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The formation of polymers on the surfaces of disperse carbon materials

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ABSTRACT. The characteristic features of the synthesis of polymers (radical and ionic polymerisation, polyaddition, polycondensation) on the surfaces of disperse carbon materials (graphite, carbon black, and diamond) are examined. The processes involving the formation of polymers, their structures, and their properties are analysed taking into account the chemistry of the surfaces of disperse carbon fillers, which plays an important role in the preparation of filled polymeric materials by the method of polymerisation filling.
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I. Introduction

The introduction of solid disperse or fibrous substances into the polymer phase makes it possible in a number of instances to improve significantly the physicochemical, mechanical, thermal, electrical, frictional, and other properties of the polymers. The chemical properties of the solid surfaces of fillers influence the efficacy of their use in compositions with high molecular weight compounds. The surfaces of fillers frequently contain functional groups, which can participate in various chemical reactions and determine to a large extent the character of the solid–polymer interaction. By altering specifically the chemical properties of the surface, it is possible to influence the nature of the interaction of the polymer with the filler surface and ultimately to improve significantly the operating properties of the polymeric material.

The graft polymerisation of monomers initiated by complex catalysts, organometallic compounds, free radicals, or ions fixed on the surface is a promising method, from the theoretical and applied points of view, of obtaining filled polymeric materials.

Among the fillers used to obtain filled polymeric materials, disperse carbon materials (carbon black, graphite) are widely used. In connection with the wide-scale development of the manufacture of synthetic diamond powders in our country, there has been a sharp increase in the interest of investigators in the creation on their basis of filled polymeric materials having many interesting and even unique properties.

However, the results of numerous novel investigations of the corresponding polymerisation processes have not so far been subjected to a due analysis, especially from the standpoint of the influence of the chemistry of the surfaces of carbon fillers and the formation processes and structures of the polymers. The aim of the present review is to fill this gap.

II. The chemistry of the surfaces of disperse carbon materials and the structure and morphology of their particles

Since carbon atoms are capable of forming chemical bonds of different types as a result of the different degrees of hybridisation of the orbitals of their valence electrons, there exist a wide variety of structures of solid carbon compounds. Among them three principal forms can be distinguished—diamond, graphite, and carbyne and in addition carbon fibres and carbon black. We shall consider briefly the chemical structure and the properties of the surfaces of these materials.

Diamond. The surface of diamond, like that of any other solid, can be regarded as one of the main defects of the three-dimensional structure of the crystal.[1] The edge of the structure of the diamond skeleton, where the coordination sphere of the surface carbon atoms is altered, as well as the high enthalpy of formation of the ideal surface promote the spontaneous occurrence of processes lowering the energy of the system. One of such processes may be the formation of surface functional groups.[2]

The existence of unsaturated bonds on the diamond surface ensures the possibility of the formation of various surface compounds. The interaction of the atomically clean diamond surface with low-molecular-weight compounds leads to the appearance of surface functional groups. Using chemical analytical, spectroscopic, and resonance methods,[2] the existence on the surface of diamond of carboxy-, hydroxy-, carbonyl, lactone, ether, $=CH_2$, $=CF_2$, and $-CH_3$ groups has been established.

Studies have been published recently concerning the fixation on the surfaces of carbon materials, including diamond powders, of functional groups having a definite chemical nature.[3–7] In order to remove various impurities (non-recrystallised graphite, metals, metal carbides, and organic substances) from their surface, diamond powders are first etched with $HClO_4$.[6] Concentrated HNO_3 and the chromic acid mixture (conc. H_2SO_4 + $K_2Cr_2O_7$) are also used to obtain a chemically clean diamond surface.[6]

As a result of the action of oxidants and the subsequent vacuum heat treatment, the surface of diamond powders is freed from the majority of oxygen-containing groups and can be used for the

fixation on it of various functional groups, for example, halide and hydride groups.

