

DEVELOPMENT OF CARBON FOAM USING COAL-DERIVED PRECURSORS

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Introduction

Carbon foam is a next generation porous carbon material. It has potential applications in such diverse areas as high temperature thermal insulation, high thermal-conductivity heat sinks, energy absorption material, etc. Carbon foam can be made from coal, coal/N-methyl-2-pyrrolidinone solvent extracts and pitch precursors, such as coal-based SynPitch and coal tar pitch[1-2]. The properties of these carbon foams, such as mechanical strength, thermal/electrical conductivity and foam cell structure can be tailored by adjusting the precursor's properties and foaming conditions to meet the requirement of different applications.

The coal-derived carbon foam is a thermal setting material. The foaming process does not require blowing agent or a stabilization step, but it is strongly related to the plasticity of the foaming precursor. Most raw coal and coal/solvent extracts can be foamed directly, but SynPitch and coal tar pitch can not. The major problem for the pitch precursors is that their viscosity is too low to hold the foam cell shape. Therefore, their properties have to be tailored before the foaming can be achieved. In this paper, the foaming mechanism, the pretreatment of foaming precursors and the comparison of the foams derived from different precursors will be discussed.

Experimental

Coal and coal extracts were ground to the prescribed mesh size, e.g., 50-100 mesh and 100-200 mesh. SynPitch and coal tar pitch were pre-treated by heat treatment under N₂ atmosphere. Foaming is carried out in a pressure foamer heated up to 500°C in N₂ under a pressure up to 500psi. All the foams samples were calcined at 1000°C in inert atmosphere. The Gieseler fluidity and dilatation rate were measured by means of a Preiser Plastometer and Dilatometer. SEM images were taken with a Hitachi 4700 FE-SEM. Compressive strength was measured by Instron 5869 using a cylinder shape sample(25mm diameter by 20~30mm height) with a matched stainless steel sample holder and piston.

Results and Discussion

The foaming process requires materials with specific fluidity and dilatation rate. During the heating, volatiles from the light fractions and decomposition products serve as the foaming agent. But only when the material's fluidity is located in a certain range, can the bubble shape be held and the foam matrix created.

Figure 1 shows the Gieseler Fluidity, Dilatation rate and TGA data of typical foaming precursor, i.e., raw coal. As the temperature increases, the material first softens and then turns fluid. The fluidity continues to increase with temperature until finally the material re-solidifies at higher temperature. During the heating, the volume of the fluid material expands and reaches the maximum dilatation at the temperature of the maximum fluidity. The TGA curve indicates that the maximum weight loss overlays nicely with the maximum fluidity and dilatation rate. The TGA data also show that the volatiles keep evolving till the re-solidification temperature of the material is reached. This may be one of reasons why most coal-based carbon foams have an open-cell structure. The dilatation curve reveals the volume expansion at atmospheric pressure. It is obviously too much dilation for generating a normal carbon foam with the acceptable strength and cell size. Therefore, an external pressure has to be applied to the system to decrease the dilatation rate and control the foam cell size.

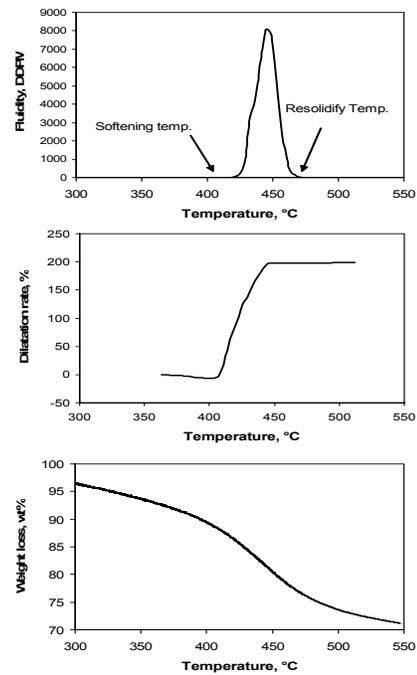


Figure 1 . Gieseler Fluidity curve (top), dilatation rate curve(middle) and TGA curve (bottom) of a typical foaming precursor(coal).

