
MACROMOLECULAR CHEMISTRY
AND POLYMERIC MATERIALS

Criteria of Polymer Carbonization

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Abstract—The possibility of using numerical criteria of polymer carbonization was considered based of experimental data on the kinetics of thermal degradation and cross-linking of various polymers. The main methodological approaches to determining the parameters of thermochemical carbonization reactions and evaluating the prospects for predicting the properties of carbon materials on the basis of the existing carbonization criteria are assessed.

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Attempts to find relationships in formation of polynuclear carbon compounds from heterocyclic polymers on the basis of experimental data on thermolysis of these polymers in many cases run into the lack of systematic studies in this field and/or of possibility of comparing the results of different experiments. We can agree with the statements made in some reviews [1–6] that the experimental data are insufficient for using a statistical approach to choose the most probable criteria for assessing the specific features of carbonization of organic compounds.

Additive schemes. Attempts to calculate probable pathways of thermochemical transformations of polyaromatic structures are still on the level of discussions, even for the case of carbon-chain compounds. An interesting approach is to construct relationships based on homological criteria and structure. Such an attempt was made by Van Krevelen [7] for the polymer combustibility. For a series of synthetic and natural macromolecular compounds, the oxygen index (OI) was determined, which appeared to be comparable with the coke residue (CR) of the polymer on heating to 850°C. The correlation with these parameters is given by the formula

$$\text{OI} \times 100 = 17.5 + 0.4\text{CR}. \quad (1)$$

The coke residue, in turn, depends on the unit cell structure of the polymer. Based on experimental data on OI and CR, a dependence allowing evaluation of

the contribution made by the polymer unit structure to the carbonization was derived. The corresponding quantity was termed the carbon formation tendency (CFT), and the following formula was obtained:

$$\text{CR} = \frac{1200\text{CFT}}{M}, \quad (2)$$

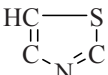
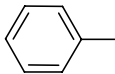
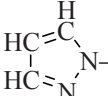
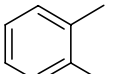
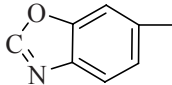
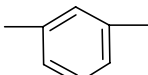
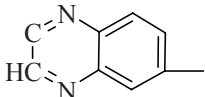
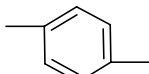
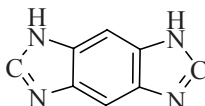
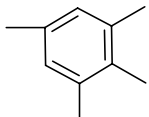
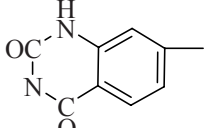
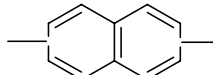
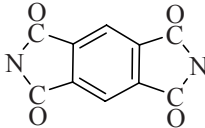
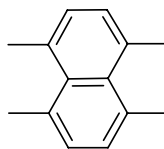
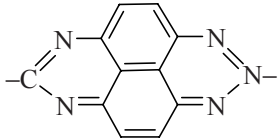
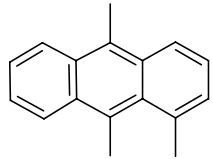
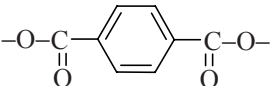

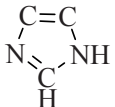
where 1200 is the carbon equivalent; CFT, dimensionless quantity characteristic of each monomer unit; and M , molecular weight of the unit.

In Tables 1 and 2 we give as examples the CFT values for various monomer units and the OI and CR values obtained experimentally and calculated by Eqs. (1) and (2).

Based on experimental data on the kinetics of thermal degradation and cross-linking of various polymers, the possibilities of using numerical criteria of polymer carbonization are considered. The main methodological approaches to determine the parameters of thermochemical carbonization reactions and evaluate the prospects for predicting the properties of carbon materials on the basis of the existing carbonization criteria are assessed.