Experimental data have established that, when the diamond surface is halogenated, the following chemical reactions take place:[5]

$$2[C]+Hal_2 \rightarrow 2[C-]-Hal,$$
$$[C-]-H+Hal_2 \rightarrow [C-]-Hal+HHal.$$

The maximum amount of chloride groups (~ 11 μmol m^{-2}) add to the diamond surface at 523–673 K which corresponds to a monolayer surface coverage.[5] When the surface of diamond which is modified with Cl groups is hydrogenated and treated with methane, the following reactions take place:[4]

$$[C-]-Cl+H_2 \rightarrow [C-]-H+HCl,$$
$$[C-]_m-Cl_n+nCH_4 \rightarrow [C-]_{m+n}-H_{3n}+nHCl.$$

An increase in temperature promotes a gradual increase in the degree of surface coverage by hydride and methyl groups (the maximum chemical monolayer coverage is attained at 823 K).

The formation of highly polar reactive functional groups of the type OH, COOH, and NH_2 on the surface of carbon, including diamond, powders, is of special interest. Thus the substitution of chlorine atoms on the surfaces of carbon substances on treatment with steam at 373–733 K results in the formation of an equivalent amount of surface OH groups:[4,8]

$$[C-]-Cl + H_2O(steam) \rightarrow [C-]-OH + HCl.$$

The fixation of COOH groups is observed when specimens of carbon materials are heated with concentrated HNO_3 for 5 h.[9]

Apart from nitric acid, the chromic acid mixture and perchloric acid are also used to oxidise carbon-graphite materials.[5] When carbon substances are boiled for 3 h in the oxidants indicated, acid groups and activated hydrogen are produced on the surfaces of the carbon-graphite materials. The number of these groups increases in the sequence initial powder < HNO_3-treated powder < chromic acid mixture-treated powder < $HClO_4$-treated powder.[5]

The NH_2 functional groups are fixed on the carbon surface when its chlorine atoms are treated with gaseous ammonia at 623–673 K:[4–6]

$$[C-]-Cl+NH_3 \rightarrow [C-]-NH_2+HCl.$$

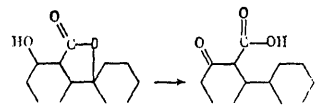
Graphite. One of the crystalline forms of carbon, widely used in various branches of industry and technology, is graphite.[10] The prospects for the intensive utilisation of graphite are associated, in particular, with the creation on its basis of anti-friction materials and filled materials with optimum properties.[11]

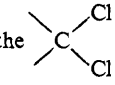
The interaction of graphite with polymers is known to be influenced significantly by the nature and concentration of its surface functional groups. Various oxygen-containing functional groups, both acid and basic, are present on the surface of graphite stored in air,[12,13] their ratio depending on the method of preparation, the subsequent treatment, and the conditions of storage of the specimens. Sub-groups include the carbonyl, phenolic, hydroxy-, and lactone groups.

The results of chemical analysis[16] indicate a relatively high concentration of COOH groups and also the presence of hydroxy- and hydroperoxy-groups, which arise on hydration of the oxidised graphite surface by water vapour. Apparently, unidentified oxygen partly enters into the composition of heterocyclic compounds, radicals, and internal oxygen bridges.[14]

It is notable that the names employed above for the oxygen-containing groups are rather conventional in character, since neighbouring groups interact in solid carbon compounds, especially in conjugated systems, which results in the formation of oxygen-containing groups with a more complex polyfunctional composition.[14]

Analysis of the real surfaces of graphites with the aid of physico-chemical (mass spectrometric and IR and EPR spectroscopic) and chemical (reactions with CH_3Mg and CH_2N_2) methods established the structures of the acid oxygen-containing groups, which were identified as cyclic esters (lactones) existing as tautomeric forms:[13,15]



