Fabrication of Solvent –Free Polyacronitrile (PAN) Hollow Microspheres and Its Pre-oxidation Microspheres

Shixiang Dong^{ab}, Wei Han^a, Meifang Liu^b, Zhangwen Zhang^b, Bo Li^{*b} and Liqin Ge^{*a}

^aState Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, P. R. China

^bLaser Fusion Research Center, China Academy of Engineering Physics, Mianyang 621900, P. R. China

Abstract: The control PAN plastic microsphere were obtained after the evaporation of the middle solvent from silicon oil/PAN in DMF solution/silicon double emulsions(O1/W/O2) which were prepared with stirring method. The pre-oxidation PAN microspheres were successfully prepared after the heating treatment of the PAN plastic microspheres. The structures of the PAN pre-oxidation microspheres were characterized by the Stereomicroscope, Field Emission Scanning Electron Microscope (FESEM), and Fourier Transform Infrared spectroscopy (FTIR). It was found that the pre-oxidation PAN microspheres at 300°C have best mechanical performance than the others. The pre-oxidation microspheres' pressure-resistance results showed that they can bear greater pressure than the plastic ones, which means that the microspheres' mechanical strength has been enhanced after the heating treatment. Most pre-oxidation microspheres can bear the pressure higher than 17 MPa, which provide a great prospect in the target application.

Keywords: Polyacrylonitrile (PAN); Double emulsion stirring method; Pre-oxidation; The pre-oxidation PAN microspheres; Pressure resistant

1. Introduction

With the ongoing development of human society, energy issues have become increasingly prominent.[1, 2] Traditional fossil fuels are non-renewable sources of energy that lead to a variety of serious environmental problems with long-term use; the dual challenge of environmental problems with future energy shortages is gradually becoming a hindrance to further development.[3] To address these issues from a traditional vantage point, clean and efficient sources of energy have been

* Corresponding authors at: State Key Laboratory of Bioelectronics, Biological Science and Medical Engineering Department, Southeast University, Nanjing 210096, PR China. Tel.: +86 025 83619983; fax: +86 025 83795635.
E-mail addresses: lb6711@126.com (B. Li), lqge@seu.edu.cn (L. Ge).

utilized, including wind, solar, and nuclear energy. Of these new energy sources, nuclear energy is currently the energy source being most widely researched for its potential applications.

As is well known, there are two methods to generate nuclear energy, nuclear fusion and nuclear fission, both of which produce large amounts of energy. However, nuclear fission can produce a large number of gamma rays, and materials and byproducts contain a high level of radioactive isotopes of heavy metals.[4, 5] If handled improperly, these materials and waste products have a very serious adverse impact on both the environment and with human exposure. Given this circumstance, nuclear fusion is currently the energy-providing method of choice for those interested in nuclear energy.

The ICF (Inertial Confinement Fusion) experiment has recently drawn greater attention from researchers.[6-8] In this experiment, a key step was to fabricate desirable targets.[9] As a fuel container, targets must satisfy the geometric parameter requirements and have specific physical and chemical properties.[10, 11] Polymer targets have the advantages of low density, permeability and atomic number, and good resistance to radiation corrosion.[12] Compared with traditional polystyrene (PS) and polymer vinyl acetate (PVA) targets, polyacrylonitrile (PAN) targets possess higher mechanical strength and lower deuterium–tritium permeability.[13-15] PAN, an important precursor of polymer materials, is known for its chemical stability and strong anti-corrosion and anti-radiation properties, characteristics that effectively prevent the penetration of gas.[16-19] PAN contains a strong -CN structure that is similar in effect to that of hydrogen bonds.[20] This structure (in which nitrile groups form strong bonds) is conducive to maintaining fuel storage, as it ensures firm binding between the molecular chains, greatly reducing the permeability to hydrogen isotopes. Accordingly, PAN is a potential material for the fabrication of ICF targets.

PAN (which attains its mechanical strength and chemical stability through heat treatment) is widely used for carbon fibers.[21] The process of converting PAN fibers into PAN carbon fibers mainly includes molding, pre-oxidation, and a carbonization process that was also investigated in early research.[22, 23] The PAN-based pyrolysis

reaction combines prestabilization and carbonization and contains intrachain cyclization, dehydration and denitrogenation.[24, 25] The whole chemical reaction can convert a linear polymer into turbostratic carbon by increasing the heating temperature.[26, 27]

In this paper, we characterize and detect the microstructures and properties of pre-oxidation PAN microspheres at different treatment temperatures. Additionally, we hope to prepare the hollow PAN microspheres with higher intensity and better performance with respect to gas retention so that suitable polymer or carbon targets are developed for use in the fusion process.