A contribution to the understanding of the polymer carbonization mechanism is made by numerous studies on determining various parameters of pyrolysis of low-molecular-weight compounds [8–11]. In these studies, the mechanism of thermochemical reactions in a wide

Table 1. CFT values for various monomer units

Unit	CFT	Unit	CFT
CH-OH-	1/3		3 1/2
	1		3 1/2
	2		7
	3		9
	4		10
	6		11
	6		12
	10		15
	14	>CH ₂ and >CH-CH ₂ - ^a	-1
	1 1/4	CH ₃ ^a	-1 1/2
	3 1/2	>C(CH ₃) ₂ ^a	-3
	3 1/2	-CH(CH ₃) ₂ ^a	-4

^a CFT corrections for groups directly linked to aromatic rings.

Table 2. Experimental and calculated [formulas (1), (2)] values of CR and OI

Polymer	CR		OI		
	experiment	calculation	experiment	calculation by formula (1)	calculation by formula (2)
Polyoxymethylene	0	0	15.3	17.5	17.5
Poly(methyl methacrylate)	0	0	17.3	17.5	17.5
Polyethylene	0	0	17.4	17.5	17.5
Polystyrene	0	0	18.3	17.5	17.5
Cellulose	5	5	19.9	19.5	19.5
Poly(ethylene terephthalate)	8	8	20.6	20.7	20.7
Polycarbonate	24	24	29.4	27.5	27.5
Poly(<i>m</i> -phenyleneisophthalimide)	35	30	29.8	31.5	29.5
Poly(phenylene oxide)	28	30	30.5	28.9	29.5
Phenol–formaldehyde resin	45	45	35.5	35.5	35.5
Polybenzimidazole	70	67	41.5	45.5	43.6
Carbon	100	100	56–64	57.5	57.5

temperature range is correlated with structural features of the organic compounds.

(1) Nonaromatic hydrocarbons undergo almost 100% degradation with the release of volatile carbon and hydrogen compounds.

(2) Cyclization of all hydrocarbon chains with the formation of aromatic compounds or low-boiling degradation products occurs depending on the presence of side substituents.

(3) Aromatic hydrocarbons undergo cyclization to bulky polycyclic aromatic and heterocyclic structures.

As a rule, reactions of the second and third types occur with macromolecular compounds.

Topological indices. The trends in formation of graphitizing carbon materials were studied on the basis of ample experimental data on pyrolysis of aromatic hydrocarbons: diphenyl, naphthalene, acenaphthene, stilbene, and durene [12–14]. Based on the data obtained, a formula was suggested for calculating the degree of graphitization from mutual approach of graphite networks, according to X-ray diffraction patterns of pyrolyzed hydrocarbons:

$$\gamma = \frac{d_{\max} - d_{002}}{d_{\max} - d_{\min}}, \quad (3)$$

where d_{\max} is the interplanar spacing in the turbostratic structure, equal to 0.343 nm; d_{\min} , interplanar spacing

in the maximally graphitized material, 0.335 nm; and d_{002} , experimentally determined interplanar spacing.

Formula (3) allows prediction of the capability of pitches, cokes, and certain organic compounds for graphitization.

Proceeding with indexing of aromatic compounds, with a homologous series of 11 fused compounds (from benzene to benzperylene) as example, Rudkevich et al. suggested the information capacity index [15]. They found satisfactory correlations between this index and the melting and boiling points of these compounds.

Another attempt to reveal certain structure–property relationships is the use of correlations between topological indices or indices of various molecules and the properties of compounds in homologous series. The topological method and procedures for finding specific criteria are described in [15–17].

Active attempts to find quantitative relationships between physicochemical and formal topological characteristics of organic compounds were made as applied to thermochemical transformations.

In organic chemistry, the Wiener, Randic, and Balaban criteria were used for predicting the octane number of liquid fuel and yield of carbon black in incomplete combustion of hydrocarbons. In the latter case, a linear correlation based on a mathematical

combination of two indices, degree of unsaturation (measure of cyclicity of independent rings) and index of the sum of averaged distances [18], was obtained between the carbon black yield and structural characteristics of approximately 100 hydrocarbons of various classes. Sannikov et al. [19], when developing criteria for evaluating the graphitization ability of organic substances, performed modification of the Randic criterion (criterion A) on the basis of the previously considered [20] relationship between the structure of individual organic compounds and graphitization ability of carbon residues.