Some coals are perfect foaming precursors. Their foaming behavior is strongly related to the maceral composition of coal, e.g., exinite and resin exhibit strong dilatation, inertinite does not exhibit dilatation and vitrinites are in between [3]. SynPitch and coal tar pitch normally can not be foamed directly. The main reason is their viscosity is too high to hold the foam cell shape. Their plastic properties have to be tailored before foaming can be achieved. Heat treatment is a simple and effective way to adjust the properties of pitches to meet the requirement of foaming. In a N_2 atmosphere, heat treatment generates more planar and condensed molecules, which increases the molecular weight and viscosity of the pitch. Meanwhile, heat treatment is sometimes accompanied by the formation of mesophase [4]. Therefore, the foam prepared from this kind of material will be anisotropic. The chemical reaction involved in heat treatment under N_2 is mainly polymerization and condensation via de-hydrogenation[4-5]. Table 1 presents the effect of the heat treatment on the properties of pitch precursors. Heat treatment significantly increases the softening temperature and narrows the plastic range.

Table 1 Effect of heat treatment on the properties of foaming precursors

Sample	Softening Point, °C	Plastic range, °C
Coal Tar Pitch	117*	>400
Treated Coal Tar Pitch	350**	185
SynPitch	110*	>400
Treated SynPitch,	320**	202

*Mettler Softening point, **from plastometer

Table 2 General properties of the coal and pitch based carbon foams

Samples	Bulk density, g/cc	Porosity, %	Open-cell, %	Compressive Strength, MPa
Kingwood coal	0.32	84.1	96.8	2.9
Lower War Eagle coal	0.33	82.7	98.4	5.5
Bakerstown coal-01	0.38	86.3	98.0	8.0
Bakerstown coal-02	0.40	79.3	97.7	9.9
Powellton extract-01	0.25	87.0	97.1	2.5
Powellton extract-02	0.31	83.6	39.1	18.7
Coal tar pitch based	0.67	64.8	83.5	18.2
Coal SynPitch based	0.42	79.7	95.6	2.8

Table 2 lists the general properties of coal and pitch-based carbon foams. The bulk density ranges from 0.25 to 0.67g/cc. Most of these foams have over 95% open cell structure according to the He density method. The compressive strength is obtained from the yield strength of the stress-stain curve. The compressive strength of these foam samples covers a wide range depending on the precursor used. Most coal-based carbon foams have compressive strength around 2~10MPa. One special coal extract-based foam exhibits a 60% closed cell, which shows a significant high strength. Two pitch-based carbon foams are very different. Coal tar pitch based carbon foam has much higher compressive strength than the one derived from SynPitch, although their densities are comparable, e.g., relative density is 0.35 for coal tar pitch-based foam and 0.20 for SynPitch-based foam.

The strength of carbon foam mainly depends on the foaming precursor and the foam cell structure. Although the relation of foam strength and structure is still under investigation, for open cell foam, the cell size has significant effect on the foam strength. The thickness of cell-wall, t , and the length of the cell-edge, l , are used to describe the cell structure of the foam. The measurement of t and l of the foam seems to be difficult, but for a regular cell structure, the following relation is known [6].

$$(t/l)^2 \propto (D^*/D_s)$$

where D^* , bulk density; D_s , true density of foam, D^*/D_s , relative density.

Coal derived carbon foam usually does not have a perfect, regular cell structure. To simplify, relative density is still used to describe the foam cell structure to compare the

carbon foam derived from similar foaming precursors. Figure 2 exhibits the relation of foam strength with the corresponding relative density of four foam samples derived from very similar bituminous coals. The increase of relative density corresponds to an increase of the thickness of cell wall, t , or decrease of the length of the edge, l . The results clearly confirm that cell size significantly affects the compressive strength of carbon foam. Thicker cell wall and short edge exhibit higher compressive strength. For the closed cell foam, the situation is more complicated. The membrane of closed cell has to be considered. During the crushing, the stretching of the membrane also prevents the foam structure from collapsing. This may be one of the reasons why closed cell foam is stronger.