2. Experimental Section

2.1 Materials

PAN powders (Mw: 60000) and N, N-dimethylformamide (DMF) were obtained from Sigma-Aldrich CO. Ltd and Sinopharm Chemical Reagent Co. Ltd. Aliquat 336 was bought from Alfa Aesar A Johnson Matthey Company, England. The KF-96-1cst /KF-96-5cst /KF-96-10cst /KF-96-50cst silicon oils were obtained from Shin-Etsu Chemical Co. Ltd. Japan. The PAN powders were dissolved in DMF (1:6.67 (w/v)) homogeneously. All the chemicals were used as received without any purification.

2.2 Preparation of PAN solution

4.5g PAN powders were dissolved in 30ml DMF with 3 ml Aliquat 336 to form 15% PAN (m/v) solution.

2.3 Preparation of PAN microspheres using the double emulsion stirring method

To obtain PAN hollow microspheres, one should prepare the double emulsions: the oil / PAN solution/ oil (O1 / W / O2) system. The first step is that silicone oil is dropped into PAN solution during stirring ($V_{O1} : V_{PAN}$ is 1:2 to 1.5:2),

The second step is that single emulsion droplets which obtained in the first step were added in the bulk same viscosity of silicone oil ($V_{O1}/w : V_{O2}$ is 1:100) and stirring constantly. Thereafter, the mixed solution was kept stirring 24 h at room temperature in order to volatilize DMF organic solvents, promoting PAN hollow microspheres solidification (Fig.1).

2.4 Preparation of solvent-free hollow PAN microspheres

Three different drying methods were studied in order to remove the silicon oil in the PAN microspheres: n-hexane, nature volatile and supercritical drying, respectively. According to these methods, the CO₂ supercritical drying method was selected as the best method to obtain the solvent-free PAN microspheres, because other two methods cannot completely remove the silicon oil, and make the collapse of the microspheres, wrecking the wall surface of the spheres. The main experimental steps for supercritical drying are: First, the inner silicon oil will be replaced with different low viscosity silicone oil: 30cst, 10cst, 5cst, 1cst, 0.65cst; Second: isoamyl acetate was used to replace the silicone oil; Third: liquid carbon dioxide replaced the isoamyl acetate and carbon dioxide is evaporated in supercritical environment. The non-solvent hollow PAN microspheres were obtained.

2.5 Heat treatments of solvent-free PAN microspheres

Solvent-free PAN microspheres were oxidated under at 260 °C、280 °C、300 °C、320 °C、340 °C respectively with a heating rate of 3 °C/min, and kept at 260 °C、280 °C、300 °C、320 °C、340 °C for 2 h in air. Then the pre-oxidation microspheres were carbonized at 800 °C with a heating rate of 16 °C/min, and kept for 3 min under the protection of high purity Argon (Ar).

2.6 Characterizations of PAN microspheres

Photographs of the microspheres were taken by optical stereo scopic microscope (Olympus U-LH75XEAP0, Tokyo, Japan) equipped with charge couple-device camera (Evolution MP 5.0 and DP72, Olympus Corporation) based on different amplification factor. The morphology images of the microspheres were taken with a Zeiss Ultra Plus field emission SEM operating at 2 to 7 kV (Zeiss, Oberkochen, Germany). The elemental analysis was conducted by energy dispersive X-ray analysis (EDS) attached to the FESEM.

Fig.1. Sketch of formation for PAN emulsions by the double emulsion stirring method

3 Results and discussion

3.1 Effect of pre-oxidation temperature on the structure of hollow PAN microspheres

Hollow PAN microspheres cannot meet the experimental requirements with respect to gas security, as their surface morphology is vulnerable to cracks due to vapor. With storage time, the number and size of cracks increases, seriously affecting the gas retention of the PAN microspheres. Therefore, we can learn from the preparation process of the PAN-based carbon fibers with the aim of increasing the tightness of the PAN microspheres through a pre-oxidation process. Currently, the polymer capsules can be used by coating their surfaces two or three times; in contrast, PAN microspheres can be formed via a core-sheath double structure in the oxidation process by controlling the experimental conditions. Through generation of this structure, the natural coating structure can be exactly formed, reducing the number of subsequent processing steps. Since each treatment of the outer surface increases the loss rate for the microspheres, reducing the number of steps that comprise the coating step (i.e., the number of treatments) equates to an increase in the success rate of the

microsphere preparation.

Pre-oxidation PAN microspheres were obtained at different temperatures (260 °C, 280 °C, 300 °C, 320 °C, and 340 °C) with a heating rate of 3 °C/min; microspheres were kept at each temperature for 2 h in air. Figure 2 shows the scanning electron microscopy (SEM) images of these microspheres. These images show that the skin–core structure of the pre-oxidation PAN microspheres was not obvious at 260 °C or 280 °C. Compared with the microspheres obtained at other temperatures, the skin–core structure is very apparent for those treated at 300 °C. The dense layer is on the outside and the loose core layer is in the inside, consistent with the layers in the pre-oxidation fiber.[28]

With the increase in the treating temperature, the difference of the skin–core structure is increasingly obscure, as the interior density of the core layer increases with the temperature increase. Simultaneous to this process, the wall thickness is reduced by cyclization and oxidation reactions. In particular, the wall thickness of the pre-oxidation PAN microspheres is down to about 2-3 μm at the pre-oxidation temperature of 340 °C. This can lead to a substantial decrease in intensity of the microspheres after the pre-oxidation. The space between the macromolecular chains constituted the wall of spheres during the pre-oxidation reaction, which grows smaller due to the mutual coupling between the molecular chains. With disappearance of the space between the chains, the wall thickness of the microspheres declined.

