The Study of High Strength Reticulated Vitreous Carbon Preparation Method

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Abstract. Reticulated vitreous carbon (RVC) is a very promising functional material but the lower strength of foamed carbon greatly limits its application range. In order to increase the strength of the reticulated vitreous carbon, we used to add graphene during the preparation process because of its high strength. The foams were manufactured by multiple replication of a polyurethane foam template structure using ethanolic solutions of phenolic resin and graphene. Then the foams of preparation were carbonized in an inert atmosphere 700ºC-1000ºC by polyurethane foam impregnated with phenolic resin precursor. The proper addition of graphene was sought by testing the mechanical properties of the reticulated vitreous carbon and observing its microstructure. The results show that the addition of graphene could improve the mechanical properties of reticulated vitreous carbon.

1. Introduction
Carbon foams were first developed in the 1960 by Ford [1]. At the beginning, the Carbon foams were made by carbonized of the Phenolic foam to obtain reticulated vitreous carbon (RVC) foam. In the decades of years that followed, researchers did a great deal of work on the preparation and modification of reticulated vitreous carbon foam [2]. In the 1990s, new foam carbon materials were prepared using bitumen and coal instead of resins as precursors. Researchers at the U.S. Air Force Materials Laboratory formed a carbon foam by applying "blown" technology to mesophase pitch. Before they carbonized and graphitized foam oxidation stability [3]. The foams was developed primarily to replace the expensive three-dimensional braided fiber preforms in polymer composites and honeycomb materials. West Virginia research team developed a method of using coal as high-strength foam precursor, the foam has excellent thermal insulation properties and high strength. Reticulated vitreous carbon has a porous network structure of light materials, with porous, low density, large specific surface area, good corrosion resistance, high temperature thermal stability, thermal conductivity and conductivity adjustable [4]. So these can be widely used in aerospace and industrial applications, including thermal insulation, impact absorption, catalyst support, and gas filtration. Due to the fact that most of the resinous polymers were precursors, the prepared carbon foam has general strength, high brittleness and no graphitization [5]. In order to overcome the shortcomings of the mechanical properties of carbon foam and broaden its application fields, researchers used a variety of methods to modify their structure, including adding enhancers, optimizing process parameters and using different raw materials.

In 2004, the Geimteamatthe University of Manchester in the UK produced stable graphene for the first time [6]. Graphene is the only two-dimensional free-state atomic crystal that has been discovered.
so far. Graphene is the basic structural unit of sp² hybrid carbon, such as zero-dimensional fullerene, one-dimensional carbon nanotube and three-dimensional bulk graphite. This has drawn great attention from scientists in other fields such as chemistry and materials. Graphene is one of the most known materials known to date, and has good toughness and can be bent. The theoretical Young's modulus of graphene is 1.0 TPa, and the inherent tensile strength is 130 GPa. Hydrogen plasma-modified reduced graphene also has very good strength, with an average modulus of 0.25 TPa. The researchers of University of Manchester found that adding graphene can make the mechanical properties of the tire has been significantly improved, the tensile strength increased by about 50%.

In the short period of time, graphene has been rapidly excavated and developed for its excellent performance and potential application prospects. At the same time, a large number of high quality and structured graphene materials are needed. The preparation of graphene can be roughly divided into physical methods and chemical methods. Among them, the chemical method was studied earlier, mainly benzene ring or other aromatic system as the core, through the coupling reaction of the benzene ring are replaced by six carbon, and then between adjacent substituents to form an evaromatic ring, So multi-step reaction to make the aromatic system larger, but the method cannot be synthesized with a larger planar structure of graphene. The physical method is mainly to graphite as raw materials to synthesize, not only cheap and readily available raw materials, but also get a larger planar structure of graphene.

2. Experiment
Materials. The polyurethane foams were hydrolyzed in sodiumhydr oxide solution with different mass fraction (6%~12%). The foam after the hydrolysis treatment was repeatedly washed with deionized water to neutral to remove residual alkali in the foam. After drying in an oven, the mass of the foam was weighed with an electronic balance. The phenolic resin was then dissolved in ethanol and 0%, 0.5%, 1%, 2% by mass of graphene was added as the carbon source of the foamed carbon. The polyurethane templates were respectively immersed in the carbon source for 30 minutes and then the excess liquid was removed and cured in an oven at 180ºC for 30 minutes and repeated several times. Finally, the precursor was carbonized at 1000ºC in an inert atmosphere at a rate of 1ºC per minute and incubated for 1 hour.

Testing. The compression strength was examined by electronic universal testing machine (MTS, CMT5105). The morphology and structure of samples were analyzed by the scanning electron microscope (Quanta250 FEG). The pore size distribution were measured by the mercury method (QuantaPoreMaster60).

Figure 1. The degree of hydrolysis of the polyurethane.
3. Results and discussion

A large number of closed cells exist in the polyurethane foam. The closed cells were composed of a layer of polyurethane film. A large number of polymer films affect the open porosity of the carbon foam after carbonization. These closed cells obstruct the impregnation of the polyurethane foam with the phenol resin. The amount of impregnation was greatly reduced. The presence of closed cells in the polyurethane foam can have a severe effect on the impregnation of the phenolic resin so as to affect the pore structure characteristics and compressive strength of the final foam carbon product.

