We are IntechOpen, the world's leading publisher of Open Access books Built by scientists, for scientists



186,000

200M



Our authors are among the

TOP 1% most cited scientists





WEB OF SCIENCE

Selection of our books indexed in the Book Citation Index in Web of Science™ Core Collection (BKCI)

Interested in publishing with us? Contact book.department@intechopen.com

Numbers displayed above are based on latest data collected. For more information visit www.intechopen.com



Chapter

Determining the Filler Activity in the Sintering of Pitch Composites

Vladimir Shmalko, Valeriia Karchakova, Oleh Zelenskyi and Fedir Cheshko

Abstract

Evaluation of the activity of fillers for sintering composites can be obtained from the results of testing the mechanical strength, in particular, the shear strength of pitch composites. The dependence of the strength of composites on the content of fillers is described by an extremum curve. At the point of maximum strength of the composites, the optimum ratio of components is realized. At this moment, the whole pitch matrix is in the interfacial layer on the surface of the filler particles. The contact angle of fillers wetting with binders is a necessary but not sufficient condition. The activity of the fillers with respect to the particular binder is characterized by the adhesive strength of the material obtained after carbonization of the "binder-filler" system. The activity of the fillers determines caking and sintering capacity of the pitch binders. It is shown that anthracite is the most active filler for the investigated pitches. Several methods for determining caking and sintering capacity of pitches are given. One of them is the determination of these indicators by the work of destroying the pitch composites. It is shown that fillers have a significant influence on the structure of the pitch matrix in composites.

Keywords: filler, activity, pitch, adhesion, sintering

1. Introduction

The properties of traditional materials, such as metals and their alloys, do not always allow, even with the most modern processing methods, to achieve such characteristics in strength, durability, and reliability, in order to provide the highest operational capabilities for a variety of designs and equipment. In areas such as missile technology, aviation, automotive, chemical industry, and many others, the optimum characteristics of materials have long been achieved through the use of composites [1]. The composites can be defined as materials that consist of two or more chemically and physically different phases separated by a distinct interface [2]. It is known that the structure of the matrix in composites is formed with a significant influence of the filler. The division of fillers into active and inert or active, semi-active, and inactive [3] is overly simplistic, since the activity of the filler is not its specific feature or fundamental property. Nevertheless, the activity of the filler, especially for sintering pitch composites, is a very important characteristic. The activity of the filler determines their behavior during sintering and the final properties of the composite.

The activity of the filler is mainly determined by three factors:

- The ratio between the adhesion energy of the matrix to the filler and the cohesive energy of the matrix [4].
- The amount of filler introduced.
- The degree of dispersion of the filler particles, which determines the area of the contact surface of the matrix with the filler. The particle size of the filler is the most important property that affects the hardening of the composite. For each type of binder and filler, there is an optimum degree of filling [5].

Filler activity refers to certain properties of the filled system. Therefore, the concepts of structural, kinetic, and thermodynamic activity were introduced [6].

The structural activity means the ability of the filler to change the molecular and supramolecular structures of the composites (the degree of crystallinity, the size and shape of the elements of the structure, etc.).

Kinetic activity is the ability of the filler to influence the mobility of certain kinetic units of the polymer, the relaxation processes, and the viscoelastic characteristics during the deformation of the composite.

Thermodynamic activity is the ability of the filler to influence the state of thermodynamic equilibrium, the phase, and thermodynamic parameters of the filled polymer.

The free surface energy of the filler particles has a basic value and determines the adhesion interaction and wettability of the surface. In this connection, the role of functional groups on the surface plays an important role and their reactivity [7].

Unfortunately, until now there is no single approach to measure the degree of activity of fillers. This is due, in particular, to the lack of theoretical developments for sintering composites, in which the adhesive strength varies with the sintering temperature. In the sintering of pitches with fillers, the cohesive strength of the cement matrix increases with carbonization, thereby increasing the adhesive strength of the composite. Since the basis of the activity of fillers is their adhesive interaction with the binder, it seems that the measure of their activity should be the methods of determining the adhesive strength.

The interaction of the filler with the binder is most often evaluated on the basis of wetting, while the quantitative characteristic is the wetting contact angle [8].

Wetting is the result of an adhesive interaction between the surface of the solid (filler) and the contacting liquid (binder). Quantitatively, adhesion is characterized by the work of adhesion, which is expressed by the equation of Dupree:

 $W_a = \gamma_L + \gamma_S + \gamma_{SL},$

where γ_L is the surface energy (tension) of the liquid phase, γ_S is the surface energy of the solid phase, γ_{SL} is the interfacial surface tension, and W_a is the work of adhesion. A rise in the interfacial attraction results in an increase in the work of adhesion. Eq. (1) can be rewritten to determine the work of cohesion (W_c) when the two phases are identical and no interface is present as shown in Eq. (2) for a solid phase:

$$W_c = 2\gamma_S \tag{2}$$

(1)

Adhesive strength—W_s—work of bond failure:

$$W_s = W_a + W_{def} \tag{3}$$

 W_{def} can be very large and differs from W_a by n times.

The wetting contact angle (Young's equation) is associated with the work of adhesion W_a:

$$\cos\theta = 2W_a/W_c - 1 \tag{4}$$

where W_a is the work of adhesion of the wetting liquid to the solid body and W_c is the wetting cohesion work.