Fig.2. The FESEM images of the wall section of PAN pre-oxidation microspheres under different temperatures: 260 °C(a), 280 °C(b), 300 °C(c), 320 °C(d), 340 °C (e)

3.2 Elemental analysis

The EDS elemental energy spectrum analysis was located on the wall of the pre-oxidation PAN microspheres, as the microspheres' outer and inner walls are affected by the dense oxide layer. The statistics in Table 1 show how the analysis of the elements will be obtained. In Table 1, it can be seen that the content of the C atoms for the PAN microspheres declines with pre-oxidation increases in temperature. The content comprising O atoms gradually increases, with the number of N atoms remaining relatively stable. When the temperature reaches 300 °C, the element content of the microspheres remains relatively stable, even as the pre-oxidation temperature rises again. PAN microspheres can become fully oxidized at heating conditions of 300 °C; the loose structures of the walls of the PAN microspheres become dense at this temperature. With continued increases in temperature, the degree of close connection

between the molecular chains also continues to increase (without having much of an impact of the course of the pre-oxidized microsphere) to form an intramolecular ladder structure. This also leads to reduction in the wall thickness of the PAN microspheres, impacting their hardness. In conclusion, 300 °C is the optimal processing temperature.

Table. 1. Element analysis under the different pre-oxidation temperature

Atom Percentage	260°C	280°C	300°C	320°C	340°C
C	77.19%	65.55%	56.28%	59.73%	56.92%
N	15.23%	15.31%	23.07%	18.94%	22.57%
O	7.58%	16.08%	19.39%	19.97%	16.76%

3.3 Infrared analysis

As-prepared PAN pre-oxidized microspheres at different temperatures were obtained under infrared analysis. The sample was prepared by using a small amount of pre-oxidized PAN microspheres crushed in a tablet together with KBr as a sample for the purpose of infrared detection. As-prepared samples developed at processing temperatures of 260 °C, 280 °C, 300 °C, 320 °C, and 340 °C were obtained for the purpose of comparison (shown in Fig. 3). These results from infrared processing showed that absorption peaks of pre-oxidation PAN microspheres remain relatively stable, as the amount of the sample preparation process is not consistent, with large differences between each sample. Therefore, the heights of the different absorption spectra peaks do not have good comparability.

Fig.3. Infrared spectrogram under the different pre-oxidation temperature

The spectrum line of the PAN pre-oxidation microspheres at 300 °C is shown in Fig. 4. The absorption peak at 800 cm^{-1} is caused by an aromatic ring = CH plane bending vibration; this absorption peak proved that the original straight-chain molecules for PAN became an unsaturated aromatic ring structure in the cyclization reaction during the pre-oxidation process. However, the absorption peak between 950 cm^{-1} to 1290 cm^{-1} is caused by oxygen-containing groups; the two absorption peaks between 1024 cm^{-1} and 1096 cm^{-1} are related to the oxygen-containing groups in the PAN linear molecular, and the absorption peak at 1261 cm^{-1} is caused by the vibration of oxygen-containing groups in excited-state branching or the between-molecules bridge, indicating the completion of the oxidation reaction.

Fig.4. Infrared spectrogram and absorption peak under the 300 °C pre-oxidation temperature of the PAN pre-oxidation microspheres

3.4 Effect of pre-oxidation times on the PAN microspheres

Then as-prepared pre-oxidation PAN microspheres underwent infrared detection for the purpose of exploring the effect of pre-oxidation times on the PAN microspheres with the temperature at 300 °C at different times (2 h, 3 h, 4 h, 6 h, 8 h), during which the pre-oxidation heating rate was not changed; any temperature increases were only carried out to maintain time.

With increases in processing time, two new absorption peaks appeared at 1392 cm^{-1} and 1608 cm^{-1} ; the 1608 cm^{-1} absorption peak was caused by the vibration of the aromatic ring $\text{C} = \text{C}$ skeleton structure, indicating that with time increases, the dehydrogenation reaction occurred in the form of oxygen in the air, O atoms and H atoms in the molecular combination to lead to the formation of water molecules, and the subsequent generation of a large number of double bonds of unsaturated $\text{C} = \text{C}$ in the main chain. However, the absorption peak at 1392 cm^{-1} is likely to come from the pre-oxidation process, where the branched chain of cyano C and (on the other chain) cyano N became an amide $-\text{CO}-\text{NH}-$ structure with the role of the O atom; the amide structure $-\text{C}-\text{N}-$ vibration culminated with this absorption peak. These two new peaks

can be attributed to increases in processing time, during which the degree of intermolecular oxidation reactions is carried out to a greater degree, with closer connection between the molecular chains (Fig. 5).