The quantities A were calculated for 33 individual organic compounds isolated from pitches, belonging to the pyrene, anthracene, fluorene, tetracene, perylene, and coronene series. Comparison of the values obtained with the published data [21, 22] showed that the modified topological Randic criterion allows evaluation of the influence exerted on the graphitization ability of carbonization products of organic substances by physicochemical quantities such as oxidation and hydrogenation numbers, and also by the size and number of aromatic rings and certain substituents.

It should be noted, however, that topological methods applicable and useful for calculation of certain relationships in homologous series of organic compounds are of little use for studying thermochemical reactoins of macromolecular compounds. For example, Sannikov et al. [19], when discussing carbonization, proceeded from doubtful interpretation of this process as a system of condensation (polymerization and polycondensation) reactions.

This approach does not take into account the whole complexity of thermochemical transformations of the initial, intermediate, and final carbonization products, characterized by superposition of high-temperature degradation and cross-linking reactions developing in time.

The need for a certain comparative characteristic of the carbonization ability of organic compounds, mostly of aromatic structure, also arose from comparison of various products of petrochemical and coal-chemical synthesis (coals, oils, pitches, etc.) as starting products for preparing carbon materials. This trend can be seen in a number of papers dealing with comparative indexing of various fused aromatic compounds [13, 17, 20–22]. In these studies, correlations are considered between certain physicochemical parameters of model

compounds and the complexity (extent of fusion) of their composition, growing with an additive increase in the number of elementary units participating in formation of bulky carbon clusters. However, as seen from comparison with real carbonization products identified in the course of thermochemical transformations, topological indices do not reflect the physicochemical nature of carbon structures obtained by carbonization of polymers and can be used only for tentative estimation of the tendency of certain substances to carbonization.

As for evaluation of the applicability of topological indices in organic chemistry, Rouvray [23], with references to a number of papers on topology of organic compounds, discusses certain limitations in applicability of topological indices to prediction of properties of organic compounds, because of problems with taking into account forces of intra- and intermolecular interaction forces. As noted in [24], topological indices are rather formal parameters for characterizing the properties of organic compounds. Certain monotonic trends in properties, observed in series of homologs, isomers, conglomerates, associates, clusters, and other sets, are expressed in many cases by chaotic arrangement of points in the topological index–property coordinates. Using mathematical manipulations, this disorder can be expressed in the form of linear correlations. This is done by taking logarithms (once or twice) or by introducing topological indices derived from the quantities taken previously. Such combinations of graphs and their separate elements are often constructed with certain arbitrary assumptions. For example, experimental check of [19] reveals certain discrepancies between the calculations made and the structure of certain organic compounds.

However, despite these drawbacks, the use of topological indices for predicting the properties of unknown compounds and for revealing trends in certain processes in homologous series of unstudied compounds is of apparent sense. Firstly, these procedures are simpler and more versatile than quantum-chemical calculations. Secondly, in some cases the results obtained allow definite conclusions on whether it is appropriate to perform numerous labor-consuming experiments. Certain published examples confirm this viewpoint, e.g., studies [25–27] giving much attention to the topology of branching and cyclicity of isomers of organic compounds, using the Wiener index.

From the viewpoint of polymer carbonization, the conclusions made in the published papers give certain insight into the structural directions of thermochemical reactions. The cyclicity (branching) is defined as a quantity inversely proportional to the sum of topological distances in a molecule. Comparison of the topological indices for growing cyclic sequences in fused polycyclic compounds and polymers demonstrates regular increase in the π -electron energy. In other words, in the case of intrachain cyclization of polymers as, e.g., for polyacrylonitrile, this means an increase in electron delocalization over the chain and in the length of the polyconjugation chain.

The progress of chemical topology led to the development of indices which, with certain assumptions, came into use for characterizing a series of cyclic compounds. Wiener, Randic, Balaban, and Hosoya indices, as well as the other quantities, take into account the geometric size of molecules. They are based on the matrices of the interatomic distances. Each index is applicable to compounds of a definite group. For example, the Wiener index $W = 0.5 \sum d_{ij}$ is the half-sum of matrix elements of the shortest distances (edges) of a graph whose vertices are atoms of the molecule under consideration.