Systems of pitch-carbon filler are very difficult to describe. The properties of the binders are always more detailed than the properties of the fillers. Usually, as a direct evaluation of the quality of the binder, the contact angle of surface wetting of the filler uses their adhesion interaction during mixing. The pitch filler systems are thermodynamically nonequilibrium, and the equilibrium contact angle in such a system is unattainable [9]. When describing composites, the binder properties are always paid more attention. Evaluation of the filler is more modest. Therefore, for pitch filler compositions, one can speak of an "apparent" contact wetting angle or of a "dynamic edge angle," as it is determined in some works [10].

The pitch matrix is a self-filled system that, when heated, even without an external filler, gives a solid residue (semicoke, coke), which can be considered as a dispersed-hardened system, i.e., as independent composite material with all the features of physicochemical and mechanical properties [5].

The wetting angle for the pitch filler compositions is determined by sessile drop, spreading drop, pendant drop, and other methods [11–13].

In addition to the wetting contact angle, the surface tension and capillary pressure are used as a quantitative evaluation of the filler-binder contact interaction [14].

The softening temperature determines its chemical composition, surface tension, viscosity, the particle size of the coke, its texture, chemical functional groups on the surface and porosity [15]. The final properties of carbonized pitch composites (e.g., electrodes designed for high current densities) are largely determined by the interaction of pitch with the filler surface. Pitch should penetrate into the pores of coke and fill the voids between the coke particles. It is believed that the wettability of coke by pitch is a direct indicator of the degree of their interaction. A good wetting of the filler surface with a pitch is a necessary, but insufficient, condition for a strong adhesion bond and high physical and mechanical properties of the resulting composite material.

Imperfection of existing estimates of binder-filler interaction leads to new attempts to assess the process of wetting fillers with pitch. In Ukraine, the technique [16] is used, according to which the determination of the wetting power of the pitch is carried out in metal or glass tubes into which the filler (coke) and pitch grains are loaded in a ratio of 15:5. The tubes loaded in this manner are placed in a laboratory electric oven, where they are kept for a certain time at a temperature of 200°C, which ensures the flowability of the test pitch, but does not lead to caking of the test coke. Then, the tubes are cooled and the coke is removed, not bound (not impregnated) with a pitch.

The wetting power (m) of pitch is calculated by the following formula:

$$m = m_{coke}/m_{pitch} \tag{5}$$

where m is the mass of bound coke (the difference between the initial sample of coke (m_{coke}) and the removed part of the latter), g, and m_{pitch} is the initial mass of the pitch buried in the tube, g.

In the apparatus for determining wetting characteristics, according to the procedure of [17], granular coke 0.25–0.5 mm in size is placed in a cylinder on top of which a layer of solid pitch with a grain-size composition of 1–2 mm is applied. This composition is heat treated in a drying chamber with forced air supply at a predetermined temperature and a time of thermal aging.

The prototype of method [16] is the method for determining the sintering ability of coals [18]. Caking coal is used instead of pitch, and anthracite is used instead of coke. It should be noted that in the prototype, the determination temperature reaches 600°C, which has a decisive influence on the physics-chemistry of the processes taking place.

In our opinion, for pitches as caking binders, it is important to evaluate the adhesive strength of their contact with fillers. In this case, the activity of the fillers will be the "sintering strength" and/or the "sintering capacity" of the pitch [19].

By the strength characteristics of the pitch composites, quantitative estimates of the quality of pitch as a binder relative to the selected filler can be obtained, as well as evaluation of the activity of the fillers with respect to the selected pitch. It is assumed that the use of this approach will allow to determine the optimal mass ratios of the binder-filler. In this case, the transition of the pitch to a solid state must be irreversible. Only then will it fully reproduce the physicochemical processes of interaction between the binder and the filler that occur during the production of the composite.

2. Experiment

In our work, we used industrial pitches as binders. Pitch samples were taken in the production conditions of coke plants. The volume of the sample was up to 4 dm³; the pitches were mixed, quartered, and sieved through a sieve to a laboratory sample with a fraction of 0.5–0.25 mm. **Table 1** presents their characteristics.

| Characteristics | | | Pitch mark | | | | |
|--|-----------------------|--------------------------------|----------------------------------|------------------------------------|---|-----------------------------------|--|
| | | | V | | B ₁ | | |
| Softening point, °C | | | 85.0 | | 72.0 | | |
| Yield of volatiles, % | | | 53.8 | | 59.0 | | |
| Quinoline insoluble, % | | | 10.5 | | 8.2 | | |
| Toluene insoluble, % | | | 33.2 | | 28.2 | | |
| Ash, % | | | 0.11 | | 0.13 | | |
| | | | | | | | |
| Samples | W ^a | V ^{daf} | A,% | d _t , g/cm ³ | Elemental com % | position, | |
| Samples | W ^a | V ^{daf} | A,% | d _t , g/cm ³ | | position, H | |
| - | W ^a 3.0 | V ^{daf} 0.8 | A,% | d _t , g/cm ³ | % | | |
| Pitch coke (PC) | | | | - | % C | Н | |
| Pitch coke (PC) Shale coke (SC) Shale coke > heated at 250 C | 3.0 | 0.8 | 0.3 | 1.53 | % C 96.5 | H 0.45 0.22 | |
| Samples Pitch coke (PC) Shale coke (SC) Shale coke > heated at 250 C (SC-T) Anthracite (A) | 3.0 2.8 | 0.8 | 0.3 0.25 | 1.53 1.50 | % C 96.5 97.2 | H 0.45 0.22 | |
| Pitch coke (PC) Shale coke (SC) Shale coke > heated at 250 C (SC-T) | 3.0 2.8 0.9 | 0.8 0.9 0.5 | 0.3 0.25 did not determine | 1.53 1.50 2.0 | % C 96.5 97.2 did not deter | H 0.45 0.22 rmine 4.1 | |

Table 2.Characteristics of the fillers.

