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Preparation and Performance of Anisotropic Mesophase of Coal Pitch in Chemical Industry Based on Computer Monitoring Technology

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Asphalt and other organic compounds form an anisotropic structure in lithification. Its product is mesophase which has excellent property and low cost so that it has been widely used in carbon fiber, carbon foam, needle coke and lithium ion secondary battery and many other areas. It can be said that the studies of preparation and structure of anisotropic mesophase of coal asphalt have significance to process improvement and cost savings in these areas. This research carries out an in-depth study in this regard. The selected coal asphalt is used as the raw material to analyze the influence of constant temperature and thermal polymerization temperature to the softening point, yield, group composition and optical microform. The experimental results show that coal asphalt turns into mesophase pitch with softening point of 312□ and yield of 79.1% if it is kept in a constant temperature of 420□ for 5 hours. However, it turns into mesophase pitch with softening point of 305□ and yield of 81.4% if it is kept in a constant temperature of 400□ for 8 hours. It shows that high-quality mesophase can be obtained with scientific control of the duration of constant temperature and the thermal polymerization temperature.

1. Introduction

In recent years, technology development highlights the application of coal asphalt so that mesophase pitch is also put into use. It is a nematic liquid crystal material with the birefringence feature of planar molecule. It can not only be obtained through the extraction of raw material bitumen but also from the polymerization of coal asphalt. Since the 1960s when anisotropy was discovered, people have carried an in-depth research in this area and successfully made some breakthrough. In 1965, the concept of mesophase was officially named by Professor Brooks and Professor Taylor. Then the study of mesophase carbon microspheres began (Yue et al., 2017). Thanks to the continuous development of science and technology, people have been able to prepare a variety of mesophases and their ancillary products through the application of carbonization reactive synthesis or other technologies. Mesophase is more widely applied because of a lower cost and a higher oxidation of the mesophase as well as a high carbon char yield and purity, which makes it possible to produce various advanced carbon materials through mesophase. These carbon materials include carbon microspheres, fluorocarbon materials, carbon plate and carbon film, ultra high modulus carbon fiber, high-temperature lubricant, carbon foam and other complex materials, which greatly promote the scientific and technological development in society and technological level of all walks of life (Cui et al., 2017). Therefore, the development of anisotropy with high content and high property, the pursuit of matrix asphalt at lower cost and easier operation has become one of the important tasks at this stage.

The purpose of this paper is to investigate the preparation technology and structure of the anisotropic mesophase of coal asphalt in order to explore the preparation method of mesophase with higher content and higher property at lower costs and easier operation. It can further help people to research and produce more mesophase pitch and its accessory products, speed up their development and application and improve the overall development level in various fields. In this paper, the following work has been done. Firstly, the structure of coal asphalt including the main components, chemical composition and physical structure of coal asphalt has been deeply studied. Then the structure analysis method of coal asphalt has been clarified to

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analyze the composition and property of coal asphalt; secondly, the formation mechanism of anisotropic mesophase pitch is analyzed; finally, coal asphalt is used as experimental material to study the effects of the duration of constant temperature and thermal polymerization temperature on mesophase pitch softening point, yield, group composition and optical microform in order to explore optimal preparation process of anisotropic mesophase.

2. Coal asphalt structure research

2.1 Major Components

The chemical structure and physical properties of coal asphalt are very complex, so people generally use the method of group composition to present their traits. At present, people mainly make use of three types of toluene dissolution and quinoline or pyridine to measure the composition of coal asphalt and its products. In this paper, toluene and pyridine are selected and divided into three components. Figure 1 shows the analysis of coal asphalt of different solvent components.