The specificity of the above indices is associated with their limited use. With the index W , it is possible to obtain certain relationships for acyclic graphs, but it is not applicable to cyclic and polycyclic graphs. In these cases, it is necessary to use other indices or combinations of indices, which complicates finding real structure–property relationships because of formalization of the initial postulates. Furthermore, the use of topological indices is justified when, first, intramolecular interaction in the solid phase is described by a certain additive relationship remaining unchanged with an increase in the molecular size; second, intermolecular interaction is characterized by an equivalent correlation between the forces of interatomic interactions in molecules constituting a common series; third, there are no “disorder” factors (steric hindrance, electrostatic effects, etc.) [28]. Therefore, the use of topological indices for structural analysis of macromolecular compounds and, the more so, for characterization of complex polyreaction processes such as thermochemical reactions of polymer carbonization is hardly promising today.

Materials-science parameters. For more complex organic systems, in particular, macromolecular compounds, the carbonization criteria are based, to a

greater extent, on experimental data on the yields of volatile and solid thermal degradation products in comparison with the results of elemental analysis and molecular-weight characteristics. Such an approach was successfully used in studying carbonization of wood materials [29] by the Van Krevelen method [30] using the formula

$$R/C = (9.9 + 3.1H/C + 3.75O/C + 1.5N/C - M_{av}/d) \times (9.1 - 3.65H/C)^{-1},$$

where R/C is the ring fusion parameter, or the number of carbon rings per carbon atom; M_{av} , weight of “averaged carbon atom” (statistical mean atom) constituting the coal molecule; this quantity takes into account the atomic ratio of the elements, i.e., $M_{av} = 12.01 + 1.008H/C + 16.00O/C + 14.008N/C + 32.0064S/C$; d is the true density of the coal organic matter; and H/C , O/C , and N/C are the atomic ratios of the elements according to elemental analysis.

Examination of the thermal behavior of a series of wood samples revealed a significant growth of the ring fusion parameter with increasing temperature, and also an increase in the degree of carbonization (evaluated by the C/O and C/H ratios) with simultaneous increase in the true density of the samples. Such a definition is somewhat formalized, as it suggests a structure consisting of six-membered rings whose fusion leads to the formation of hexagonal network structures. However, a calculation of the degree of aromatization f_a from the yield of volatiles V_M by the formula

$$f_a = \frac{(100 - V_M)1200}{1200C}$$

and comparison of the data obtained with Veselovskii's formula [10]

$$C_i = \frac{H + 1/8(O + N + S)}{1/3C}$$

demonstrated good agreement of the degrees of aromatization in the examined temperature range (300–700°C).

One more index of carbonization of wood materials was suggested by Schnekkel et al. [31] and was termed the relative mass yield (RMY). This index is determined from the yield of the carbonized mass and fixed carbon content in the carbon residue:

$$RMY_x = 0.2724 \left(\frac{0.8}{FC_x} \right)^{0.78},$$

where FC_x is the fixed carbon content at the volatile component content equal to x .

The independence of the suggested carbonization index and carbon yield was checked and confirmed with more than 50 different kinds of wood materials using published data from 11 countries [31].

An example of mathematical simulation of thermal decomposition of macromolecular compounds at intense heating is the consideration of the parameters of weakening of intermolecular interaction in a narrow temperature interval (about 20°C) [32]. This supplement is of practical significance for use of polymeric items under extreme thermal conditions. The suggested model allows calculation of heat-protecting coatings of aerospace apparatus, of laser-beam treatment processes, and of other processes accompanied by intense thermal impacts in coke chemistry, plasma chemistry, and solar power engineering.

Along with these parameters suggested as independent carbonization criteria, which are of applied significance for separate kinds of macromolecular compounds, there is a series of various indirect parameters associated with the specific features of particular branches of industry and reflecting variation of certain materials-science parameters that can characterize to certain extent the carbonization process. Among them are heat and electrical conductivity, density, adsorption parameters, and other physicochemical properties of carbonized materials.