Fig.5. Infrared spectrogram under the different processing times below 300 °C

3.5 Variation in inner and outer diameter before and after pre-oxidization of the PAN microspheres

As-prepared pre-oxidation PAN microspheres were measured at more than 5 temperatures for inner and outer diameter and wall thickness. Since pre-oxidized PAN microspheres become black and opaque after the pre-oxidation process, traditional instruments cannot be used to measure their parameters. X-ray diffraction is the preferred method for measuring diameter and wall thickness in this scenario. Experimental temperature treatments selected were chosen so that 5 microsphere samples could be measured. We used the 180° interval (symmetrical 2 points) to measure the wall thickness and inner and outer diameter of the PAN pre-oxidation microspheres, then compared the wall thickness and inner diameter shrinkage before and after pre-oxidation treatment.

Table. 2. The measurement data of the PAN pre-oxidation microspheres under different temperature

Temperature	Number	Mean inner diameter/ μm	Average wall thickness / μm	Inner diameter shrinkage	Wall thickness shrinkage
260	1	294.50	18.09	14.96%	5.29%
	2	334.99	12.66	15.18%	13.23%
	3	316.75	23.08	14.15%	4.94%
	4	312.95	20.18	16.89%	-4.45%
	5	300.37	16.07	18.91%	14.97%
280	1	303.47	17.23	15.56%	8.55%
	2	328.76	23.61	12.26%	5.82%
	3	304.64	18.97	14.75%	20.56%
	4	323.58	22.29	14.67%	8.98%
	5	307.09	16.61	11.78%	9.33%
300	1	295.31	16.85	14.16%	2.60%

	2	307.29	30.46	18.47%	-18.29%
	3	269.92	22.48	21.65%	-12.34%
	4	322.21	27.59	15.74%	1.08%
	5	315.83	17.63	15.53%	7.41%
320	1	290.56	18.46	17.06%	8.43%
	2	285.59	19.14	19.60%	-24.53%
	3	344.18	15.08	14.87%	13.53%
	4	301.01	17.74	18.89%	-2.66%
	5	300.69	16.21	16.25%	0.55%
340	1	257.44	21.08	17.05%	6.68%
	2	264.26	23.45	18.72%	-0.47%
	3	321.65	23.95	6.01%	20.35%
	4	263.54	19.65	20.80%	7.05%
	5	305.71	30.99	21.84%	3.46%

The results show that the inner diameter of PAN pre-oxidation microspheres shrinks significantly with increases in pre-oxidized temperature, with further

reductions in diameter with continued increases. Wall thickness also is reduced, but with no obvious relationship to the treatment temperature. Anomalously, at points the wall thickness of the pre-oxidation PAN microspheres increased with increases in temperature (Table. 2). We hypothesized that these results may have stemmed from the use of different methods of measurement, leading to the emergence of a large measured error. Perhaps the wall-thickness uniformity of the pre-oxidation PAN microspheres is not very good when a given measurement position is selected; the selected measurement locations, in fact, are not likely to have a common representative. However, from the overall situation, since the cyclization reaction and the oxidation reaction proceed in the pre-oxidation process and molecular chains and intramolecular structures are constantly engaged in cross-linking reactions, the closeness of intermolecular bonding likely results in the inner and outer diameter and wall thickness generally contracting for PAN microspheres.

3.6 Pressure-resistant experiments in PAN pre-oxidation microspheres

As-prepared PAN pre-oxidation microspheres were used for pressure-resistant experiments (Fig. 6). PAN microspheres became rigid after the pre-oxidation process. Rigid spheres break when the pressure applied is more than the tolerance pressure; however, relatively speaking the resistance to pressure of rigid spheres is better than that of the elastic balls prepared with polymers.

Fig. 6. Sketch diagram of equipment serve for pressure-resistant experiments on PAN pre-oxidation microspheres

Table. 3. The pressure-resistant of PAN pre-oxidation microspheres under the different processing temperature

Temperature	Number	Tolerance pressure /MPa	Number	Temperature	Tolerance pressure /MPa
260	1	15.24	1	300	15.68
	2	6.95	2		>17.89
	3	16.08	3		>17.89
	4	13.06	4		16.26
280	1	17.67	1	320	14.75
	2	15.20	2		9.90
	3	17.55	3		8.30
	4	>17.89	4		15.08
340	1	>18.03	3	340	>18.03
	2	>18.03	4		>18.03

Table 3 shows that the pressure-resistant capability of most PAN pre-oxidation microspheres has reached more than 10 MPa, and in pre-oxidation PAN microspheres treated at 300 °C resistance to stress conditions is better than that obtained under other pre-oxidized temperature conditions. However, the resistance to pressure of PAN pre-oxidation microspheres at 340 °C has no obvious changes in the entire experiment. The possible reason is that PAN pre-oxidation microspheres obtained at 340 °C due to the thinner wall thickness led to the appearance of pores in the wall, resulting in the microsphere being unable to retain gas. In this instance, the inner and outer pressure would remain equal during the entire experiment.