Important information about the chemical nature of the graphite surface can be obtained by investigating the adsorption interaction with it by substances of different types. Only prismatic faces of graphite are known[16] to be reactive, since all the bonds in the basal plane are saturated. The sorption of hydrogen on an atomically clean graphite surface at 300 K is fully irreversible and the amount of hydrogen adsorbed on the prismatic faces is $N_H = 1.1 \times 10^{14}$ atoms cm^{-2}, which is almost 13 times smaller than the corresponding value for oxygen. The chemisorption of oxygen on a graphite specimen after it had been kept in a hydrogen atmosphere followed by desorption differs little from the adsorption of oxygen on the atomically clean surface. The number of adsorbed H and O atoms is the same as the number of carbon atoms forming the prismatic graphite faces.[16] The adsorption of molecular chlorine on an atomically clean graphite surface proceeds similarly to the adsorption of hydrogen and leads to the formation of the  groups.

Analysis of data on the surface chemistry of graphite confirms the reactivity of its prismatic faces and the possibility of the formation of surface groups of the same type as on diamond. The presence of functional groups creates the possibility for the chemical grafting of polymers on the graphite surface and for increasing its reinforcing effect in polymer compositions.

Carbon black. The wide scale and great variety of the applications of carbon blacks in the national economy makes the study of their structure, methods of preparation, and modification of current interest. The existing views on the structure of carbon black particles, as a molecular and supermolecular organisation of condensed carbon, cannot be regarded as fully established. Fairly contradictory views are frequently expressed in the literature on this question.[17] Apart from the generally accepted models of the structure of carbon black—the 'graphite' and condensed carbon models—others have also been suggested on the basis of all the forms of the organisation of carbon known at the present time. Furthermore, there exist views in conflict with traditional ideas about the structure of carbon materials and especially carbon black.[18]

Transitional forms of carbon, including carbon black and carbon fibre, have a more complex structure, in contrast to the principal crystalline forms (diamond and graphite) owing to the different nature of the surface carbon atoms on the carbon black particles, existing in different hybrid states (sp^3, sp^2, sp). The edge atoms in carbon black crystallites, like those in the graphite crystal, have less than three neighbours, i.e. their valences are not fully saturated. They are saturated by hydrogen or hydrocarbon radicals formed in the carbon black formation process.

Apart from carbon, carbon black also contains hydrogen, sulphur, oxygen, and minerals. Hydrogen and oxygen enter into the composition of various chemical groups of the surface layer, determining its chemical properties. The existence on the surface of carbon blacks of both acid and basic groups, whose ratio depends on the method of preparation and the subsequent treatment of the carbon blacks, has been established by physicochemical and chemical methods.[14] Carboxy-, carbonyl, phenolic, and lactone groups[19,20] as well as the groups formed by nitrogen and sulphur atoms[19] have been detected on the surfaces of carbon black and graphite.

The functional groups are bound mainly to edge carbon atoms in the basal planes. These carbon atoms influence strongly the properties of the groups linked to them. Thus the COOH groups retain their acidity, which may even increase: they are in fact responsible for the low pH of aqueous suspensions of certain carbon blacks and also for their ability to absorb bases. The carboxy-groups bound to aromatic rings enter into the composition of quinones. The quinone oxidation and reduction processes can occur on the surfaces of carbon blacks, which determines certain properties of the surface layer.[13,15]

The presence of oxygen on the surface of the carbon black predetermines to a large extent its physical, physicochemical, and operating properties.[21] The enhancement of the polar character of the surfaces of carbon blacks when they are partly coated by oxygen has a significant influence on the adsorption properties: the degree of adsorption of polar substances increases in this case[22,23] but the ability of carbon blacks to absorb non-polar substances never fully disappears under these conditions.[20]

The oxygen-containing groups formed on the surfaces of graphite and carbon black are in principle identical. However, it has been demonstrated by enthalpymetric titration that the acidity of the oxygen-containing groups on graphite is greater than on carbon black.[15] Consequently, the nature of the substrate undoubtedly influences the properties of the surface compounds (the degree of conjugation of the chemical bonds in graphite is greater and the proton participating in the reaction is therefore more mobile).[16]

Carbon blacks contain (mainly in the bulk of the particles) paramagnetic centres which do not interact with free radicals under the usual conditions. The complexity of the EPR spectra of carbon black[24,25] is explained by the presence of at least two types of paramagnetic centres and several types of unpaired electrons weakly interacting with one another. Furthermore, the form of the EPR spectrum may become complicated as a result of the appearance of lines corresponding to the radical oxidation products.

