Applied Surface Science 261 (2012) 415–421

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Comparison studies of surface cleaning methods for PAN-based carbon fibers with acetone, supercritical acetone and subcritical alkali aqueous solutions

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ARTICLE INFO

Article history:
Received 11 June 2012
Received in revised form 6 August 2012
Accepted 6 August 2012
Available online 14 August 2012

Keywords:
Carbon fiber
Surface cleaning
Supercritical acetone
Subcritical aqueous

ABSTRACT

Four kinds of polyacrylonitrile-based carbon fibers were cleaned by three methods and were characterized by X-ray photoelectron spectroscopy, monofilament tensile strength test and atomic force microscopy (AFM). Experimental results of these tests reveal that the method using supercritical acetone or subcritical potassium hydroxide aqueous solution act as the processing medium shows a better cleaning effect compared to the traditional method, Soxhlet extraction with acetone. The method using supercritical acetone is more appropriate to wipe off the oxygenated contaminants on carbon fibers' surfaces and causes a relatively smaller damage to the bulk strength of each carbon fiber. As far as treating method using the subcritical alkali aqueous solution, it can thoroughly remove silicious contaminants on the surfaces of treated fibers.

1. Introduction

As a kind of important reinforced material and catalyst carrier, carbon fiber has gained increasing attention from more and more researchers and was investigated extensively in labs all over the world [1]. When used as experimental subjects, especially for surface modification, manufacture of non-resin matrix composite material and applied as catalyst carrier, epoxy resin coating layer on the surface of carbon fiber, which formed in commercial manufacture, becomes an interference factor and is intractable to be removed [2–4].

Presently, prevailing methods to remove epoxy resin coating layers on the surfaces of carbon fibers include three categories: Soxhlet extraction with organic solvent, ultrasonic cleaning in organic solvent and thermolysis in an inert atmosphere. Each of these three methods has its disadvantages, therefore, cannot meet the requirements of experiment research satisfactorily [5]. Normally, the Soxhlet extraction process cannot remove residual layers thoroughly within a reasonable period [6,7]. Because carbon fiber has a significant brittleness, ultrasonic cleaning usually leads to a relatively extreme injury to monofilament tensile strength of the fibers. For another traditional cleaning method, the nature of thermolysis is an elimination process of heteroatom on the surfaces of treated carbon fibers [8,9]. In fact, it is not a cleaning process and may change surface appearances of the cleaned fibers irretrievably.

Supercritical fluid has both liquid-like and gas-like characteristics and possesses a complete solvency for most gases and organic compounds. Moreover, a lot of reactions were usually catalyzed by protons or hydroxyl ions occur in near-critical water without the addition of acids or bases, simply because of the high ionic product of water under this condition. Jiang et al. [10] recycled three different PAN based carbon fibers from epoxy resin/carbon fiber composites using supercritical n-propanol. The tensile strength and modulus of the recycled carbon fiber was very similar to the corresponding as-received carbon fibers and the surface oxygen concentration decreased significantly. Hernanza et al. [11] investigated chemical recycling of carbon fiber reinforced composites using subcritical and supercritical alcohols as reactive-extraction media. After recycling the produced fibers that retained 85–99% of the strength of the virgin fibers.

In this study, we designed two novel methods to clean the surfaces of polyacrylonitrile-based (PAN-based) carbon fibers, based on the properties of supercritical and subcritical fluid, such as high diffusivity and special catalytic action [12,13]. In comparison with the traditional Soxhlet extraction process with acetone, the two cleaning methods with supercritical acetone and subcritical potassium hydroxide solution are proven to be more feasible and show a better cleaning efficiency.

2. Experiment

2.1. Materials

The sources of experimental materials engaged in this study are given in Table 1.

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0169-4332/$ – see front matter
http://dx.doi.org/10.1016/j.apsusc.2012.08.025

Table 1
The source of experimental materials.

Materials	Source of materials
No. 1 carbon fiber	T700, Japan Toray
No. 2 carbon fiber	T300, Japan Toray
No. 3 carbon fiber	GuangWei Group, Weihai, PR China
No. 4 carbon fiber	Jilin Carbon Co. Jilin, PR China
Acetone	The First Factory of Chemical Agents, Tianjin, PR China
Potassium hydroxide	Shanghai Chemical Reagent Co.
Deionized water	Made in lab

2.2. Surface cleaning processes

Method I: each kind of PAN-based carbon fibers were extracted by Soxhlet with acetone for 24 h, then they were dried in a dry oven at 393 K for 24 h.

Method II: each PAN-based carbon fiber was placed into a batch autoclave (95 ml, with 25 ml acetone and 5 ml deionized water) and sealed. The sealed autoclave was heated by salt-base at 623 K for 20 min. The purpose of mixing water in this system is to provide a protons environment and augment the dissolving capacity of supercritical acetone for polar groups. After cleaned, the fibers were washed with acetone and then dried in a dry oven at 393 K for 24 h.

