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Preparation and Characterization of PAN/SiO_2 Hybrid Fibers

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Summary

Two kinds of hybrid PAN/SiO_2 sols were prepared via either sols blend or *in-situ* polymerization, respectively, and their spinnability was investigated. Hydrolysis time (t_l) and spinnable time (t_2) of both hybrid sols increased with PAN content. The hybrid fibers were characterized with FTIR, DSC, SEM and TG. As evidenced from the FT-IR spectra and DSC measurements, different chemical structures of hybrid fibers were different with CN groups hydrolyzed in the hybrid fibers via *in-situ* polymerization. SEM measurements showed the interior structures of the hybrid fibers via *in-situ* polymerization were more homogeneous. TG measurements suggest both of the hybrid fibers show better resistance to heat than pure PAN.

Introduction

Sol-gel process has been widely used to prepare inorganic-organic hybrid materials [1-3]. Accord to different preparation method and reaction degree, different materials with shapes of bulks, films and fibers were made [4]. The preparation of continuous fibers by sol-gel containing Si[4], Ti[5], Zr[6], Al[7], Cu[8] has gained considerable attention recently. Among them, SiO_2 fiber has been investigated extensively, and applied in different areas, such as optical and electronics fields [4,9].

Recently, some inorganic-organic hybrid continuous fibers made *via* sol-gel method have been reported [10-11], and these novel fibers showed excellent physical properties. For example, Hasewaga et al [12-15] reported a series of inorganic-organic hybrid continuous fibers prepared via sol-gel method from organic polymers with metaloxyalkyllide. These hybrid fibers have been used as precursors and combined with carbothermal reduction to prepare continuous SiC, Si_3N_4, ZrC and Si-Zr-C fibers.

PAN is a kind of linear polymer with excellent spinnability and used widely as general fiber. Therefore, a new class of hybrid fiber from PAN and SiO_2 via sol-gel process caught our attention. To our knowledge, up till now, there is seldom report available on the preparation and the property investigation on PAN/SiO_2 hybrid fibers. In this paper, two kinds of hybrid PAN/SiO_2 sols were prepared via sols blend method and sol-gel *in-situ* polymerization method, respectively. The reaction mechanism of the hybrid sols and their spinnability, as well as performance of the PAN/SiO_2 hybrid fibers was investigated.

Experimental

Materials

Polyacrylonitrile (PAN, Mn 80,000) was purchased from Anqing Petrochemical Co. (China), and tetraethyl orthosilicate (TEOS), DMF, EtOH and Acrylonitrile (AN) from Xilong Pure Chemical Co. (China). Vinyltriethoxysilane (VTEOS) was obtained from Zhangjiagang Fine Chemicals Co. (China). Azobis(isobutyronitrile) (AIBN) was recrystallized in EtOH before use.

Instruments

SEM measurements were performed on a SIRION 200 field emitted SEM eqiupment. DSC measurements were performed on a Meterlo-Toledo DSC-821E differential scanning calorimeter in the temperature range of ambient temperature to 300°C at a heating rate of 10°C/min. TG measurements were performed on a Shimadzu DTG-60H thermogravimetric analyzer under nitrogen atmosphere. FTIR spectra were recorded on a Nicolet-IR200 FTIR spectrometer with a resolution of 1 cm^{-1}.

Preparation of PAN/ SiO_2 hybrid sols

via in-situ polymerization method

TEOS, VTEOS, EtOH, distilled water and 0.1mol/L HCl was added successively into a 250-mL three-neck glass-flask equipped with a condenser, and the mixture was mixed by vigorous stirring for about 1 h at ambient temperature, thus a reactive silica sol was made. Then stoicheiometric (see Table 1) AN containing AIBN (AIBN:AN = 0.01:1, mol ratio) was added to the above reactive silica sol with stirring, and the mixture was kept at a temperature of 70°C for about 2 h. After that vacuum was exerted for about 1 h to distal out the residual monomer AN, and then a hybrid sol was prepared.

via sols blend method

PAN was washed firstly with water and dried, then was dissolved in DMF in a mass ratio of 5% in order to prepare PAN/DMF solution. This solution was added into a 250-mL three-neck glass-flask, and then stoicheiometric TEOS (see Table 1), distilled water and 0.1mol/L HCl were added successively with stirring. After vigorously stirring for 2 h, a viscous hybrid sol of PAN/SiO_2 was obtained.