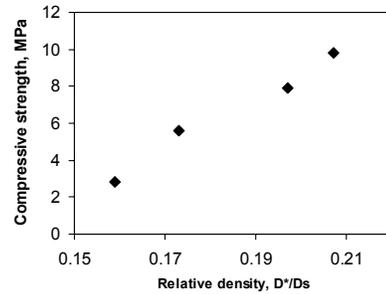


Figure 2 Relation of compressive yield strength with relative density

Figure 3 shows the optical texture of carbon foam derived from coal(a) and pitch(b and c). The coal and extract based carbon foams show an isotropic texture (coal extract derived picture is not shown). However, pitch-derived carbon foams show some anisotropic domains. Figure 3(b) is the foam derived from coal-based SynPitch, which shows large anisotropic domains aligned in parallel along the cell wall, indicating heat treatment of this pitch generates some mesophase. Figure 3(c) is the foam derived from coal tar pitch containing quinoline insoluble(QI). Here, only small anisotropic domains are observed. This is because QI prevents the coalescing of the anisotropic domains. This kind of carbon foam will be less graphitizable but it will be mechanically stronger. Therefore, the foam properties could be controlled and tailored by using the different precursors to meet the requirements of different applications.

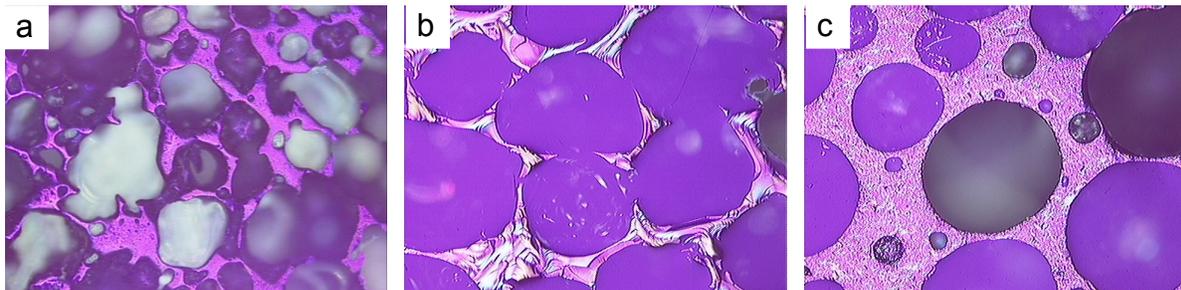


Figure 3 Polarized optical microscope images of raw coal(a), coal tar pitch, (b, c) derived carbon foams

Figure 4 presents the SEM images of typical coal and pitch derived carbon foams. Image (a) is a coal-based carbon foam, while (b) is a special foam derived from coal solvent extracts, which has ~60% closed-cell structure. The closed-cell membranes are clearly observed. Image (c) is a coal tar pitch-based carbon foam, which shows a thicker cell wall along with some closed-cell structure.

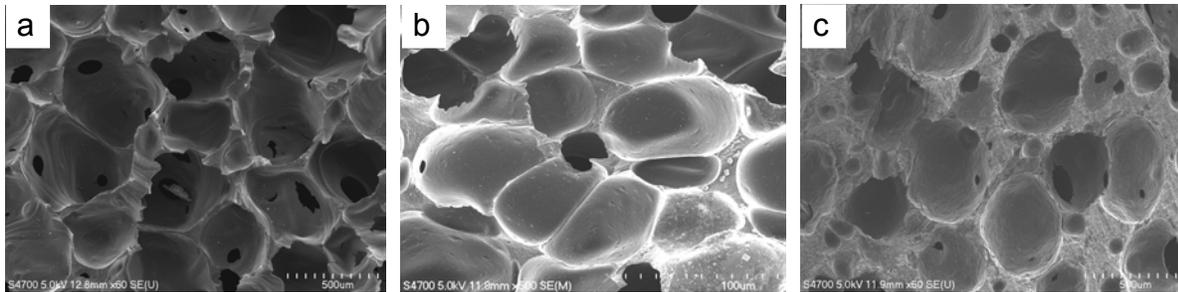


Figure 4 SEM images of raw coal(a), coal extract(b) and coal tar pitch derived carbon foams(c)

Conclusion

Coal and coal extracts are the suitable foaming precursors. They generate a strong, isotropic foam suitable for structural applications and energy absorption. Pitch precursors, on the other hand, have to be tailored before foam can be created. After adequate pretreatment, pitch can be used to generate anisotropic carbon foam.

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