Method III: each kind of PAN-based carbon fiber was placed into a batch autoclave (95 ml, with 80 ml 0.1 mol/L potassium hydroxide aqueous solution) and sealed. The sealed autoclave was heated by salt-base at 613 K for 20 min. After treated, carbon fibers were wished by deionized water and acetone respectively, then dried in a dry oven at 393 K for 24 h.

2.3. Performance testing

The surface composition analysis was performed on a Scienta ESCA 300 X-ray photoelectron spectroscopy (XPS) system equipped with a monochromatic Al Kα X-ray source (1486.60 eV). The pass energy was set at 187.83 and 29.35 eV for the survey and the high resolution spectra, respectively. The instrument was operated with an analyzer chamber pressure of 2.6×10^{-7} Pa at 25 °C. Single fiber strength tests were carried out according to ASTM-D3379. Atomic force microscopy (AFM) images were obtained using an NT-MDT Solver P47H system.

3. Results and discussion

3.1. Surface chemical composition analysis by XPS

Survey spectrograms of twelve specimens (four kinds of PAN-based carbon fibers cleaned by three methods) are given in Fig. 1, and the detailed analysis results are shown in Table 2. As can be seen that after cleaning by Soxhlet extraction with acetone for 24 h the oxygen content on the surfaces of No. 1 carbon fiber and No. 2 carbon fiber are 26.42% and 9.73% respectively. When cleaned with supercritical acetone act as treated medium, the oxygen content on the surfaces of No. 1 carbon fiber and No. 2 carbon fiber are 4.94% and 4.30% respectively. After cleaned by subcritical potassium hydroxide aqueous solution such values are 8.80% and 7.18% respectively. These results show that the cleaning method using supercritical acetone and subcritical potassium hydroxide aqueous is preferred to Soxhlet extraction with acetone for these two kinds of carbon fibers.

For No. 4 carbon fiber, all of these three methods displayed favorable cleaning effects. But for No. 3 carbon fiber, cleaning effect of each method is dissatisfactory, but the latter two methods are still far better than the former one. Further, we hold the opinion that the advantage of using supercritical acetone as cleaning media rather than using acetone lies in its high diffusivity and good heat-transporting properties. As to subcritical potassium hydroxide aqueous, this cleaning treatment is more like a pyrogenic decomposition and hydrolyzation process, therefore can remove the layers on the surfaces of carbon fibers more thoroughly.

A further contrast can be performed between cleaning process through supercritical acetone and subcritical potassium hydroxide aqueous solution. The former is more appropriate to remove oxygenous groups on the surfaces of the cleaned carbon fibers. The latter possesses a better cleaning effect for silicious groups. (After cleaning by subcritical potassium hydroxide aqueous solution, there is no Si be detected on the surfaces of carbon fibers.)

Table 3
The mechanical data and the results of Weibul analysis.

Specimens	R_a	m	σ_0	Expectation (GPa)
No. 1-I	0.992	−6.23	3.79	4.68
No. 1-II	0.993	−6.15	3.81	4.54
No. 1-III	0.987	−5.74	3.56	4.52
No. 2-I	0.997	−8.29	6.21	3.53
No. 2-II	0.998	−7.77	5.73	3.60
No. 2-III	0.997	−8.41	6.36	3.50
No. 3-I	0.994	−6.48	4.17	4.31
No. 3-II	0.994	−7.49	4.76	4.43
No. 3-III	0.993	−8.08	5.24	4.30
No. 4-I	0.995	−5.03	3.59	3.66
No. 4-II	0.992	−5.30	3.67	3.82
No. 4-III	0.982	−4.96	3.62	3.55

3.2. Single filament strength tests

Since Soxhlet extraction with acetone has widespreadly been seen as a feasible cleaning method leading an acceptable strength loss, another two methods are compared with it. The results of Weibul analyses of single tensile tests are presented in Fig. 2 and Table 3. It can be seen that the regularity of monofilament tensile strength distributions of the carbon fibers basically remains

Table 2
Surface composition of the treated carbon fibers.

Specimens	Composition of C (%)	Composition of O (%)	Composition of N (%)	Composition of Si (%)
No. 1-I	64.41	26.42	2.97	6.20
No. 1-II	87.89	4.94	6.01	1.16
No. 1-III	86.58	8.80	4.61	–
No. 2-I	82.18	9.73	3.52	4.57
No. 2-II	88.14	4.30	5.25	2.31
No. 2-III	88.44	7.18	4.38	–
No. 3-I	59.41	25.79	4.95	9.86
No. 3-II	79.36	8.97	6.59	5.08
No. 3-III	79.51	15.86	4.63	–
No. 4-I	82.70	12.00	2.94	2.36
No. 4-II	92.79	3.50	3.36	1.35
No. 4-III	94.65	2.69	2.67	–