Spinnability of the hybrid sols and preparation of the hybrid fibers

The hybrid sols were kept still for aging with designed time. During this period, a glass rod with a diameter of 8 mm was immersed into the above hybrid sols repeatedly, and drawn up slowly. According to reported process [16], if a hybrid fiber could be drawn from them, the drawing-ability of the hybrid sols was called “yes”, otherwise, the drawing-ability of the hybrid sols was called "no". The time interval between the hybrid sols prepared and when they become viscous enough to be drawn up is defined as the hydrolysis time (t_1). The time between the beginning when the hybrid sols become viscous enough to be drawn out and when they become cured gradually to not able to be drawn out is defined as the spinnable time (t_2).

Results and discussion

The preparation conditions for the hybrid sols are compiled in Table 1, and the effect of PAN on their spinnability parameters are compiled in Table 2. The contents of PAN inside the hybrid sols are varied.

In sol-gel transition of PAN/SiO_2 hybrid sols, the main chemical reaction was hydrolysis and condensation of TEOS. According to the reported mechanism [4,16], the reaction included three stages. The first chemical reaction was the hydrolysis of TEOS and compounds with –OH groups, thus formed silanol groups. Subsequently, condensation between silanol groups or TEOS with silanol groups, and low molecular polymers were formed. Finally, condensation between low molecular polymers formed the crosslinked silica network. Generally, a spinnable hybrid sols can be produced in the third stage[10-11], which has a suitable molecular structure for drawing. According to Ref.[10-11], the molecules of the spinnable hybrid sols must be big enough but with lower cured degree.

From Table 2, the hydrolysis time (t_1) and spinnable time (t_2) increased gradually with PAN content. The increase of t_1 and t_2, in fact, was the elongation of the time needed to produce the macromolecules suitable for drawing. PAN is linear macromolecule, the presence of PAN in the hybrid sols decreased the relative content of TEOS, which reduced the speed of the hydrolysis and condensation of TEOS, therefore, t_1 increased with PAN content increased gradually. In the meantime, as the decrease of SiO_2 content, the linear degree of the hybrid sols increased, the formation of silica cured network delayed, which resulted in the prolongation of t_2.

Table 1. Conditions for the hybrid sols preparation.

Sample order	Method	TEOS /mol	VTEOS /mol	EtOH /mol	HCl /mol	H_2O /mol	AN /mol	5%PAN solution/g	PAN content in sols/ %
Hybrid Sol-1	In-situ	0.25	0.025	1.0	0.0025	0.5	0.040	/	12.5%
Hybrid Sol-2	In-situ	0.25	0.025	1.0	0.0025	0.5	0.094	/	25%
Hybrid Sol-3	In-situ	0.25	0.025	1.0	0.0025	0.5	0.283	/	50%
Hybrid Sol-4	Blend	0.125	/	0.5	0.00125	0.25	/	150.0	50%
Hybrid Sol-5	Blend	0.05	/	0.2	0.0005	0.10	/	180.0	75%
Hybrid Sol-6	Blend	0.02	/	0.08	0.00002	0.04	/	168.0	87.5%

Table 2. Spinnability of the hybrid sols.

Sample order	method	spinnability		
		t_1/h	t_2/h	Fiber length/cm
Hybrid Sol-1	In-situ	~94.5	2.7	>50
Hybrid Sol-2	In-situ	~121	3.1	>50
Hybrid Sol-3	In-situ	~147	3.3	>50
Hybrid Sol-4	Blend	~93	2.5	>50
Hybrid Sol-5	Blend	~177	2.9	>50
Hybrid Sol-6	Blend	~216	3.1	>50

FT-IR spectroscopy was used to check the chemical compositions of the hybrid sols with different SiO_2 content, and resultant spectra are compiled in Figure 1. For comparison, the IR spectrum of pure PAN was also included. For the hybrid sols from blend, there were relative intensive peaks around 2245cm^{-1} in curves 1b–d, which suggests –CN group existence in the PAN/SiO_2 fibers. Comparing with the spectra of pure PAN, new peaks around 800cm^{-1}and 1087cm^{-1} were found, which were corresponding to the scissor vibration and symmetric flexible vibration of Si-O-Si. With the increase of SiO_2 content, the relative intensity of these peaks increased gradually. Intensive peak around 1664cm^{-1} was observed, which suggests existence of $CO-NH_2$ groups from solvent DMF. But for in-situ hybrid fibers, there was no peak around 2245cm^{-1} as illustrated in curves 1e–g, but new peak around 1659cm^{-1} was observed. According to Ref.[17], this signal demonstrates existence of $CO-NH_2$ groups.