Methods of formal kinetics. In connection with the development of thermal analysis methods, numerous papers dealing with application of the data obtained to characterization of thermal transformations of polymers have been published. Some of these data are recorded directly in the course of experiments in the temperature–property (at nonisothermal heating mode) or time–property (at isothermal heating mode) coordinates. The most widely used parameters in thermal analysis are the sample weight change in the course of heating (thermogravimetric analysis) and variation of thermal characteristics (temperature, enthalpy; calorimetric analysis: DTA, DSC). There are also other complex methods of thermal analysis, but they do not alter the essence of the dualistic approach to interpretation of the results of thermal analysis. One of them directly uses the experimental quantities, e.g., the weight loss at a definite temperature or in a definite interval, or actual change in the temperature or enthalpy in the same coordinates. This approach can be conventionally termed the materials-science approach, as in practice it characterizes the new properties of a

heat-treated material and can serve as a certain indicator for predicting the service conditions for items made of this material.

Another approach is related to calculated data obtained by mathematical processing of the experimental results of thermal analysis. With this approach, it is possible to gain insight into the mechanism of thermochemical reactions yielding new compounds on the basis of very limited experimental data. Such an approach, however, requires much caution, especially in thermal analysis of complex organic and macromolecular compounds. It is well known that heat treatment of polymers initiates degradation reactions, often developing concurrently. With increasing temperature, the competition is enhanced, with each reaction being affected by numerous kinetic and diffusion factors altering the reaction course even at slight changes in any reaction conditions. Hence, it is hardly of any sense to speak of quantitative characteristics of thermochemical reactions for macromolecular compounds.

In practice, conclusions on the realization of specific reaction mechanisms are frequently based on the results of mathematical processing of experimental TGA, DTA, or DSC curves. As a rule, the authors use such terms as activation energy, reaction order, exponential factor, and frequency factor. For example, calculations of the kinetic parameters from the TGA curve are initially based on a formal rate equation [33]

$$-dx/dt = kx^n,$$

where x is the weight of the converted substance; n , reaction order; and k , specific rate constant of the reaction.

The latter quantity as a function of temperature is described by the Arrhenius equation

$$k = Ae^{-E/RT}, \quad (4)$$

where A is the preexponential factor; E , activation energy; and R , universal gas constant.

Using the parameters of these equations, the authors of many papers mentioned in monographs [34–37] do not explain the kinetic parameters used. This particularly concerns the definition of the activation energy. It is unclear what is meant by the activation energy in a conglomerate of mutually superimposing and competing thermochemical reactions. Somewhat the term overall, or apparent, activation energy is used. This inconsistency in terminology apparently hides

poor understanding of thermochemical processes in polymers or serves as a certain formal criterion in comparison of data for different polymers. Unjustified efforts are made to define these parameters which have neither physical nor chemical sense. In calorimetric practice, determination of the activation energy is, as a rule, reasonable in analysis of thermal degradation of simple inorganic solids in which the activation energy is related to cleavage of a definite chemical bond.

Calculations of formal kinetic parameters from the data of nonisothermal methods do not allow elucidation of the reaction mechanism and determination of the corresponding parameters at all, because of mathematical shortcomings of each of the three methods used for this purpose. As shown in [34], there are numerous modifications of kinetic equation (4) derived from the TGA curve and modified by the differential, integral, or approximative method. The Freeman–Carroll, Horowitz–Metzger, Coats–Redfern, Doyle, and Ozawa methods are still frequently used in thermal analysis of macromolecular compounds and polymeric materials, with the result being the same as 40–50 years ago [38–43]. As a rule, the authors do not use the critical approach and do not follow the required rules for thermal analysts, formulated by Flynn [44] and still topical.

(1) The experimental conditions of thermal analysis should be identical in calibrations and real experiments.

(2) It is necessary to use the smallest samples that can be measured with the highest accuracy.

(3) The heating rates (or temperatures) should be as low as possible.