4. Conclusion

In this work, PAN microspheres were prepared using the double emulsion stirring method and pre-oxidation microspheres were successfully prepared with the heating treatment. Supercritical drying is the most efficient method to remove the silicon oil in the PAN microspheres. It was found that treatment of PAN microspheres at 300 °C for 2 hours provided the most conducive conditions for the creation of pre-oxidation PAN microspheres. The skin–core structure of these microspheres can be conducive to gas retention. The pressure-resistance test on the pre-oxidation microspheres showed that, after the pre-oxidation process, microspheres can bear greater pressure than microspheres that did not undergo the pre-oxidation heating treatment; this increase in mechanical strength is another obvious enhancement. Most microspheres can bear the pressure of more than 17 MPa, providing a great prospect for future ICF target application.

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^aState Key Laboratory of Bioelectronics, School of Biological Science and Medical Engineering, Southeast University, Nanjing 210096, P. R. China

^bLaser Fusion Research Center, China Academy of Engineering Physics, Mianyang 621900, P. R. China

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Keywords: Polyacrylonitrile (PAN); Double emulsion stirring method; Pre-oxidation; The pre-oxidation PAN microspheres; Pressure resistant

1. Introduction

With the ongoing development of human society, energy issues have become increasingly prominent.[1, 2] Traditional fossil fuels are non-renewable sources of energy that lead to a variety of serious environmental problems with long-term use. The dual challenge of environmental problems and future energy shortages are

* Corresponding authors at: State Key Laboratory of Bioelectronics, Biological Science and Medical Engineering Department, Southeast University, Nanjing 210096, PR China. Tel.: +86 025 83619983; fax: +86 025 83795635.
E-mail addresses: lb6711@126.com (B. Li), lqge@seu.edu.cn (L. Ge).

gradually becoming hindrances to further development.[3] To address these issues from a traditional vantage point, clean and efficient sources of energy have been utilized, including wind, solar, and nuclear energy. Of these new energy sources, nuclear energy has been most widely researched currently for its potential applications.

Nuclear fusion and nuclear fission are the two methods to generate nuclear energy . However, nuclear fission can produce a large number of gamma rays, and materials and byproducts contain a high level of radioactive isotopes of heavy metals.[4, 5] If handled improperly, these materials and waste products would have a very serious adverse impact on the environment and human. Given this circumstance, nuclear fusion is currently the energy-providing method of choice for those interested in nuclear energy.

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Table.1. Comparisons the property of PAN materials with other materials

	PS	PAN	PVA
The gas permeability	$\sim 10^{-14}$	$\sim 10^{-17}$	$10^{-18} \sim 10^{-20}$

coefficient of the			
deuterium gas/			
mol.m-1.s-1.Pa-1			
Tensile strength /MPa	80	» 600	60-100
Low temperature			
resistance	bad	well	bad
Irradiation resistance	well	well	bad

PAN (which attains its mechanical strength and chemical stability through heat treatment) is widely used for carbon fibers.[21] The process of converting PAN fibers into PAN carbon fibers mainly includes molding, pre-oxidation, and a carbonization which was also investigated in early researches.[22, 23] The PAN-based pyrolysis reaction combines prestabilization and carbonization and contains intrachain cyclization, dehydration and denitrogenation.[24, 25] The whole chemical reaction can convert a linear polymer into turbostratic carbon by increasing the heating temperature.[26, 27]

In this paper, we characterize and detect the microstructures and properties of pre-oxidation PAN microspheres at different treatment temperatures. Additionally, we hope to prepare the hollow PAN microspheres with higher intensity and better performance with respect to gas retention so that suitable polymer or carbon targets are developed for use in the fusion process.

2. Experimental Section

2.1 Materials

PAN powders (Mw: 60000) and N, N-dimethylformamide (DMF) were obtained from Sigma-Aldrich CO. Ltd and Sinopharm Chemical Reagent Co. Ltd. Aliquat 336 was bought from Alfa Aesar A Johnson Matthey Company, England. The KF-96-1cst /KF-96-5cst /KF-96-10cst /KF-96-50cst silicon oils were obtained from Shin-Etsu Chemical Co. Ltd. Japan. The PAN powders were dissolved in DMF (1:6.67 (w/v)) homogeneously. All the chemicals were used as received without any purification.

2.2 Preparation of PAN solution

4.5g PAN powders were dissolved in 30ml DMF with 3 ml Aliquat [®]336 to form 15% PAN (m/v) solution.

2.3 Preparation of PAN microspheres using the double emulsion stirring method

To obtain PAN hollow microspheres, one should prepare the double emulsions, the oil / PAN solution/ oil (O1 / W / O2) system. The first step is that silicone oil is dropped into PAN solution during stirring ($V_{O1} : V_{PAN}$ is 1:2 to 1.5:2).