In a word，FTIR spectra reveal different chemical structures formed in the above two kinds of the hybrid fibers. Among them, CN groups hydrolyzed thoroughly in the latter, and transformed into $CO-NH_2$ groups. The formation of different chemical structures in the above two kinds of the hybrid fibers were resulted from their different preparation methods and reaction conditions. According to Ref.[18-19], CN groups become unstable in acidic solution or alkaline solution and their hydrolysis will happen. In general, the hydrolysis of CN group can be a complex process and different types of hydrolyzed products may be obtained. From acidic hydrolysis of CN group, the products may include –C=N–, acrylamide, acid acrylate, and from different stages of the hydrolysis. These two kinds of the hybrid sols were all acidic. In the case of the hybrid sols prepared by in-situ polymerization, monomers AN mixed with water more easily, the hybrid sols were prepared at a higher temperature (70°C), and they had a relative higher content of H_2O and HCl, so the hydrolysis of CN groups was more easily. Oppositely, the sols prepared by blend, less H_2O and HCl were added, and they were kept at a temperature as low as ambient temperature, in such conditions, no or less CN groups hydrolyzed.

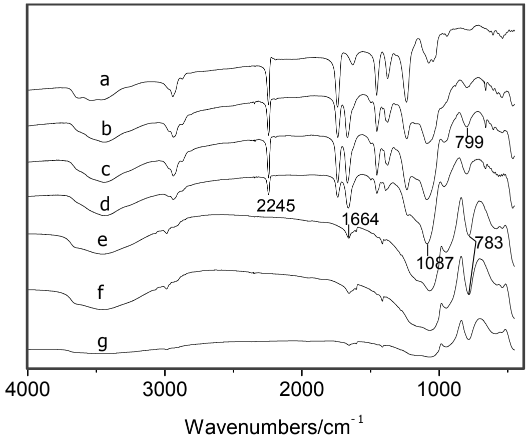

Figure 1. FTIR spectra of the samples. Content of PAN : a, 100%; b, 87.5%; c, 75%; d, 50%; e, 50%; f, 25%; g, 12.5%. Preparation method : b-d, blend; e-g, in situ.

DSC measurements were conducted and resultant curves are shown in Figure 2. Curves a-c were the DSC curves of hybrid fibers prepared by blend. Weak endothermic peaks around 64°C were due to re-arrangement of molecular chains of PAN, which was caused by swell of amorphous areas of PAN by residual DMF, the endothermic peaks around 115°C were caused by re-arrangement of molecular chains of PAN in crystalline areas. Endothermic peaks around 260°C were caused by cyclization of PAN [20]. Curves d-f were the DSC curves of the hybrid fibers prepared by in situ polymerization. Comparing with the curves of the hybrid fibers prepared by blend, only endothermic peaks around 130°C could be found in these curves, which was caused by volatilization of absorbed moisture and/or with the evaporation of trapped solvent (H_2O or EtOH from TEOS) in the fibers. But it should be noted that endothermic peaks around 260°C disappeared in the fibers, which was caused by oxidation and cyclization of PAN. That the AN groups in the hybrid fibers

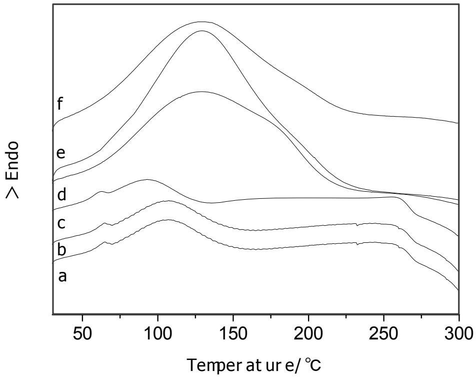

Figure 2. DSC curves of the hybrid fibers. PAN content : a, 50%; b, 75%; c, 87.5%; d, 12.5%; e, 25%; f, 50%.

prepared by in situ polymerization had been hydrolyzed could be also demonstrated from the DSC curves, and this conclusion is in good agreement with the results from FTIR experiments.

The TG curves of SiO_2 gel fiber, PAN/SiO_2 hybrid fibers and pure PAN were compared in Figure 3. As observed in curve a and d, pure PAN showed poor heat resistance with a residue weight only about 42.1%, while SiO_2 gel fiber showed excellent heat resistance, and the weight residue kept about 80.6%. For PAN/ SiO_2 fibers (curves b and c), three degradation steps could be observed. Firstly, for blend type PAN/ SiO_2 fibers, the first step was between 27 and 318°C, which was associated with the loss of absorbed moisture and/or with the evaporation of trapped solvent (DMF and H_2O or EtOH from TEOS), weight loss was about 10%. The second step was between 318 and 375°C, which is corresponded to the cyclization of PAN[20]. The third step was after 375°C with a weight loss about 28%, which was dependent on further degraded of the polymer residues and further reaction of inorganic phase. Weight loss at this stage was about 12%. The total weight residue was about 48%. It should be noted that, pure PAN reached the temperature of maximum weight loss at 301°C, while PAN/SiO_2 fibers reached this at 318°C. This suggests that heat resistant of PAN was improved by the interaction of PAN and SiO_2.