We used both carbon and noncarbon fillers. All the fillers were crushed to the size of particles passing through a sieve with a size of 0.5–0.2 mm holes. **Table 2** gives an overview of the filler characteristics. These are pitch coke (PC), shale cokes (SC), and shale coke after heat treatment (SC-T), which we preheated for 2 hours at a temperature of 250°C to remove moisture. For comparison, we took hardened glass, washed bank-run sand, and anthracite.

3. Results and discussion

The photographs of the surface of the filler grains (**Figure 1**) clearly show the difference in their structure. For shale coke (**Figure 1a**, **b** and **e**, **f**), there are at least two types of structures: sponge (**Figure 1a**) and layered fibrous structures (**Figure 1b**). The grain sizes with a spongy structure in **Figure 1a** are about 180–450 μ m, and the grains of shale coke with a layered structure are 100–300 microns in diameter and 800 μ m in length. The thickness of the layers in the grains of the layered structure according to optical microscopy is <2–5 μ m. The surface of the pitch coke grains is most rough with numerous pores (**Figure 1c**, **g** and **i**), which coincides with the data [20]. Lamellar anisotropic structures are visible on the pitch coke (**Figure 1g**). In the case of good wettability, the caking can give a strong adhesive bond and a significant proportion of adhesion due to the capillary penetration of the pitch in the pores of the filler.

The surface of anthracite grains is the smoothest. It is well visible that the surface is sometimes chipped with folded structures. Anthracite grains have a large variation in size from 20 μ m to 100–160 μ m. Anthracite dust is present on the surface of the grains in the photographs (**Figure 1d**).

Samples of composites for mechanical testing were prepared as follows. Mixtures of pitch and an inert filler (anthracite, sand, glass, pitch coke (PC), shale coke (SC), and shale coke after heat treatment (SC-T) at 250°C) in different proportions (from 1:1 to 15:1) are charged in cells of ceramic cassette (**Figure 1**), preliminarily placed in a special coking chamber (**Figure 2**). One loading of the cassette camera allows to receive 14 samples of char from the pitch composites. The heat input in the coking chamber was carried out from below, since radial heating of the cylindrical sample has a temperature gradient along the radius of the cylindrical charge—the outer layers of the charge in the coking chamber undergo heat treatment for a longer time than in the central part. With one-sided heating (from below), the temperature gradient in the loading of the coke composition is available in the height of the load. Therefore, semicoke samples of the pitch composite for mechanical testing had a gradient of strength in height, but in the fracture region, samples were prepared at the same temperature (500°C).

Isothermal aging at the final treatment temperature is designed to increase the homogeneity of the composite in the radial plane.

Mechanical test samples of solid residue from the pitch composites are carried out according to the procedure described in [4], using a cassette chamber (**Figure 2**).

Each semicoke sample of the pitch composite was placed in the test cell (**Figure 3**), and mechanical strength tests were carried out so that the fracture region of all samples was in the semicoke plane heated to a temperature of 500°C. All the samples in the fracture region had the same final heating temperature, and the strength of the semicoke sample of the pitch composite was determined in an isothermal layer.

We believe that since the strength of the coke (filler) is higher than that of the semicoke matrix, the destruction of the sample during our tests was mainly carried out on the pitch matrix (cohesive failure), and the filler grains were not destroyed.

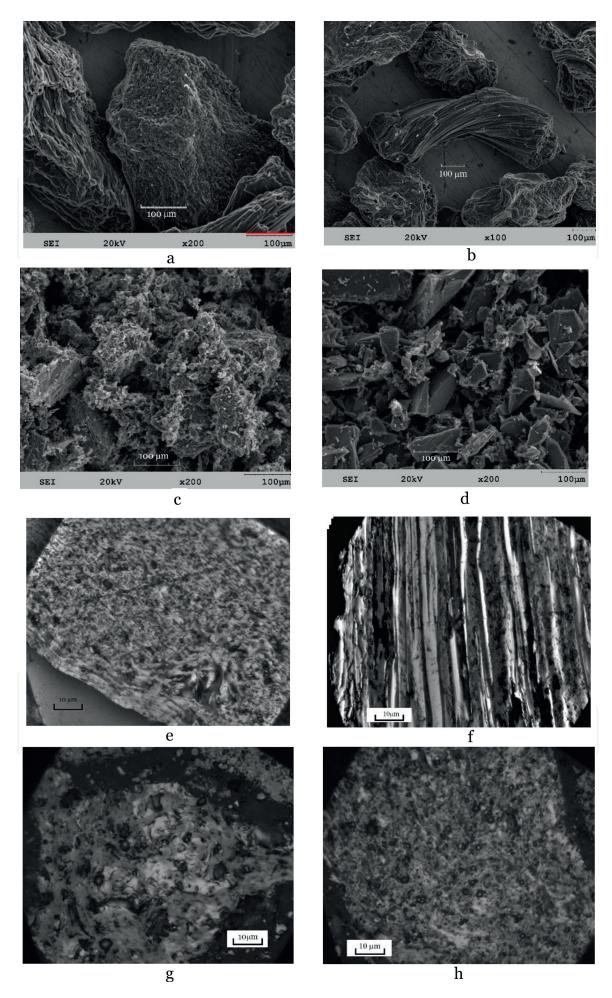


Figure 1. Structure of filler surface (SEM): $a - shale coke (\times 200)$; b - shale coke x 100; $c - pitch coke (\times 200)$; $d - anthracite (\times 200)$. Optical microscope, polarized light, $\times 500$): e, f - shale coke; g, h - pitch coke.