The second step is that single emulsion droplets which obtained in the first step were added in the bulk with same viscosity of silicone oil ($V_{O1}/w : V_{O2}$ is 1:100) and stirring constantly. Thereafter, the mixed solution was kept stirring 24 h at room temperature in order to volatilize DMF organic solvents, promoting PAN hollow microspheres solidification (Fig.1).

2.4 Preparation of solvent-free hollow PAN microspheres

Three different drying methods were studied in order to remove the silicon oil in the PAN microspheres: n-hexane wash, nature volatile and supercritical drying. Compared to the others, the CO₂ supercritical drying method is subject to keep the PAN capsules integrity. CO₂ supercritical drying process consists of two steps, the first, solvent exchange, where the PAN capsules were immersed in sequence silicone oil with different low viscosity with 30cst, 10cst, 5cst, 1cst, 0.65cst. Finally, immersed in the isoamyl acetate to remove silicone oil. The second, supercritical drying, substituted the isoamyl acetate for liquid carbon dioxide and carbon dioxide evaporated in supercritical environment. The non-solvent hollow PAN microspheres were obtained.

2.5 Heat treatments of solvent-free PAN microspheres

Solvent-free PAN microspheres were oxidated at 260°C、280°C、300°C、320°C、340°C respectively with a heating rate of 3 °C/min, and kept at 260°C、280°C、300°C、320°C、340°C for 2 h in air. Then the pre-oxidation microspheres were carbonized at 800 °C with a heating rate of 16 °C/min, and kept for 3 min under the protection of high purity Argon (Ar).

2.6 Characterizations of PAN microspheres

Photographs of the microspheres were taken by the optical stereo scopic microscope (Olympus U-LH75XEAP0, Tokyo, Japan) equipped with the charge

couple-device camera (Evolution MP 5.0 and DP72, Olympus Corporation) based on different amplification factors. The morphology images of the microspheres were taken with the Zeiss Ultra Plus field emission SEM operating at 2 to 7 kV (Zeiss, Oberkochen, Germany). The elemental analysis was conducted by the energy dispersive X-ray analysis (EDS) linked to the FESEM.

Fig.1. Sketch of formation for PAN emulsions by the double emulsion stirring method

3 Results and discussion

3.1 Effect of pre-oxidation temperature on the structure of hollow PAN microspheres

Hollow PAN microspheres cannot meet the experimental requirements with respect to gas security, as their surface morphology is vulnerable to cracks due to vapor. With storage time, the number and size of cracks increases, seriously affecting the gas retention of the PAN microspheres. Therefore, we can learn from the preparation process of the PAN-based carbon fibers with the aim of increasing the tightness of the PAN microspheres through a pre-oxidation process. Currently, the polymer capsules can be used by coating their surfaces two or three times. In contrast,

PAN microspheres can be formed via a core-sheath double structure in the oxidation process by controlling the experimental conditions. Due to the generation of this structure, the natural coating structure can be exactly formed, simplifying the subsequent process. Since each treatment of the outer surface increases the loss of the microspheres, reducing the number of steps that comprise the coating step (i.e., the number of treatments) equates to increasing in the success rate of the microsphere preparation.

Pre-oxidation PAN microspheres were obtained at different temperatures (260 °C, 280 °C, 300 °C, 320 °C, and 340 °C) with a heating rate of 3 °C/min. and the microspheres were kept at each temperature for 2 h in air. Fig.2 shows the scanning electron microscopy (SEM) image of PAN microsphere. Fig.3 shows the cross section of PAN pre-oxidation microspheres at the different treatment conditions. Fig.3a and Fig.3b show that the skin-core structure of the pre-oxidation PAN microspheres was not obvious at 260 °C or 280 °C, it is difficult to distinguish the dense layer and loose core layer. Compared with the microspheres obtained at other temperatures, the skin-core structure was very apparent for those treated at 300 °C (Fig.3c). The dense layer is on the outside and the loose core layer is in the inside, consistent with the layers in the pre-oxidation fibers.[28]

With the treating temperature increase, the difference of the skin-core structures is increasingly obscure, as the interior density of the core layer increases. Simultaneous to this process, the wall thickness is reduced by the cyclization and oxidation reactions. In particular, the wall thickness of the pre-oxidation PAN microspheres is down to about 2-3 μm at the pre-oxidation temperature of 340 °C (Fig.3e). This can lead to a substantial decrease in intensity of the microspheres after the pre-oxidation. The space between the macromolecular chains constituted the wall of spheres during the pre-oxidation reaction, which grows smaller due to the mutual coupling between the molecular chains. With disappearance of the space between the chains, the wall thickness of the microspheres declined.