Polyurethane foam was immersed with 6%, 8%, 10%, 12% mass fraction sodium hydroxide at 50°C for 1 hour. The degree of hydrolysis was calculated by comparing the mass of the polyurethane template before and after hydrolysis. The Figure 1 shows the hydrolysis of a polyurethane template at 50°C for 1 hour with different sodium hydroxide mass fraction. Figure 1 shows that the degree of hydrolysis of polyurethane foam was increased with the mass fraction of sodium hydroxide.

![Figure 1](image1.png)

**Figure 1.** Hydrolysis degrees of polyurethane foam with different sodium hydroxide mass fraction.

The hydrolyzed polyurethane template was immersed in phenolic resin for 30 minutes and then cured at 180°C for 30 minutes. The unhydrolyzed polyurethane foam was chosen to repeat the same procedure as a reference sample. The Figure 2 shows phenolic resin impregnation curves of sodium hydroxide with different mass fraction. Compared with the unhydrolyzed polyurethane foam, the hydrolyzed polyurethane foam phenolic resin impregnated more. The high degree of hydrolysis of the template could make the polyurethane foam deformation was too large, the hole wall weakened obviously, significantly reduce the resilience of polyurethane foam in the pretreatment difficult to restore the original state, the mechanical strength greatly reduced, lost the porous structure. When the degree of hydrolysis of the template was too low, it could affect the amount of phenolic resin impregnated and reduce the mechanical strength of the foam carbon. According to the Figure 1 and Figure 2, when the mass fraction of sodium hydroxide was 6%, the degree of hydrolysis of the template is only about 6.3%. In this case, the amount of carbon source impregnated was insufficient, so that the strength of the foam carbon was low. When the mass fraction of sodium hydroxide was 8%, the degree of hydrolysis of the polyurethane template was about 10.1%. In this case, it has the same situation as the sample above. When the mass fraction of sodium hydroxide was 10%, the degree of hydrolysis of the polyurethane template was about 14.1%. In this case, it has better impregnation amount of the phenolic resin and the structural integrity of the polyurethane template. When the mass fraction of sodium hydroxide was 12%, the degree of hydrolysis of the polyurethane template was about 19.2%. In this case, the sample lost its resilience and could not serve as a template. According to Figure 1 and Figure 2, when the mass fraction of sodium hydroxide was 10%, the template effect hydrolysis treatment was preferably.
Figure 3. The compressive strength curves of different graphene mass fraction.

During the phenolic resin impregnation, different mass fractions of graphene were added. After carbonization, the compressive strength of the test specimen was tested. The compression strength of the reticulated vitreous carbon prepared by carbonizing the samples with different mass fraction of graphene was shown in Figure 3. The results show the compressive strength of the reticulated vitreous carbon increases as the amount of graphene increases. This indicates that the strength of foamed carbon could be effectively increased by adding graphene. The phenolic resin impregnation of the unhydrolyzed template was only 50.7%, resulting in a lower mechanical strength foam carbon made. When the degree of hydrolysis of template was 6%, 8%, 10%.

Figure 4. SEM images of Samples before carbonization and after carbonization.

According to the Figure 4, the results show that the carbon foam was produced after carbonization retains the structure of the polyurethane template. The carbon foam have a similar pore size distribution. In the Figure 5 and Figure 6, the results show that graphene could be fixed in the reticulated vitreous carbon’s ligament structure department where prone to brittle fracture by adding graphene. The greater the graphene mass fraction, the more graphene was attached around the ligament structure. During the carbonization of the sample, graphene mixed with phenolic resin was carbonized in the ligament structure. Graphene was closely linked to the ligament structure of the sample, supporting the structure where easy to break.
Figure 5. SEM images of reticulated vitreous carbon with 1% grapheme.

Figure 6. SEM images of reticulated vitreous carbon with 1.5% grapheme.

Figure 7. Pore size distribution plots of reticulated vitreous carbon.
In the Figure 7, the results show that the combination of mercury intrusion porosimetry can measure reticulated vitreous carbon’s holes pore size were mainly distributed in 5-10μm. The reticulated vitreous carbon retained the structure of the phenolic resin as a template. The reticulated vitreous carbon has a large number of pores, can be used as a catalyst carrier or thermal insulation with good heat insulation properties.

4. Conclusions
(1) The choice of 10% sodium hydr oxide for hydrolysis can maintain the structural integrity of the template and increase the amount of phenolic resin impregnated. This was a suitable method for template pre-processing.

(2) Adding graphene can effectively improve the strength of reticulated vitreous carbon. At a certain mass fraction, with the increase of graphene, the compressive strength of reticulated vitreous carbon also increased. Adding graphene was a suitable method to increase the compressive strength of reticulated vitreous carbon.

(3) Reticulated vitreous carbon prepared by this method retained the structure of the template. It can be applied in the field of thermal insulation and catalyst support.

References
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