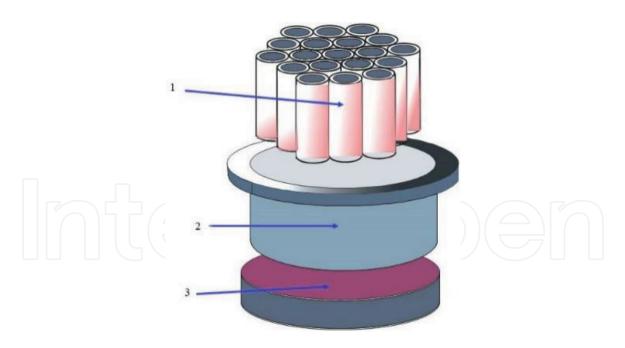
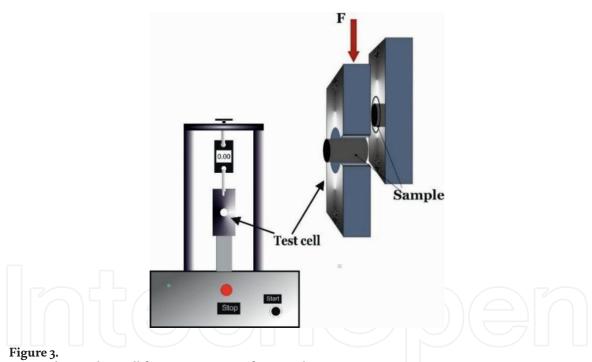


Figure 2.

Coking chamber for samples of pitch composites: 1 – cassette of ceramic cells; 2 – coking chamber; 3 – heater.



Test machine and test cell for testing composite for strength.

3.1 Determining the filler activity by the positive root of the parabola equation, which describes the dependence of the pitch composite strength on the filler content

The dependence of the pitch composites of the semicoke's strength on the mass ratio of the pitch and filler is investigated. As a rule, an extreme dependence of the strength on the degree of filling was observed, characterized by the presence of a concentration maximum.

A second-order equation is a reasonable approximation. For all the equations, we calculate the discriminant and determine the roots.

Table 3 shows the equations of the second-order curves describing the dependence of the strength of the semicoke from the pitch composites on the composition

| Fillers | Equation | R ² | Roots of equation | |
|------------|--------------------------------|----------------|-----------------------|-----------------------|
| | | | x ₁ | x ₂ |
| SC-T | $Y = -0.28x^2 + 2.80x + 54.42$ | 0.92 | -9.81 | 19.81 |
| SC | $Y = -3.69x^2 + 39.2x - 18.8$ | 0.90 | 0.5 | 10.1 |
| PC | $Y = -1.33x^2 - 19.2x + 40.2$ | 0.76 | 1.86 | 16.29 |
| Glass | $Y = -1.3x^2 + 17.9x + 2.02$ | 0.81 | -0.1 | 13.9 |
| Sand | $Y = -2.77x^2 + 34.1x - 23.6$ | 0.96 | 0.74 | 11.6 |
| Anthracite | $Y = -2.58x^2 + 48.96x + 77.5$ | 0.96 | -1.47 | 20.45 |

of all the excipients that were tested, the roots of these equations x_1 and x_2 , and the determination coefficients (R^2) of the interaction y = f(x).

We do not consider the negative values of the roots x_1 because they do not match the condition of the problem.

The physical meaning of the roots x_2 of the parabola equation is some hypothetical ratio of filler binding, in which the strength of the pitch composite falls to zero. The x_2 indicator can be used as an indicator of the activity of the filler. The higher the value of x_2 , the greater the filler activity.

There is some physical meaning of the roots x_2 of the parabola equation. The x_2 indicator can be used as a measure of the activity of the filler or of the sintering ability of the pitch. The higher the value of x_2 , the greater the activity of the filler is. That is, the more active the filler, the more its quantity will be agglomerating. By x_2 , it is possible to rank the binders for the sintering ability to the fillers. The activity of the filler is the amount of the inverse sintering power of the pitch [21]. In accordance with this indicator, fillers are located (in descending order) in a row:

3.2 Determining filler activity by sintering ability

As an example, let us consider the curve for the change in strength of pitch composites with anthracite (**Figure 4**). The strength of the pitch composite increases (the left branch of the curve in **Figure 4**), because the high modulus filler reduces the ability of the entire composition to deform. With an increase in the degree of filling, the individual particles of the filler approach and their boundary (interphase) layers begin to interact with one another, forming a film structure of the matrix between the particles (**Figure 5a**).

We do not take into account here that individual particles in composites are rarely observed [22]. Since binders that solidify are typical nonequilibrium systems, the loss of stability leads to the spontaneous formation of primary clusters—a decrease in surface energy occurs due to a reduction in the interfacial surface and, as a consequence, aggregation of the filler particles. The filler particles on their surface have a layer of a pitch matrix, the so-called interfacial layer (IFL) [23]. There is no clear boundary between IFL and the pitch matrix, but it is established that IFL reduces the concentration of stresses on the surface of the matrix and filler, which affects deformation and fracture in composites [24]. The thickness of the interphase layer

depends on the radius of the filler particles and the fractal dimension of its surface [25]. At low filler concentrations in the matrix, the interphase layers are not an independent phase in the volume of the composite, which does not affect its properties.