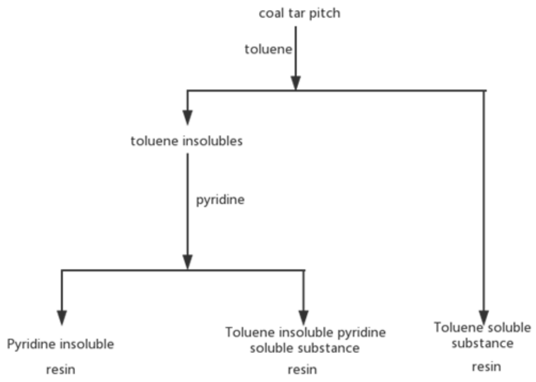

Figure 1: Coal asphalt of different solvent components analysis

Figure 1 shows that the three components are toluene insoluble and pyridine soluble (TI-PS), pyridine insoluble (PI) and toluene soluble (TS) substances (Xing et al., 2017).

2.2 Chemical Composition

The chemical composition of coal asphalt is a mixed multi-molecular system. The components in this system are extremely complex and the component molecular weight is widely distributed. A variety of analytical methods show that coal asphalt consists of 1,2-BCZC 1,2-pyrene and 1,2-benzofluorene (Chang et al., 2017).

2.3 Physical Structure

At room temperature, raw asphalt, after heated at a certain temperature, softens and melts into viscous liquid as the temperature rises, which proves that raw asphalt is a solution system and the degree of dissolution of raw asphalt will change into a three-dimensional gradient micellar tissue solution during mutual dissolution. The heat of mixing of this micellar system is very small (Li et al., 2017). The experimental data shows that temperature control can not only turn coal asphalt into glassy state but also colloidal state. The system of coal asphalt is dispersed, the effect of phase and matrix has a direct influence on all properties of coal asphalt. Since coal asphalt usually exists in bulk solids, it should be crushed before the reaction in order to facilitate the subsequent catalytic polymerization (Xiao and Qiu, 2016).

2.4 Structural Analysis Methods

Common methods for determining the aromaticity of coal asphalt include X-ray diffraction and infrared spectroscopy. The method of determining the average molecular weight distribution of coal asphalt mainly includes VPO, permeation chromatography and resolution mass spectrometry. In addition, the most important analytical methods for presenting the internal structure of coal asphalt include nuclear magnetic resonance spectrometry, elemental analysis and infrared spectroscopy, among which elemental analysis is most common (Cao et al., 2016).

2.5 Relation between structure, property and composition of coal asphalt

The relation between the structure, properties and composition of coal asphalt equals to that between the softening point, residual carbon rate, density and its structure and composition. The relation between the softening point and the structure and composition of coal asphalt can be expressed by the formula $\lg\eta_t = \frac{711.8}{t+(86.1-t_m)} - 4.175$. η_t represents the viscosity of the coal asphalt at temperature t. The viscosity unit is Pa.S while the softening point is t_m with its unit □. The relation between the residual carbon ratio and the structure and composition of coal asphalt can be expressed by the formula $\mathrm{BY} = \mathrm{BY}_{max} - B \cdot h_0^{-1} \cdot k^{-0.5}$. In this formula, the maximum carbonization yield, the coking value, the height of container loading and the system pressure during carbonization are $\mathrm{BY}_{\max}$, BY, h_0 and k. The relation between density and structure and composition can be expressed by the formula $\mathrm{Cq} = 10^{-2}(1.68(primRI) + 1.47\beta + 1.21\gamma + 1.35(\sec RI))$. In the formula, the density, the a1 resin content and the a2 resin content are presented by Cq, primRI and sec RI. β and γ stand for the respective resin content. This equation shows that β and γ have the greatest impact on asphalt density while the two are opposite to each other (Cao et al., 2017).