The interaction of free radicals, including growing polymer radicals, with radicals present on the surface of the carbon black leads to the firm fixation of the macromolecules or to grafting. The fixation of free radicals on carbon black can also be due to the presence of surface quinonoid groups, since the number of radicals bound to the surface is greatly diminished when such groups are reduced.[26]

The surface of carbon black particles is physically and chemically inhomogeneous. In many instances, this makes it impossible to obtain sufficiently reliable results in the study of chemical processes with its participation. In order to impart to the surface of the carbon black specific properties and to improve the adhesion interaction in carbon black compositions, specific modification of the chemical composition of the surface is carried out.[24,27-29] The methods used to obtain functional groups on the surface of the carbon black are analogous to those already described for diamond and graphite.

The specific features of carbon fillers of different types are determined by two principal factors: the structure of the skeleton of the particles and the chemistry of the surface which depends on it. In particular, the presence in the structure of graphite (and partly also carbon black) of aromatic rings increases the reactivity of the surface groups bound to the carbon atoms in these rings. The identical chemical reactivities of the functional groups on the surface of diamond is due to the equivalence of all the carbon atoms in its crystal structure.

III. The formation of polymers on the surfaces of disperse carbon materials

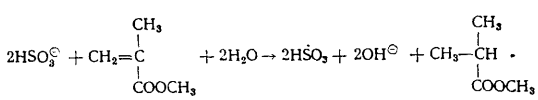
Much attention has been devoted in recent years to the preparation of composite polymeric materials by synthesising polymers in the presence of fillers.[30,31] Carbon materials with a fairly high reactivity in polymerisation initiation processes, which in many cases makes it possible to obtain graft polymers even without any preliminary treatment of the filler surface, are therefore of considerable interest. The nature of the interaction of polymer molecules with the carbon black surface has been investigated fairly thoroughly, while the monomer polymerisation processes on the surfaces of carbon black and graphite have been inadequately studied. Very few studies have been devoted to the nature of the active polymerisation centres on the newly formed surfaces of carbon blacks and graphite and for diamond such data have until recently been virtually lacking.

1. Free-radical polymerisation in the presence of carbon substances

Vibromilling of carbon blacks and graphite without access of air in vinyl monomers results in the graft polymerisation of the latter.[16] The ground carbon substances retain for a long time their ability to initiate polymerisation after dispersion. It has been suggested[16] that polymerisation is initiated by the free radicals formed on rupture of the C–C bonds and also by carbon atoms in the singlet state.

In the presence of graphite, the rate of polymerisation of methyl methacrylate under the influence of $NaHSO_3$ in an aqueous medium increases while the activation energy falls compared with the unfilled monomer.[32,33]

The molecular weight of poly(methyl methacrylate) diminishes with increase in the amount of filler, which is apparently due to processes involving the transfer of the growing chain to graphite. It has been suggested that polymerisation is initiated by the radicals $H\dot{S}O_3$ formed on interaction of $NaHSO_3$ with methyl methacrylate and water in accordance with the following scheme:



In general, much attention has been devoted to the thermal graft polymerisation of vinyl monomers on the surface of carbon black. It has been established that, when a carbon black is introduced into the monomer during the thermal polymerisation of styrene, the yield of the polymer diminishes.[34] The inhibiting effect of carbon black has been explained[16] by the interaction of the growing polymer radicals with the free radicals on the carbon black surface. It has been pointed out that the carbon black free radicals are incapable of initiating the polymerisation of monomers under the usual conditions

but they readily interact with the radicals of the growing macromolecular chain. The duration of the inhibition period is a function of the amount of carbon black introduced into the monomer.[35]