Considering the fact that the interfacial layer is an oriented ordered structure, the film has enhanced strength compared to the structure of the remaining volume of the pitch matrix. At the critical point, the complete transition of the pitch matrix to the film structure of the IFL is the main factor of strength increasing of the pitch composites. In addition, the filler-binder ratio at this point is optimal, which corresponds to the maximum on the curve (**Figure 4**).

In the case of a critical binder-filler ratio, the pitch matrix is completely on the surface of the filler particles in a structured (interfacial) layer (**Figure 5a**). The activity of the filler is maximum. With a further increase in the content of the filler in the composite (the right branch of the curve in **Figure 4**), the activity of the filler does not decrease, but the pitch matrix cannot cover the entire surface of the filler grains. The film is not enough to cover the entire surface of the filler grains. The binder film is divided into separate fragments (**Figure 5b**), which is accompanied by a sharp decrease in the strength of the final composite. In this consideration, we do not take into account the effect of agglomeration of filler particles.

Although the amount of the matrix and probably its cohesive strength does not change, the strength of the composite decreases. The strength of the matrix on the surface of the filler particles can be another indicator of the activity of the filler.

In the actual conditions of formation of the contact surface of the filler with a liquid binder, the processes of diffusion of the adhesive into the filler play an important role. A part of the pitch can penetrate into the surface layer of the filler due to capillary phenomena.

The removal of volatile substances from the pitch when carbonized leads to the appearance of shrinkage stresses and defects and, as a result, to rupture the film. That is, a pitch that is carbonized to the semicoke state may not completely cover the filler surface and not create a continuous "carbon skeleton," the ideas of which were previously expressed [26].

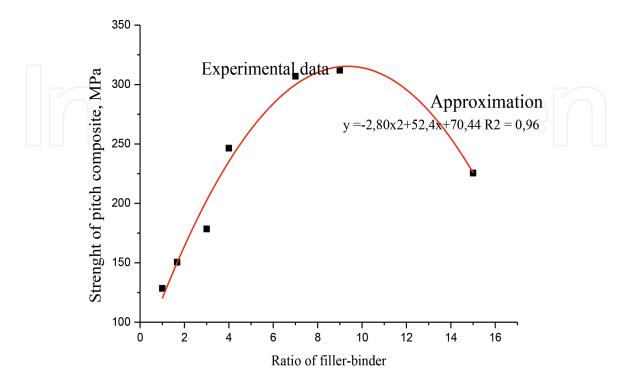


Figure 4.

Experimental points and approximation by the parabola equation for the dependence of the strength of a pitch composite on the amount of filler (anthracite) in it.

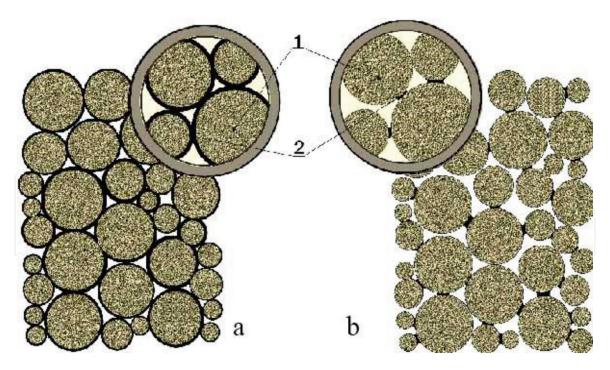


Figure 5.

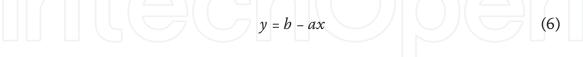
The microstructure model of the pitch composite: a - a binder in the film on the surface of the filler; b - with pitch deficit: 1 - filler particles, 2 - semi-coke of the matrix.

3.3 Determining filler activity by cohesive strength of the pitch matrix film on the filler surface

Another way to determine the activity of the filler is determining the cohesive strength of the pitch composite in the film state on the filler surface. The more active the filler with respect to the pitch binder, the more IFL is structured on the surface of the filler and, correspondingly, the higher its strength.

We solved the problem of determining the strength of the matrix in the film as follows.

In the filling region, which is characterized by the falling section of the curve of the dependence of the strength of the composite on the degree of its filling (**Figure 4**), the strength of the pitch matrix does not change, despite the reduction in the overall strength of the pitch composite. The loss of strength curve in this descending section is approximated by a straight line:



where *y* is the strength of the composite and x is the filler content. One can estimate the strength of the "film" pitch matrix by extrapolating this linear dependence on the ordinate axis, which gives the value of the strength of the semicoke of the pitch matrix (film) without the filler (for x = 0). The extrapolation value obtained by extrapolation at zero fill (σ_0) (**Figure 6**) is simultaneously a measure of the activity of the filler and at the same time can serve as a measure of the sinter ability of the pitch.

The sintering thus determined is an indicator of the peculiarity of the pitch to a specific filler. The same pitch with another filler will have a different sintering, because the sintering process depends on the nature of the filler and its physical–chemical interactions with the binder. **Figure 6** shows the variant of approximation of the fall-ing part of the curve of the strength of the pitch composite on the content of coke in it.