3. Formation mechanism of anisotropic mesophase asphalt

Since there is no unified theory to systematically explain the formation of mesophase asphalt, a variety of theories can be used to explain its formation mechanism and be improved by other properties of mesophase. When the coal asphalt is heated to a certain temperature, the liquid phase reaction includes both thermal decomposition and thermal polymerization, but the latter takes up the majority. The original plane-like naphthenic molecules in mesophase asphalt will continue to accumulate and transform into laminated tissue. Temperature rise leads to reduction of system energy and results in the intertangling of laminate by external forces. Then mesophase sphere will be formed which will absorb the mother liquor molecules in the system, swell and merge into larger spheres due to attraction, collision, and interpenetration during expansion. Until the surface tension is too large to maintain the shape of sphere so that it transforms into non-spherical anisotropic microstructures (Xu et al., 2016). Thus, anisotropic microstructure in non-spherical form was transformed (Xu et al., 2016).

$$\begin{cases} X - Y \to X^{\circ} + Y^{\circ} \\ X^{\circ} + X^{\circ} \to XX, Y^{\circ} + Y^{\circ} \to YY \\ XX \to \text{The aggregation state of XX} \\ \text{The aggregation state of XX} \to \text{XX's heap state} \end{cases}$$

In the above four formulas, respectively represent the generation of free radicals, the merging of free radicals, the aggregation of molecules and the stacking of molecules. Coal tar has a very complex components, so the free radicals, the merger is not only the same type of free radicals can merge, different kinds of free radicals can merge, according to the molecular weight of asphalt components, it can be divided into three parts, one is the molecular weight of more than 400 and within 700 components, these components in coal tar coking reaction is the most lively performance, the polycondensation reaction tends to happen in a short time, its molecular weight also will increase sharply; The second is the composition with a molecular weight of more than 700 and less than 1200. The reaction activity of this kind of component is relatively general. When further reaction occurs in the carbonization reaction, the intermediate phase formed is also relatively stable. The third component, whose molecular weight is over 1200, is the most stable in the formation of intermediate phase, and is inert in the carbonaceous reaction. Generally speaking, in the formation process of anisotropic intermediate phase asphalt, two basic conditions must be satisfied. The first basic condition is that the plane aromatic hydrocarbon molecules should be large enough, and the larger plane aromatic hydrocarbon molecules can have stronger molecular force, which is also an important power source for the orderly arrangement of intermediate phase molecules. The second basic condition is that the viscosity category of the system needs to be reasonable, which can ensure that molecules can move freely within the viscosity category, thus creating a good external condition for the formation of intermediate phase asphalt. On the mesophase formation viscosity of the system are studied, can realize that when the temperature rises, the system viscosity will reduce gradually, when the temperature is between 360 ℃ to 400 ℃, the viscosity will there is a minimum, and the higher the temperature, the viscosity will increase rapidly, as shown in figure 2:

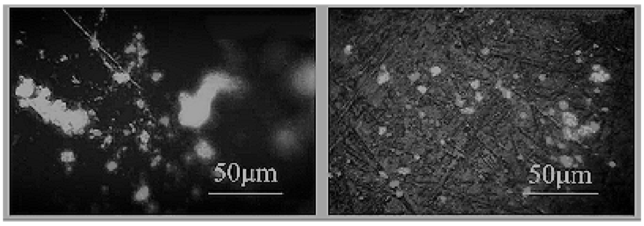

Figure 2: Polarized mi croscopic photographs of mesophase produ ced by HI1 at 380 □ for 6 h with marketers heating rate

Therefore, time and temperature must be strictly controlled to ensure that the system viscosity and reaction speed can be maintained in a good range when intermediate phase asphalt is formed. Two basic conditions for the formation of intermediate phase asphalt are shown in FIG. 3.