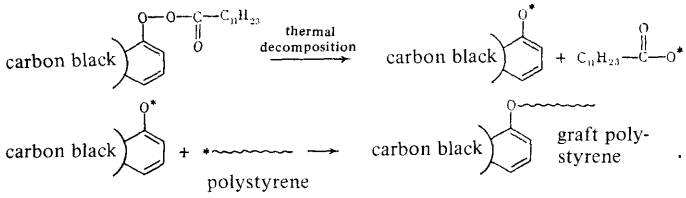
The inhibiting effect of carbon black has been attributed[34–36] to the presence on its surface of quinone groups which are reduced to hydroquinones groups in the course of polymerisation. The hydrogen atoms in the hydroxy-groups of the latter are mobile and capable of adding to the double bond of styrene, initiating its polymerisation. At the end of the inhibition period, the polymerisation of styrene is greatly accelerated in the presence of the carbon black. Both the inhibition stage and the acceleration stage are attributed to the presence on the surface of the carbon black of oxygen, which influences the duration of the inhibition period.[37–39]

The usual but accelerated thermal polymerisation takes place in the concluding stage of the reaction, which is explained by the fact that the chain termination rate constant is smaller in the presence of the carbon black than in the pure solution.[35,40]

It has been established[40] that part of the polymer formed in the presence of the carbon black is strongly bound to its surface, which indicates the grafting of the polymer chains. The amount of the grafted polymer can reach in many instances 15–20%. Since there are many radical centres on the surface of the carbon black capable of reacting with peroxy- and cyanoisopropyl radicals,[16,34] one can assume that the polystyrene radicals can also react with these centres, forming grafted chains.

In order to diminish the inhibiting effect of the carbon black and to increase the yield of the graft polymer, its surface is treated by peroxides. The surfaces of carbon substances promote in most cases the decomposition of peroxides, whose mechanism depends on the composition of the surface functional groups.[34,41–43] The fixation of peroxide initiators, especially 4,4-peroxobis(4-oxo)butanoic acid, on PM-100 carbon black[42] increases considerably their decomposition rate constant compared with the process occurring in the absence of the carbon black.

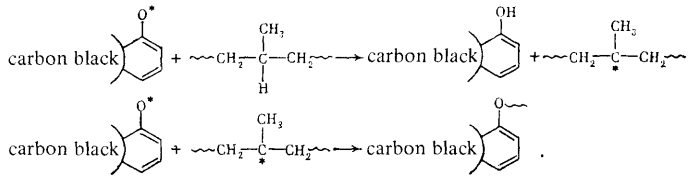
The rate of polymerisation in the presence of initiators fixed on the surface of the carbon black increases.[34] This effect can be accounted for by assuming that the growing chains are adsorbed on the surface of the carbon black and that such adsorption obeys the Langmuir–Hinshelwood law.[16] The mechanism of the formation of the graft polymer can be represented schematically as follows



As a result of the treatment of the carbon black by peroxides, the polymerisation interaction period can vanish (for example, on treatment with lauryl peroxide[16]), which indicates the blocking of the surface quinone groups or their reduction to hydroquinone groups, or it may increase (for example, on treatment with benzoyl peroxide[44]).

The efficacy of the grafting of polymers on the surfaces of carbon materials depends both on the nature of the initiator and on the chemistry of the surface. Measurements have been made[45] of the constants for chain transfer to the surfaces of oxidised carbon fibres during polymerisation carried out in the presence of lauroyl peroxide, benzoyl peroxide, and azobisisobutyronitrile. In the system with lauroyl peroxide, the chain transfer rate constant exceeds by a factor greater than 2 the corresponding value in the system with azobisisobutyronitrile. A highly oxidised surface with an increased content of carboxy-groups is the most reactive in the reaction with primary radicals.[34]

The quinone and aryloxy-groups present on the carbon black surface are capable of abstracting a hydrogen atom from a tertiary carbon atom. The radical derived from the polymer or an organic compound, formed under these conditions, can add to the surface of the carbon black:[40]



