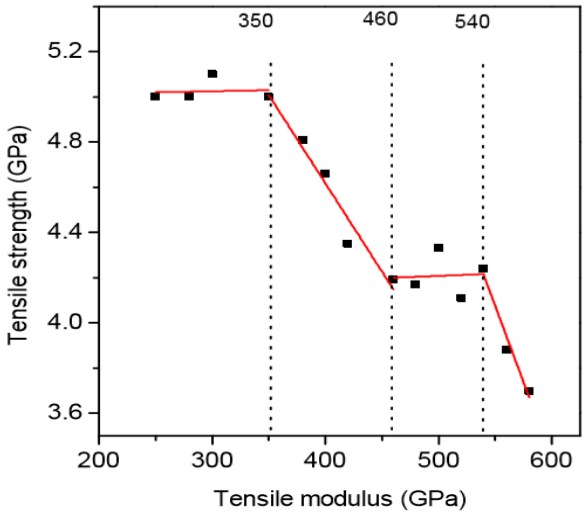

Figure 6. Tensile strength changes with tensile modulus

The carbon fiber is determined by wide-angle X-ray diffraction, as shown in Figure 7. When the tensile modulus of carbon fiber is less than 300GPa, the interplanar spacing and grain size of (002) are 3.5nm and 1.7nm, respectively. As the modulus of the carbon fiber increases, the interplanar spacing begins to decrease, and the grain size rapidly increases; when the tensile modulus is 420GPa to 480GPa, the crystal parameter of the carbon fiber changes little, and when the tensile modulus is higher than At 480GPa, the spacing between (002) planes becomes narrower, and the grain size increases rapidly. When the carbon fiber tensile modulus changes from low to high, the interplanar spacing of the (002) plane changes from 3.5nm to 3.4nm, while the grain size increases from 1.7nm to 8.6nm. It can be seen from the above that the rearrangement and growth of graphite crystals play a major role in improving the tensile modulus of carbon fibers.

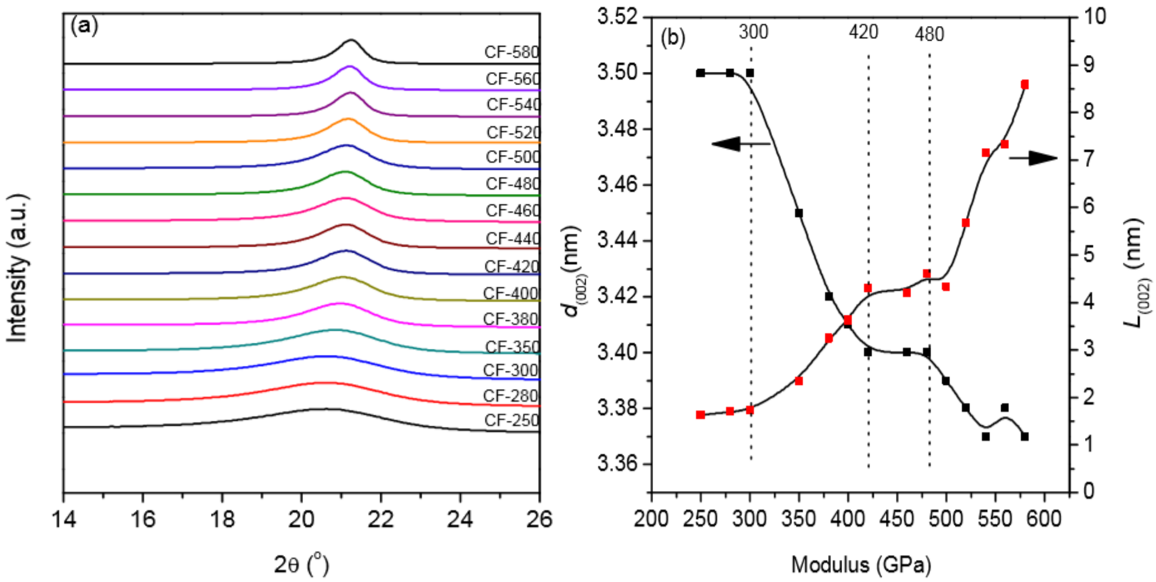

Figure 7. Carbon fiber crystallite structure parameters: (a) (002) plane wide-angle X-ray integral diagram (b) crystal plane spacing and grain size change with changes in carbon fiber modulus.

CONCLUSION

In this paper introduce investigate PAN/MWNT where the amount of MWNTs added is 3% or more, the viscosity of the spinning dope is greatly reduced, and the sensitivity to frequency is also reduced, which is beneficial to the spinning process. The tensile strength and storage modulus of PAN fiber with carbon tube increased, the loss factor decreased, and the elongation at break was also reduced. The crystallinity of the fibers was increased by the addition of carbon nanotubes.

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