In order to compare the pitch with each other, you can enter the parameters of sintering and sinter ability with respect to the filler standard, for example,

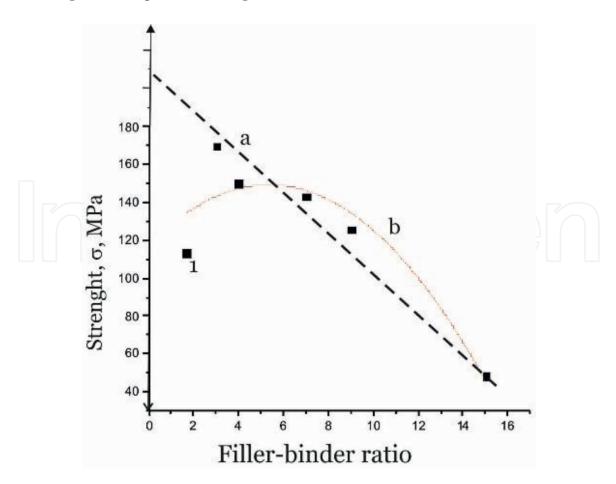


Figure 6.

Approximation of the falling branch of the dependence of the strength of the pitch composite with the coke by a straight line.

anthracite. By the way, anthracite, as a standard, is used to estimate coal by sintering in works [27, 28].

Testing the strength of a semicoke from pitch without filler cannot give an estimate of the pitch sintering. The reason is that when the pitch is heated and sintered during solidification, the solids are formed, which in fact play the role of the filler, which is unevenly distributed in volume. Therefore, such a semicoke is heterogeneous in terms of physical and mechanical properties [29]. In addition, the sintered material contains an uncontrolled amount of pores, which are, in essence, a low modulus filler.

Monitoring of the quality of the B1 (softening point 72°C) and V (softening point 86°C) at the factory (**Tables 4** and **5**) showed that the sinterability (σ_0) of the pitches was significantly higher than the other indicators' quality for these pitches. This means that it is more sensitive than the rest (the error in determining σ_0 is 5%). As a coefficient of measure, free term of the equation (**Table 4** of Eqs. (1)–(6) and **Table 5** of Eqs. (1)–(7)) is adopted. The physical meaning of the free term of these equations is the strength of the semicoke of the pitch film in the absence of the addition of a filler when x = 0.

3.4 Determining filler activity by work of destruction of pitch composite

The area under the dependence curve of the strength of semicoke samples from composites is an integral characteristic—the work of destruction. The term "work of destruction" is used in the physics of polymers [30, 31]. The work of destruction, in fact, is the energy used to overcome the forces of grip (in our case, the sintering) between the pitch matrix and the filler, so this figure can be taken as a measure

Fillers - Synthesis, Characterization and Industrial Application

| N⁰ | Softening point _. °C | V ^{daf} , % | Viscosity, η _{140 Pa*c} | Wetting power by [16], m | Equation |
|----|------------------------------------|-------------------------|----------------------------------|--------------------------|-----------------|
| 1 | 72 | 58.1 | 1.51 | 1.47 | y = 78.2–3.4x |
| 2 | 72 | 58 | 1.48 | 1.43 | y = 132.7–5.8x |
| 3 | 72 | 58.1 | 1.37 | 1.48 | y = 146.9–6.9x |
| 4 | 72 | 57 | 1.37 | 1.37 | y = 192.6–10.3x |
| 5 | 72 | 57.7 | 1.42 | 1.55 | y = 83.8–3.8x |
| 6 | 72 | 57.5 | 1.58 | 1.28 | y = 115.8–6.9x |

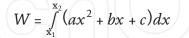
| Nº | Softening point. °C | V ^{daf} , % | Viscosity, $\eta_{140 Pa^*c}$ | Wetting power by [16], m | Equation |
|----|------------------------|-------------------------|-------------------------------|--------------------------|-----------------|
| 1 | 85 | 53 | 2.89 | 0.8 | y = 206.8–11.6x |
| 2 | 87 | 53 | 3.97 | 0.785 | y = 207.8–9.8x |
| 3 | 86 | 53 | 3.96 | 0.86 | y = 263.0–21.7x |
| 4 | 86 | 53.8 | 3.29 | 0.94 | y = 263.0–21.6x |
| 5 | 86.5 | 53.7 | 3.88 | 0.9 | y = 150.3–8.6x |
| 6 | 86 | 54.5 | 3.59 | 1.0 | y = 345.8–31.3x |
| 7 | 86 | 54.5 | 3.42 | 0.85 | y = 275.2–21.3x |

Table 5.

Results of monitoring quality for pitch V.

of the sintering ability of the pitch and filler activity. It seems that this definition of the term "sintered ability" has a definite physical content, in contrast to that adopted in coal chemistry: the sintered ability—the property to bake one or another amount of inert material [32].

Since we have a parabolic plot (**Figure 4**), the work of destruction (W, c.u.) will be equal to the area under the parabola:



Eq. (7), after simple transformations, gives a formula for calculating the work of the destruction of pitch composites:

$$W = \frac{a}{3}\left(x_2^3 - x_1^3\right) + \frac{b}{2}\left(x_2^2 - x_1^2\right) + c\left(x_2 - x_1\right)$$
(8)

(7)

The coordinates of the maximum of the parabola with respect to Eq. (8) were constructed using the well-known equations.

The results of calculations of the destruction of pitch composites with different fillers are given in **Table 6**.

As follows from data of **Table 6** and diagrams of **Figure 7**, the greatest sintering ability of the studied pitch is in relation to anthracite, and the smallest—in relation to sand and glass. That is, adhesive interaction is the most potent in a pair of pitch-anthracite. Anthracite is the most active filler. In this regard, anthracite is the reference filler for assessing the sintering ability of coal, as it is customary in the Roga test [33].

| Fillers | Coordinates of maximum | | The work of destruction, <i>W</i> , cond. Ur | |
|-----------|------------------------|-------|--|--|
| | x_0 | Уo | | |
| SC-T | 5.4 | 149.4 | 2417.5 | |
| SC | 9.0 | 126.2 | 1602.3 | |
| Glass | 8.0 | 64.0 | 646.6 | |
| Sand | 6.3 | 88.7 | 498.1 | |
| Anthracte | 9.4 | 315.6 | 4468.6 | |

Table 6.