For in situ polymerization type hybrid silica fibers, the first step was between 27 and 153°C, which was associated with the loss of absorbed moisture and/or with the evaporation of trapped solvent (H_2O or EtOH from TEOS), weight loss was about 10%. The second step was between 153 and 480°C, corresponded to the further reaction of residual Si-OH, Si-O-Et and hydrolysates of PAN. The third step was after 480°C, weight loss was about 8%, which was dependent of the further degradation of polymer residues and further reaction of inorganic composition, weight loss was about 5%, the last weight residue was about 77.5%.

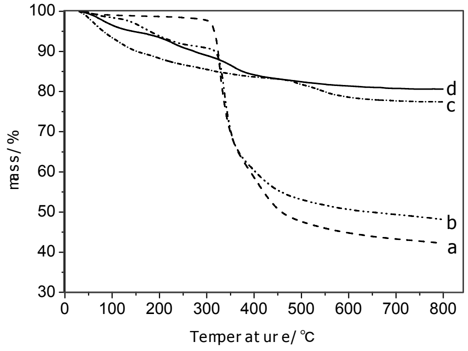

Figure 3. TG curves of the samples. a, SiO_2 gel fiber; b, hybrid fiber by in situ; c, hybrid fiber by blend; d, pure PAN. mPAN/mSiO_2: a, 100:0; b, 87.5:12.5; c, 12.5:87.5; d, 0:100.

SEM was applied to examine the morphologies of the hybrid fibers, and the photographs are compiled in Figure 4. The appearance of the hybrid fiber made by blending was very coarse. Hybrid fiber composed of some beams of fibers could be clearly observed, which aroused from orientation of PAN macromolecules chains after being drawn, which demonstrated from another aspect that the chemical structure of organic composition of PAN didn't change in the hybrid fiber. As showed Figure 4b, some groove and fractures were found on the surface of the hybrid fiber, which was understood due to the poor miscibility of PAN and SiO_2. There were some defects caused in the hybrid fiber by SiO_2 while the sols were drawn. In contrast, the hybrid fibers made by in situ polymerization were transparent, and showed smooth appearances. The pictures also indicated that homogeneous structure formed in the interior of the hybrid fibers. In a word, it was demonstrated by the SEM pictures that different morphology existed in two kinds of the hybrid fiber, which may be resulted from the difference in their chemical structure.

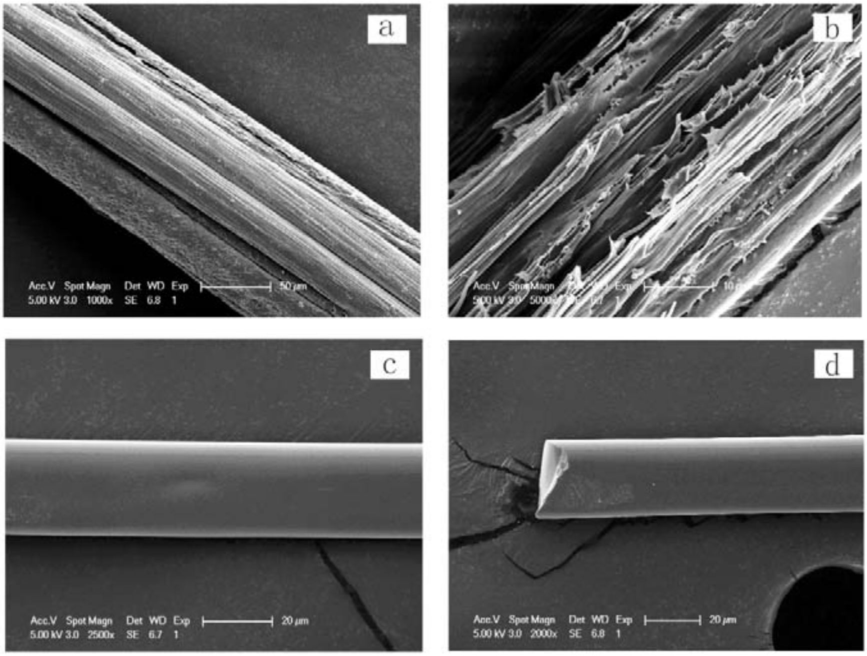

Figure 4. SEM photographs of the hybrid fibers. a-b, hybrid fibers by blend; c-d, hybrid fibers from in situ polymerization.

Conclusions

Hybrid fibers of PAN/SiO_2 with different SiO_2 content were prepared by sol-gel method. The chemical structures of the hybrid fibers were influenced greatly by their preparation method and conditions, which resulted in different micro-morphology and performance of the hybrid fibers. These fibers had shown some super properties of the organic–inorganic hybrid materials, especially, in heat resistance.

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