(4) For theoretical studies, it is necessary to vary each methodical factor (one after another).

(5) For practical use of kinetic data, all the methodical factors should be the same.

(6) To determine the transformation parameters from the degrees of conversion, it is necessary to use the data of isothermal experiments.

(7) To determine a temperature parameter, it is necessary to use data for the same degree of conversion.

(8) When comparing the kinetic parameters from different experiments, the initial sample weight should be constant.

(9) The thermal history of the sample should be evaluated.

With these rules observed, the use of too “simple” and formal methods for analysis of kinetic data will be avoided, and their use in chemical or physical interpretation of thermochemical reactions will be reasonably restricted.

Neglecting these conditions and ignoring the main specific feature of thermochemical reactions of polymers, namely, superposition of competing reactions in the course of nonisothermal heating, will make the kinetic studies too formalistic and give rise to rather doubtful postulates, as it is reflected, e.g., in [38–40]. The dependence of the results of thermal analysis on the experimental conditions and initial structure of the samples, repeatedly indicated in papers dealing with thermal degradation of polymers, is clearly and convincingly seen from the primary results of thermal analysis, and determination of energetic and kinetic characteristics requires performing numerous experiments under comparable conditions. However, the sense of the physical or chemical interpretation of the activation energy still remains unclear. Numerous researchers adhere to this opinion [45, 46].

Fractal approach. Recently a fractal approach came into use in studying carbonization of various polymers and properties of carbon materials [47–50]. Application of relationships of fractal physics is based on mathematical postulates of non-Euclidean geometry describing bodies or objects with fractional (fractal) dimensionality. Methods of fractal geometry allow simulation of complex sizes of non-Euclidean objects whose images closely resemble those of natural objects. One of the most important properties of fractals is self-similarity, i.e., a small part of a fractal bears information on the fractal as a whole. This axiom attracted interest of chemists, especially of specialists in the field of macromolecular compounds for whom simulation of complex polymeric structures and their transformations in the course of chemical and physical processes is the starting point in elucidation of the mechanism by which a monomer transforms into a polymer.

Major attention to using fractal analysis of macromolecules for determining characteristics of network polymers was given in reviews [48, 49]. The necessity for taking into account numerous factors affecting the formation of the polymer structure in the course of the synthesis is noted. Possible development

of micro-, meso-, and macrodefects in the course of service of polymeric items requires their evaluation and prediction of their appearance. Solution of such problems is complicated by the fact that the majority of polymers used are solids occurring in a thermodynamically nonequilibrium state.

It is known that such systems can be only roughly described by methods of Euclidean geometry operating with integer dimensions. For accurate and reliable analysis of solid polymers, it is necessary to use the fractal approach, with obligatory use of three parameters: dimension of the enveloping space d , fractal Hausdorff dimension d_h , and spectral dimension d_s characterizing the connectivity of the object. Note that extensive studies of formation and transformation of network polymers based on epoxides [48, 49] demonstrated the possibility of deriving real information on the structure and properties of these compounds. The ratio of forces of chemical nodes in the polymer network and of macromolecular contacts was elucidated. The fractal structure of amorphous polymers on the 0.3–5.0-nm scale provides supramolecular local order. The fractal dimension of a chain segment between the chemical nodes or intermolecular contacts D characterizes different degrees of mobility of macromolecular segments. The quantity D is the relative measure of the mobility, independent of the macromolecular structure, and is determined by the known mechanisms of variation of the statistical rigidity.

As a network polymer is a single giant macromolecule (fractal cluster), one of its characteristics (there are also other assumptions) is the density of network nodes (chemical cross-links) γ_s or molecular weight of the macromolecular segment between cross-link points M_s , mutually related by

$$\gamma_s = \frac{\rho N_A}{M_s},$$

where N_A is the Avogadro number and ρ , polymer density.

Using various procedures for calculating D for epoxy polymers, Novikov and Kozlov [48] found γ_s and concluded that the network polymer depending on γ_s can be either a rubber or a rigid-chain polymer. It is also emphasized that, as any geometric image is more primitive than a real polymeric molecule, the quantity D varies in a wide range depending on the mutual arrangement of rigid segments of the macromolecule and conformational fractal properties.