The work of the pitch composite destruction for various fillers.

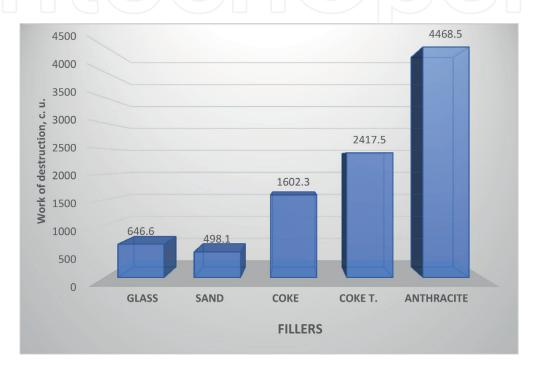


Figure 7.

The fillers activity by destruction work of pitch composite.

4. Conclusion

The generally accepted estimate of binders by the contact angle of wetting of the filler surface reflects only the initial stage of the adhesive interaction of the components of the composites. Wetting of fillers with binders is a necessary but not sufficient condition.

The activity of the fillers with respect to the particular binder is characterized by the adhesive strength of the material obtained after the carbonization of the "binder-filler" system. The activity of the fillers determines the sintering ability and sintering capacity of the pitch binders.

The external curve describes the dependence of the strength of composites on the content of fillers in them. Both step V and anthracite in the place of the extreme ratio of the filler-binder are 9:1, and the strength of the composite is 3,10 MPa. At this stage, the pitch matrix is in the interfacial layer on the surface of the filler particles. This optimal ratio is valid only for the given experimental conditions: temperature and grain size of the filler.

We show that anthracite is the most active filler for the resins under study. Some methods use anthracite as a reference filler to determine the sintering of coal and tar. Therefore, it can serve as a standard of activity in evaluating the activity of other fillers.

Acknowledgements

The authors would like to thank Dr. Bannikov, the chief of Chemical Department of the Ukrainian State Research Institute of Carbochemistry, for his valuable contribution to the evaluation and discussion of our data.

Author details

Vladimir Shmalko*, Valeriia Karchakova, Oleh Zelenskyi and Fedir Cheshko SE "UKHIN", Ukrainian State Research Institute for Carbochemistry, Kharkiv, Ukraine

*Address all correspondence to: v.shmalko@gmail.com

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (http://creativecommons.org/licenses/ by/3.0), which permits unrestricted use, dist<u>ribution, and</u> reproduction in any medium, provided the original work is properly cited.

References

[1] Klárová. Composite Materials. Ostrava: Coursebook; 2015. 43 p

[2] Jose J, Malhotra S, Thomas S,
Joseph K, Goda K, Sreekala M. In: Thomas S et al., editors. Advances in Polymer Composites: Macro- and Microcomposites – State of the Art, New Challenges, and Opportunities Introduction to Polymer Composites.
Part One, Polymer Composites. Vol. 1.
1st ed. Wiley-VCH Verlag GmbH&C; 2012. 16 p

[3] Slusarski L, Zaborski M, Donnet JB. Activity of carbon black as a filler in different elastomeric matrices. Die Angewandte Makromolekulare Chemie. 1994;**222**:49-60. DOI: 10.1002/ apmc.1994.052220105

[4] Beev AA, Beeva DA, Abaev AM, Kozlov GV, Mikitaev AK. The properties of the interphase layer of the filled polyhydroxyester compositions. Sovremennyie naukoemkie tehnologii. 2006;**3**:60

[5] Karchakova VV, Pokhilko AV, Shmalko VM. Determining the filler activity in the sintering of pitch composites. Coke and Chemistry. 2014;**57**(1):24-29. DOI: 10.3103/ S1068364X14010025

[6] Solomko VP. Interstructural filling and its effect on the properties of polymers. Mekhanika Polimerov. 1976;**1**:162-166

[7] Donskoi AA, Baritko NV. The effect of filler surface treatment on properties of low-density heat-shielding materials. In: Handbook of Polymer Research. Chapter 9, V.19. Nova Science Publishers; 2006. pp. 201-232

[8] Bogdanova YG. Adgeziya i ee rol' v obespechenii prochnosti polimernykh kompozitov: Uch. posobie (Adhesion and Its Role in the Strength of Polymer Composites: A Handbook). Moscow: Izd. MGU im. Lomonosova; 2010

[9] Montes Ruiz-Cabello FJ, Rodríguez-Valverde MA, Cabrerizo-Vílchez
MA. Equilibrium contact angle or the most-stable contact angle. Advances in Colloid and Interface Science.
2014;206:320-327. DOI: 10.1016/j. cis.2013.09.003

[10] Lu Y, Kocaefe D, Kocaefe Y, Bhattacharyay D, Huang X-A, Morais B. Study of the wetting of coke by different pitches. Light Metals. 2016:871-876. DOI: 10.1002/9781119274780.ch147

[11] Sarkar A, Kocaefe D, Kocaefe
Y, Bhattacharyay D, Coulombe
P. Prediction of contact angle of coke-pitch system from raw material properties using artificial neural network. International Journal of
Engineering Inventions. 2017;6(4):42-52

[12] Rocha VG, Blanco C, Santamaria R, Diestre EI, Menendez R, Granda M. Pitch/coke wetting behavior. Fuel.
2005;84:1550-1556. DOI: 10.1016/j. fuel.2005.02.007