Despite the large number of studies on the polymerisation of monomers on carbon black, the influence of the chemistry of the filler surface on the characteristics of the formation of polymers was not studied in most of them, since the nature and number of surface functional groups on carbon black were as a rule unknown. In connection with the recent appearance of data on the chemical homogenisation of the surfaces of disperse carbon substances,[4–7] we investigated the influence of the chemistry of the surfaces of carbon fillers on the kinetics and characteristic features of the radical polymerisation and copolymerisation of vinyl monomers.[49,50]

One of the ways of modifying the surfaces of fillers by polymers is known to be[47,48] radical polymerisation which is initiated in this instance by the radicals fixed on the filler surface and formed as a result of the thermal decomposition of the initiators.[39] In particular azoisobutyronitrile (AIBN) and 4,4′-azobis-4-cyanovaleric acid (ACVA) have been used as initiators.[49] The latter initiator is of special interest in view of its ability to be chemisorbed in a number of instances on the substrate surface. A study of the adsorption of AIBN and ACVA from solutions on powdered ASM 1/0 diamond, ARV graphite, and GG-10 carbon black with specific surfaces of 10 000, 5000, and 10 000 $m^2\ kg^{-1}$ respectively and containing surface groups of a specific type (H, Cl, COOH, or NH_2 [2–6]) made it possible to establish that the equilibrium degree of adsorption of AIBN and ACVA depends both on the nature of the surface functional groups and on the nature of the filler skeleton. In all the instances investigated, the degree of adsorption of AIBN and ACVA on carbon substances containing different surface groups increased in the sequence H < Cl < COOH < NH_2. The degrees of the equilibrium adsorption of AIBN and ACVA on fillers with identical functional groups, referred to their concentration, differ significantly and increase as a function of the nature of the filler in the sequence carbon black < diamond < graphite, which is probably associated with the different structures of the carbon skeletons of the fillers and their influence on the reactivity of the surface groups. At the same time, the degree of equilibrium adsorption calculated per unit surface of the test powders is significantly higher for ACVA than for AIBN (by a factor of 1.5 on carbon black, 3–4 on graphite, and 10 on diamond). This demonstrates a significant influence of the polarity of the COOH functional groups in the initiator molecules on its sorption interaction with the surfaces of disperse carbon substances.

In order to elucidate the characteristics of the modification of the surfaces of disperse carbon fillers by polymers, a study was made of the influence of the nature of the adsorption on the kinetic parameters of the thermal decomposition of the sorbed azo-initiators.[50] With increase in the polarity of the surface

functional groups of the carbon materials in the sequence H < Cl < COOH < NH_2, the decomposition constants of the adsorbed AIBN and ACVA increased, while their activation energy for the thermal decomposition fell. It has been suggested[50,51] that the significant influence of the adsorption of initiators on their thermal stability may be due to the following causes:

(1) the decrease in the number of degrees of freedom of the initiator molecules as a result of their fixation on the surfaces of the carbon materials;

(2) the possibility of the addition of ACVA molecules via both end groups to the surfaces of disperse carbon materials and the formation of strained rings, which are apparently less stable than the linear molecule.[52]

The fixation of initiators on a solid surface is known[35,53] to entail in many instances a sharp decrease in the rate of polymerisation. This effect has been explained by the limitation of the diffusional mobility of the primary radicals bound to the solid phase, which leads to their rapid recombination, and also by topochemical factors determined by the localisation of the chain initiation, propagation, and termination processes at the surface of the filler particles.[53]

Table 1. The influence of the chemistry of the surfaces of disperse carbon materials on the amount (wt.%) of polystyrene not extractable from their surfaces.[46,49,50]