Fig.2 FESEM image of PAN pre-oxidized microsphere

Fig.3. The FESEM images of the wall section of PAN pre-oxidation microspheres under different temperatures: 260 °C(a), 280 °C(b), 300 °C(c), 320 °C(d), 340 °C (e)

3.2 Elemental analysis

The EDS elemental energy spectrum analysis was located on the wall of the pre-oxidation PAN microspheres, as the microspheres' outer and inner walls are affected by the dense oxide layer. The statistics in Table.2 show the analysis of the elements. In Table 2, it can be seen that the content of the C atoms of the PAN microspheres declines with the pre-oxidation increases in temperature increase. The content comprising O atoms gradually increases while the number of N atoms remains relatively stable. When the temperature reaches 300 °C, the element content of the microspheres remains relatively stable, even as the pre-oxidation temperature rises again. PAN microspheres can become fully oxidized in the heating conditions of 300 °C and the loose structures of the walls of the PAN microspheres become dense at this temperature. With continued increases in temperature, the degree of close connection between the molecular chains also continues to increase (without having much of an impact of the course of the pre-oxidized microsphere) to form an intramolecular ladder structure. This also leads to reduction in the wall thickness of the PAN microspheres, impacting their hardness. In conclusion, 300 °C is the optimal processing temperature.

Table. 2. Element analysis under the different pre-oxidation temperature

Atom Percentage	260°C	280°C	300°C	320°C	340°C

C	77.19%	65.55%	56.28%	59.73%	56.92%
N	15.23%	15.31%	23.07%	18.94%	22.57%
O	7.58%	16.08%	19.39%	19.97%	16.76%

3.3 Infrared analysis

As-prepared PAN pre-oxidized microspheres at different temperatures were processed by the infrared analysis. The sample was prepared by using a small amount of pre-oxidized PAN microspheres crushed in a tablet together with KBr for the purpose of infrared detection. As-prepared samples developed at processing temperatures of 260 °C, 280 °C, 300 °C, 320 °C, and 340 °C were obtained for the purpose of comparison (shown in Fig.4). These results from infrared processing showed that absorption peaks of pre-oxidation PAN microspheres remain relatively stable, though the amount of the sample preparation process is not consistent, with large differences between each sample. Therefore, the heights of the different absorption spectra peaks do not have good comparability.

Fig.4. Infrared spectrogram under the different pre-oxidation temperature

The spectrum line of the PAN pre-oxidation microspheres at 300 °C is shown in Fig. 5. The absorption peak at 800 cm⁻¹ is caused by an aromatic ring = CH plane bending vibration. This absorption peak proved that the original straight-chain molecules for PAN became an unsaturated aromatic ring structure in the cyclization reaction during the pre-oxidation process. However, the absorption peak between 950 cm⁻¹ to 1290 cm⁻¹ is caused by oxygen-containing groups and the two absorption peaks between 1024 cm⁻¹ and 1096 cm⁻¹ are related to the oxygen-containing groups in the PAN linear molecular. The absorption peak at 1261 cm⁻¹ is caused by the vibration of oxygen-containing groups in excited-state branching or the between-molecules bridge, indicating the completion of the oxidation reaction.

Fig.5. Infrared spectrogram and absorption peak under the 300 °C pre-oxidation temperature of the PAN pre-oxidation microspheres

3.4 Effect of pre-oxidation times on the PAN microspheres

Then as-prepared pre-oxidation PAN microspheres underwent infrared detection

for the purpose of exploring the effect of pre-oxidation times with the temperature through 300 °C at different times (2 h, 3 h, 4 h, 6 h, 8 h), during which the pre-oxidation heating rate was not changed. Any temperature increases were only carried out to maintain the same time.

With increases in processing time, two new absorption peaks appeared at 1392 cm^{-1} and 1608 cm^{-1} . The 1608 cm^{-1} absorption peak was caused by the vibration of the aromatic ring C = C skeleton structure, indicating that with time increases, the dehydrogenation reaction occurred in the form of oxygen in the air, O atoms and H atoms in the molecular combination to lead to the formation of water molecules, and the subsequent generation of a large number of double bonds of unsaturated C = C in the main chain. However, the absorption peak at 1392 cm^{-1} is likely to come from the pre-oxidation process, where the branched chain of cyano C and (on the other chain) cyano N became an amide -CO-NH- structure with the role of the O atom. The amide structure -C-N- vibration culminated with this absorption peak. These two new peaks can be attributed to increases in processing time, during which the degree of intermolecular oxidation reactions is carried out to a greater degree, with closer connection between the molecular chains (Fig. 6).

Fig.6. Infrared spectrogram under the different processing times at 300 °C

3.5 Variation in inner and outer diameter before and after pre-oxidization of the PAN microspheres

As-prepared pre-oxidation PAN microspheres were measured at more than 5 temperatures for inner and outer diameter and wall thickness. Since pre-oxidized PAN microspheres become black and opaque after the pre-oxidation process, traditional instruments cannot be used to measure their parameters. X-ray diffraction is the preferred method for measuring diameter and wall thickness in this scenario. Each of experimental treatment temperature was chosen to measure 5 microsphere samples. We used the 180° interval (symmetrical 2 points) to measure the wall thickness and inner and outer diameter of the PAN pre-oxidation microspheres, then compared the wall thickness and inner diameter shrinkage before and after pre-oxidation treatment.