[13] Suriyapraphadilok U. Characterization of coal- and petroleum-derived binder pitches and the interaction of pitch/coke mixtures in pre-baked carbon anodes [thesis]. 2008

[14] Li K, Shen K, Huang Z-H, Shen W, Yang G, Yang J, et al. Wettability of natural microcrystalline graphite filler with pitch in isotropic graphite preparation. Fuel. 2016;**180**:743-748. DOI: 10.1016/j.fuel.2016.04.091

[15] Sarkar A, Kocaefe D, Kocaefe Y,
Sarkar D, Bhattacharyay D, Morais B,
et al. Coke-pitch interactions during
anode preparation. Fuel. 2014;117:
598-607. DOI: 10.1016/j.fuel.2013.09.015

[16] Rafalskiy PN, Shulga AA, Portyan II, Zharova OV. Otsenka smachivayuschey sposobnosti kamennougolnyih pekov po metodike OAO «UKRGRAFIT». Uglehimicheskiy zhurnal. 2010;**5-6**:31-34

[17] RDC-163 Wetting Characteristics [Internet]. Available from: http://www. lmltd.ru/r-d/equipment/pitch/33rdc163.html

[18] Shmalko VM, Sklyar MG, Soldatenko EM. Opredelenie spekayuschey sposobnosti ugley (Determination of the sintering ability of coals). Koks i Himiya. 1984;**10**:8-10

[19] Karchakova VV, Solovyov MA, Shmalko VM. Primenenie metoda opredeleniya spekaemosti i spekayuschey sposobnosti ugley dlya harakteristiki kamennougolnyih pekov i uglerodistyih napolniteley (The application of the method for determining the sinterability and sintering ability of coals to characterize coal tar pitch and carbonaceous fillers). Uglehimicheskiy zhurnal. 2013;**3-4**:32-38

[20] Ovchinnikova SA, Cheshko FF, Pityulin IN, Karchakova VV. Microstructure of electrode pitch at OAO Zaporozhkoks. Coke and Chemistry. 2010;**53**(1):31-34. DOI: 10.3103/S1068364X10010072

[21] Karchakova VV, Pokhilko AV, Shmalko VM. DoslIdzhennya spIkannya pekovih kompozitsIy z riznimi napovnyuvachami (Investigation of sintering of pitch compositions with different fillers). In: II International scientific and technical conference "Progress in oil and gas and petrochemical industry; May 2014; Lviv: NU Lviv Polytechnic; 2014. p. 135

[22] Kiseleva OA. Polistrukturnaya teoriya prochnosti kompozitsionnyih materialov (Polystructural theory of strength of composite materials). Tambov: GBOU VPO Tambov State Technical University; 2013. 22 p

[23] Auguie D, Oberlin M, Oberlin
A. Formation of thin mesophase
layers at the interface between filler
and binder in prebaked anodes. Effect
of mixing on mesophase. Carbon.
1981;19(4):211-284

[24] Marosi G, Bertalan I, Rusznák P. Role of interfacial layers in the properties of particle-filled polyolefin systems. Colloids and Surfaces. 1989;**23**(3):185-198

[25] Kozlov G, Yanovski Y, Zaikov
G. The experimental and theoretical estimation of interfacial layer thickness in elastomeric nanocomposites.
Chemistry and chemical technology.
2012;6(3):345-348

[26] Pitulin IN. Nauchnotehnologicheskie osnovyi sozdaniya kamennougolnyih uglerodsoderzhaschih materialov dlya krupnogabaritnyih elektrodov (Scientific and technological foundations for the creation of carbonaceous carbon-containing materials for large-sized electrodes). Kharkov: Kontrast; 2004. 480 p

[27] Shmalko VM, Solovyov MA. Metod viznachennya spIklivostI ta spIklivoYi zdatnostI sirovini dlya koksuvannya. TeoretichnI aspekti. (Method of determination of copolymer and copolymer ability of raw materials for coking. theoretical aspects). Uglehimicheskiy zhurnal. 2007;**6**:7-13

[28] Shmal'ko VM, Solov'ev
MA. Developing new methods of determining the clinkering properties of rammed coal. Coke and Chemistry.
2009;52(2):45-50. DOI: 10.3103/ S1068364X0902001X

[29] Denisov VD, Ibragimov IG, Galiev LG. Neodnorodnost fizikomehanicheskih svoystv spetsialnogo

koksa v ob'eme reaktora (Inhomogeneity of physical and mechanical properties of special coke in the reactor volume). In: All-Union conference of young scientists and specialists "Modern achievements in the field of research, production and operation of carbon materials and products"; Chelyabinsk; 1984. p. 15

[30] Korohin RA, Solodilov VI, Gorbatkina YA, Otegov AV. Fiziko-mehanicheskie svoystva dispersno-napolnenyih epoksidov (Physicomechanical properties of dispersed-filled epoxides). Plasticheskie Massy. 2013;4:37-41

[31] Volyinskiy AL. Effekt Rebindera v polimerah (The Rebinder effect in polymers). Priroda. 2006;**11**:11-18

[32] Sklyar MG, Nesterenko LL. Ob uporyadochenii terminologii v oblasti spekaniya ugley i koksoobrazovaniya (On the ordering of terminology in the field of sintering of coal and coke formation). Koks i Himiya. 1977;4:54-57

[33] ISO 335:1974. Hard coal --Determination of caking power -- Roga test. Publication date. 1974-10

IntechOpen