Initiator	Surface groups	Amount* of polystyrene not extractable from the surface		
		graphite	diamond	carbon black
AIBN	—H	1.2/0.8	0.30/—	1.4/1.0
	—Cl	1.3/0.7	0.58/—	1.6/1.2
	Initial specimen	3.2/2.2	2.0/0.6	4.0/2.4
	—COOH	3.4/2.5	3.5/2.1	5.6/2.6
	—NH_2	6.1/2.9	7.3/2.4	7.8/2.6
ACVA	—H	2.1	0.71	2.2
	—Cl	2.4	0.84	2.4
	Initial specimen	6.2	6.5	7.3
	—COOH	10.5	12.4	14.5
	—NH_2	13.5	13.8	16.1

Note. The polystyrene was obtained by radical polymerisation in suspension in the presence of the adsorbed initiators AIBN and ACVA.

*The numerator and denominator indicate respectively data obtained in the presence and absence of the initiator.

The polystyrene formed on polymerisation of styrene in the presence of an initiator sorbed on the filler surface and introduced into the monomer (0.5% relative to the monomer) is a mixture of a non-extractable polymer grafted to the surfaces of the disperse carbon materials and a homopolymer extractable by hot toluene and benzene.[46,49,50] Table 1 shows that the nature of the functional groups on the surfaces of disperse carbon materials influences significantly the amount of polystyrene non-extractable from the surfaces, which is especially notable in the polymerisation of styrene initiated by ACVA. A much greater amount of non-extractable polystyrene is formed on the surfaces of graphite and carbon black containing H groups than on the surface of diamond, which is apparently associated with the presence on the graphite and carbon black surfaces of free radicals capable of reacting with the growing polystyrene macroradicals. This leads to the termination of the polymer chain and the grafting of polystyrene to the surface. Such radicals have not been detected on the surface of diamond stored in air, which is apparently the reason for the smaller amount of polystyrene grafted to its surface.

The amount of polystyrene grafted on carbon substances containing different surface groups increases in all the systems investigated in the sequence H < Cl < initial specimen† < COOH < NH_2, which is correlated with the increase in the amount of adsorbed azo-initiators on these surfaces.[46]

As in the studies of Ivanchev and co-workers,[34,37] Bryk and Burban[46] observed a low efficacy of the initiation of the polymerisation of monomers by initiators (especially ACVA) fixed on the surfaces of carbon substances and a deviation of the kinetics of such a reaction from those characteristic of radical polymerisation. The latter is expressed by a decrease in the polymerisation reaction order with respect to the initiator from 1 to 0.3–0.7. According to Ivanchev and co-workers,[34,47] the observed phenomena can be attributed to the localisation of the initiator on the surface of the solid phase. The approach of the monomer molecules to a surface reaction centre 'shielded' by the polymer can be hindered in many instances and the rate of reaction is then controlled by diffusional factors.[34] The lower rates of formation of graft polystyrene compared with the homopolymer may be associated with the increase in the probability of the recombination of the primary radicals in the surface layer and their involvement in the termination of the growing chains.[47]

Analysis of the results of these studies carried out permit the conclusion that the grafting of the polymers onto the surfaces of carbon fillers can proceed via several mechanisms:

(1) as a result of the termination of the growing macroradicals on the radical centres present on the surfaces of the fillers.

(2) as a result of polymerisation initiated by the active centres on the surfaces of carbon black and graphite.

(3) in the interaction of the surface functional groups of the filler with the macroradicals.

(4) as a consequence of the transfer of the growing polymer chain to the surfaces of the carbon materials.

The molecular weight of the polystyrene obtained in the presence of disperse carbon materials with adsorbed AIBN and ACVA depends significantly on the chemistry of the surfaces of the fillers. The increase in the rate constant for the decomposition of the adsorbed initiators[50] leads to an increase in both the rate of initiation and in the rate of termination of the growing chains, which promote a decrease in the molecular weight of the polymer (Table 2).[34]

The presence in the polymer matrix of a solid and, what is most important, an active surface is known[54] to influence significantly the properties of the polymer. The change in the main characteristics of thermoplastics in the presence of fillers is associated with the alteration of the physical structure of the polymer at the polymer–solid interface. When disperse fillers are introduced into amorphous polymers, the adsorption interaction of the polymer molecules with the surface leads to the formation of a definite structure, inducing changes in the thermomechanical properties of the polymer.[54–56]

†The specimen of the carbon material which has not been treated in order to generate functional groups of a specific type and containing different surface functional groups.