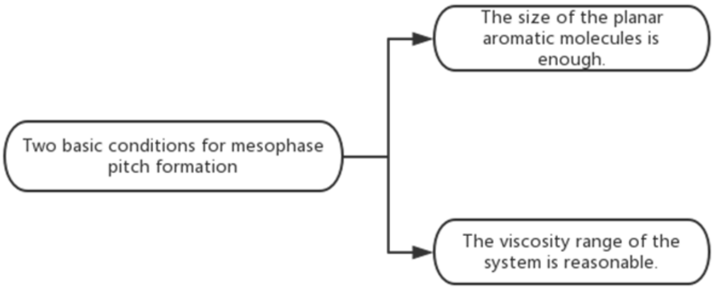

Figure 3: two basic conditions for the formation of intermediate asphalt

Will be generated in the process of molten coal tar mesophase, the process can be used as a phase transformation process, this process is the conversion between anisotropy and same-sex, therefore can be related to calculation using the thermodynamic theory, and then build a phase diagram, so can the mesophase formation condition and its transformation are discussed. In addition, because the coal asphalt composition and the complexity of the reaction is extremely high, therefore cannot be realized with the method of quantitative calculation, and this requires using the experimental data that has come, but on the theoretical guidance is relatively lack, and it also makes the researchers tried to through the establishment of statistical theory model to calculate the phase diagram, although there exist certain differences between and the test data, but of the opposite sex for coal pitch mesophase pitch thermodynamic analysis has laid a solid foundation.

4. Study of preparation of anisotropic mesophase of coal asphalt

4.1 Experiment Materials and Procedures

The raw materials used in experiment in this paper are medium temperature refined asphalt produced by Taiwan’s carbon steel, which has an ash content of only 0.24%. In the thermal polycondensation reaction, the asphalt, after being grinded, should be put into a high-temperature and high-pressure reaction still equipped with a PTC-2 temperature controller. The capacity of the reaction still is 3 liters and the high-pressure environment is 23.5 MPa. In the thermal transformation experiment, the temperature of reaction still is set to increase 5 °C per minute. It forms a spontaneous pressure under the protection of nitrogen and it is stirred at a constant rate. When the temperature is raised to 385 °C to 445 °C, it should be maintained at a fixed one for 2 to 10 hours. Then the system pressure is discharged while the reaction still is cooled to return to room temperature so as to obtain a mesophase asphalt, whose form and anisotropy are observed by OLYMPUS BX51M polarized light microscopy and recorded (Xu et al., 2016). The softening point of the mesophase asphalt is measured by a self-made tester by means of needle penetration test. Its group composition is detected by hot-melt extraction. Toluene solvent with a proportion of 30 methylbenzene every gram asphalt serves as the solvent. During it is made, the temperature should be always less than 80℃ and the stirring time is 1 hour. After it is made, the solvent is filtered so as to separate it from the toluene-soluble part. Then pyridine solvent is melt in 80℃ environment for 1 hour so as to separate the pyridine-insoluble part from the toluene-insoluble but pyridine-soluble part (Liu et al., 2015). In the observation of mesophase, the conventional methods include preparation, polishing and embedding, and observation by polarizing microscope. Figure 4 shows the schematic diagram of the preparation of anisotropic mesophase pitch.