The curing reaction additionally illustrates the advantage of fractal methods for calculating macromolecules of network polymers [48]. As it is assumed that formation of a network structure is turbulent since it occurs in a viscous medium, one of the main properties of turbulent flows, fractality, is used, which makes it necessary to take these factors into account.

Without dwelling on all the aspects of applying fractal methodology to analysis of formation and properties of network epoxy polymers, let us note the overall applied effect of fractals on the polymer chemistry, according to [48, 49]. In connection with the multilevel primary and secondary structure of the polymer, the majority of different parameters characterizing the structure and properties of polymers can be correlated only empirically. If the same parameters will be characterized by uniform fractal dimension, it will become possible to obtain analytical dependences involving no fitting parameters. This is important for computer synthesis of the structure and for prediction of the properties and behavior of polymers in the course of service. The applicability of fractal methods to studying macromolecular compounds, discussed in [49, 50], and a convincing example of using these methods for studying epoxy resins demonstrated practical significance of studying formation of cross-linked polymers and their mechanical and other materials-science characteristics. These data convince that the fractal approach is promising for formulating common criteria in characterization of numerous physical and chemical processes determining the structure and properties of polymeric materials. Apparently, the development of the above-mentioned methods will make it possible to design chemical, physical, and technological experiments taking into account multiprofile modeling in a common standard system.

We can note the first experience in applying multifractal formalism to studying carbon fibers prepared from synthetic and natural polymers [51]. Multifractal parameters of the structure of carbon fibers prepared from polyacrylonitrile and hydrated cellulose were studied and correlated with the elastic and strength properties of these fibers. Electron microscopic examination revealed multifractality of carbon fibers, which allowed the objects under consideration to be characterized as a loose network structure with a minimal amount of network points. This fact allows calculation of the optimal content of fibrils providing the maximal strength of carbon fibers.

Novikov et al. [51] believe that materials should be subdivided into brittle-deformable and nonelastically deformable on the basis of their multifractal diagram and on the correlation between the Poisson coefficient and elongation of break of the fiber.

A multifractal model of the failure of carbon fiber, based on using the Serpinskii set (one of parameters of fractal geometry), was suggested. A hypothesis that there are two types of failure, brittle and viscous, was put forward and substantiated by examples of correlation between the strength, elastic modulus, and fractal dimension of microregions in which the external energy pumped into the sample in the course of deformation is localized.

Subdivision of fiber deformation into brittle (extension) and viscoelastic (shear) is associated with an increase in latent ordering in the structures of carbon fibers and a decrease in the structure uniformity. This fact correlates with the previously observed effects of formation of "carbon plastics" in coking of coals in the temperature interval 400–600°C where the regions of structural ordering were detected [52]. Along with coal, elements of spatial orientation were found in the step of initial carbonization in the same temperature range for acrylonitrile and its cocarbonizates with some cellulose derivatives [53–55]. The occurrence of exo- and endothermic effects suggesting formation of mesogenic structures with various types of intra- and intermolecular orientation may be an object of application of fractal geometry for elucidation of the kinetics of transformation of a linear polymeric structure into three-dimensional formations of allotropic forms of carbon.

Apparently, search for optimal conditions of polymer carbonization using fractal modeling will expand the use of mathematics in polymer chemistry toward practical predictions of ways of using thermochemical reactions for preparing carbon materials with preset properties.

CONCLUSIONS

(1) A two-level approach to quantitative evaluation of polymer carbonization, scientific and applied, was developed. The first approach allows evaluation of the carbonization mechanism, and the second approach, prediction of materials-science characteristics of carbonization products.

(2) The carbonization criteria are determined using methods of material science, formal kinetics, topology, and fractal analysis.

(3) Each of the methods considered has certain advantages and drawbacks. One of the drawbacks is kinetic formalism whose application to polymers is of neither physical nor chemical sense.

(4) To date there is no common criterion of carbonization of macromolecular compounds. From the applied viewpoint, such parameter is hardly of any promise.

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