Table. 3. The measurement data of the PAN pre-oxidation microspheres under different temperature

Temperature	Number	Mean inner diameter/ μm	Average wall thickness / μm	Inner diameter shrinkage	Wall thickness shrinkage
260	1	294.50	18.09	14.96%	5.29%
	2	334.99	12.66	15.18%	13.23%
	3	316.75	23.08	14.15%	4.94%
	4	312.95	20.18	16.89%	-4.45%

	5	300.37	16.07	18.91%	14.97%
280	1	303.47	17.23	15.56%	8.55%
	2	328.76	23.61	12.26%	5.82%
	3	304.64	18.97	14.75%	20.56%
	4	323.58	22.29	14.67%	8.98%
	5	307.09	16.61	11.78%	9.33%
300	1	295.31	16.85	14.16%	2.60%
	2	307.29	30.46	18.47%	-18.29%
	3	269.92	22.48	21.65%	-12.34%
	4	322.21	27.59	15.74%	1.08%
	5	315.83	17.63	15.53%	7.41%
320	1	290.56	18.46	17.06%	8.43%
	2	285.59	19.14	19.60%	-24.53%
	3	344.18	15.08	14.87%	13.53%

	4	301.01	17.74	18.89%	-2.66%
	5	300.69	16.21	16.25%	0.55%
340	1	257.44	21.08	17.05%	6.68%
	2	264.26	23.45	18.72%	-0.47%
	3	321.65	23.95	6.01%	20.35%
	4	263.54	19.65	20.80%	7.05%
	5	305.71	30.99	21.84%	3.46%

The results indicate that the inner diameter of PAN pre-oxidation microspheres shrinks significantly with the increases in pre-oxidized temperature. Wall thickness is also reduced, but with no obvious relationship to the treatment temperature. Anomalously, at points the wall thickness of the pre-oxidation PAN microspheres increased with increases in temperature (Table. 3). We hypothesized that these results may have stemmed from the use of different methods of measurement, leading to the emergence of a large measured error. Perhaps the wall-thickness uniformity of the pre-oxidation PAN microspheres is not very good when a given measurement position is selected and the selected measurement locations, in fact, are not likely to have a common representatively. From the overall situation, since the cyclization reaction and the oxidation reaction proceed in the pre-oxidation process and molecular chains and intramolecular structures are constantly engaged in cross-linking reactions, the closeness of intermolecular bonding likely results in the inner and outer diameter and wall thickness generally contracting for PAN microspheres.

3.6 Pressure-resistant experiments in PAN pre-oxidation microspheres

As-prepared PAN pre-oxidation microspheres were used for pressure-resistant experiments (Fig. 7). PAN microspheres became rigid after the pre-oxidation process. Rigid spheres break when the pressure applied is more than the tolerance pressure; Relatively speaking the resistance to pressure of rigid spheres is better than that of the elastic balls prepared with polymers.

Fig. 7. Sketch diagram of equipment serve for pressure-resistant experiments on PAN pre-oxidation microspheres

Table. 4. The pressure-resistant of PAN pre-oxidation microspheres under the different processing temperature

Temperature	Number	Tolerance pressure /MPa	Number	Temperature	Tolerance pressure /MPa
260	1	15.24	1	300	15.68
	2	6.95	2		>17.89
	3	16.08	3		>17.89
	4	13.06	4		16.26
280	1	17.67	1	320	14.75
	2	15.20	2		9.90
	3	17.55	3		8.30

	4	>17.89	4		15.08
340	1	>18.03	3	340	>18.03
	2	>18.03	4		>18.03

Table.4 shows that the pressure-resistance ability of most PAN pre-oxidation microspheres has reached more than 10 MPa, and in pre-oxidation PAN microspheres treated at 300 °C resistance to stress conditions is better than that obtained under other pre-oxidized temperature conditions. The resistance to pressure of PAN pre-oxidation microspheres at 340 °C has no obvious changes in the entire experiment. The possible reason is that PAN pre-oxidation microspheres obtained at 340 °C due to the thinner wall thickness led to the appearance of pores in the wall, resulting in the microsphere being unable to retain gas. In this instance, the inner and outer pressure would remain equal during the entire experiment.

4. Conclusion

In this work, PAN microspheres were prepared using the double emulsion stirring method and pre-oxidation microspheres were successfully prepared with the heating treatment. It was found that treatment of PAN microspheres at 300 °C for 2 hours provided the most conducive conditions for the creation of pre-oxidation PAN microspheres. The skin–core structure of these microspheres can be conducive to gas retention. The pressure-resistance test on the pre-oxidation microspheres showed that, after the pre-oxidation process, microspheres can bear greater pressure than microspheres that did not undergo the pre-oxidation heating treatment. Consequently, the mechanical strength of PAN microspheres is obviously enhanced. Furthermore, most microspheres can bear the pressure of more than 17 MPa, providing a great prospect for future ICF target application.

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