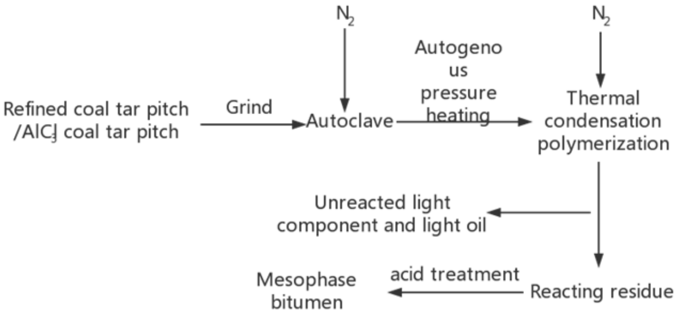

Figure 4: Schematic diagram of the preparation of anisotropic mesophase pitch

4.2 Results and Discussions

The above experiment shows that when the thermal polymerization temperature is 385□ and when the time of constant temperature is 5 hours, a large number of the mesophase asphalt has many dense anisotropic mesophase spherules which show enlarging, mutual integration and eventually formation of microstructure of anisotropic mesophase with the rise of reaction temperature. It proves that high temperature thermal conversion can lead to prepare anisotropic mesophase (Song et al., 2015). When the thermal polymerization temperature is 375 °C and when the time of constant temperature is 6 hours, the entire field of view in a polarizing microscope which is isotropic asphalt. Its softening point is 175 °C and the isotropic polymer yield of isotropic asphalt is as high as 93%. When the thermal polymerization temperature is 385□ and when the time of constant temperature is 5 hours, the mesophase sphere enlarges. When the thermal polymerization temperature rises to 400 °C and when the time of constant temperature is 5 hours, a part of polymerization product converts into mosaic structure, but also part of the merges into the streamline texture. When the thermal polymerization temperature rises to 435 °C and the time of constant temperature is 5 hours, the polymerization product had completely formed a streamlined mesophase with 100% anisotropy and a part of them shows a wide-area mesophase structure (Lin et al., 2015). When the temperature rises to 445 °C and the time of constant temperature is 2 hours, the anisotropic mesophase exhibits a semi-coke state and is harder to soften. Under the same stirring rate and heating rate but different heat treatment temperatures, the influence of heat treatment temperature on the softening point, insoluble and yield is observed (Song et al., 2015). The observation shows that temperature rise leads to higher softening point and insoluble concentration but lower yield of the polymerized product. When the reaction temperature is 395□, the softening point and insoluble content of thermopolymerization mesophase rapidly increase, but the yield of the polymerized product decreases rapidly, because the aromatic hydrocarbon molecules will be degraded due to dehydrogenation which leads to the increase of system pressure and viscosity and affects the yield of the mesophase. During this process, free radicals undergo rearrangement, cyclization and collision cross-linking and eventually develop into thick Cyclization and aromatization (Xie et al., 2014). When the temperature is between 395 °C and 420 °C and when insoluble increases, the decline of the polymerization product yield starts to slow down. This decline further slows down in the temperature is 420□ to 445□. The above analysis shows that the variation of the yield of the polymerization product is the same as the change of the optical structure observed in the polarizing microscope.

It is shown that when the thermal polymerization time is 3 hours, a rough mosaic structure is observed and only a small part is converted into a streamlined structure so that there is only a small amount of mesophase. When the thermal polymerization time is 5 hours, most of the polymerization products have been converted into short streamlined structure while only a few of them are rough mosaic structure. When the thermal polymerization time is 7 hours, it is totally streamlined while only a small part of them transforms into a wide area structure mesophase. When the thermal polymerization time is 10 hours, it has all transformed into anisotropic wide-area mesophase, which also proves that it takes time to convert the mesophase from the initial microcrystalline structure to the final wide-area intermediate structure and the thermal polymerization time plays an important role in promoting the formation, expansion and integration of mesophase (Yang et al., 2014). Therefore, the above analysis shows that although the conversion time into mesophase can be shortened by temperature rise, the polymer yield will decrease rapidly, which is not conducive to the preparation of the anisotropic mesophase. However, the lower thermal polycondensation temperature with longer time of constant temperature will increase mesophase content, which is more conducive to the preparation of the anisotropic mesophase.

5. Conclusions

In summary, when the refined coal tar pitch is used as the raw material for the preparation of the anisotropic mesophase, when the thermal polymerization temperature is controlled at 420℃ and when the temperature is constant for 5 hours, the mesophase asphalt exhibits a streamlined body structure where its softening point is temperature is 312℃ and the polymer yield is only 79.1%. When the thermal polymerization temperature is controlled at 400℃ and when the temperature is constant for 10 hours, the mesophase asphalt exhibits a wide-area structure where the softening temperature is 305℃ and the polymer yield is as high as 81.4%. This shows that at lower thermal polymerization temperature, the prolonging of the constant temperature time is constructive for the preparation of high quality anisotropic mesophase of coal asphalt.

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