Thus the introduction of carbon fillers diminishes the mobility of the polymer macromolecules as a consequence of their interaction with the surfaces of the particles.

Table 2. Dependence of the molecular weight of the polystyrene obtained at 353 K by ACVA-initiated polymerisation on the rate constant for the decomposition of ACVA.[46,49,50]

Carbon material	Surface groups	$10^{-5} k_d$, s^{-1}	Molecular weight of graft polystyrene
Diamond	—H	10.1	57000
	—Cl	10.9	52000
	—COOH	12.0	32000
	—NH_2	14.0	30000
Graphite	—H	12.0	55000
	—Cl	12.8	52000
	—COOH	13.3	30000
	—NH_2	16.0	28000
Carbon black	—H	8.97	56000
	—Cl	9.70	54000
	—COOH	10.30	36000
	—NH_2	11.70	34000

The glass point of the polymer increases in this instance in the sequence of the following functional groups present on the fillers: H < Cl < COOH.[46,57] Such variation is characteristic of polystyrene obtained in the presence of AIBN and ACVA adsorbed on the surfaces of carbon substances and is more pronounced for ACVA apparently due to the higher energy of the interaction of the ACVA molecules and of the radicals formed on their decomposition with the surface.[50]

It has been established[46,57] that the presence of a carbon filler (especially one containing the COOH and NH_2 surface groups) appreciably increases the resistance of the polymer to thermo-oxidative degradation. This can apparently be accounted for by the structure-forming effect of the filler, whose particles become the nodes of a structural network arising as a result of the interaction of the polymer molecules with the surface.[57] The stabilising effect of the filler on the thermal properties of the polymer is manifested to a greater extent the stronger the bond between the polymer and the surface.

The energy of the interaction of the polymer with the surface influences appreciably also the mechanical properties of the compositions obtained by the polymerisation of filled monomers. Thus the ultimate compressive strength of compositions of polystyrene with disperse carbon materials increases with increasing adsorption and chemical interactions of the macromolecules with the surface, which is in many respects determined by the chemistry of the surface of the solid phase.[54]

The effect involving the strengthening of the polymers depends greatly on the nature of the fillers and their structure. The number of surface functional groups and their reactivity are then of primary importance.[58] The geometry of the surfaces of the disperse materials is also very important.

Among the multiplicity of polymeric materials, filled three-dimensional polymers, in the preparation of which polymerisation and structure formation processes are carried out in the presence of a filler with an active surface, should be given special consideration.

Studies on the characteristic features of the radical copolymerisation of styrene with divinylbenzene (DVB) in the presence of disperse carbon materials with initiators (AIBN and ACVA) adsorbed on their surfaces have shown that the yield of the copolymer diminishes with increase in the polarity of the surface groups of the fillers in the sequence H < Cl < COOH < NH_2.[59] This is apparently associated with the decrease in the rate of polymerisation when the initiator is fixed on a solid surface.[34,52]

Table 3. Dependence of M_c of the styrene–divinylbenzene copolymer obtained in the presence of disperse carbon materials on the chemistry of their surfaces.[59]

Initiator	Surface groups	M_c^* of the copolymer on		
		diamond	graphite	carbon black
AIBN	—H	415	420	410
	—Cl	418	426	420
	Initial specimen	440	456	438
	—COOH	455	466	450
	—NH_2	458	470	456
ACVA	—H	418	416	415
	—Cl	422	420	425
	Initial specimen	480	490	475
	—COOH	506	517	502
	—NH_2	515	530	510

Note. Divinylbenzene content 10 wt.%; polymerisation temperature 343 K.
*M_c = 400 for the unfilled copolymer.

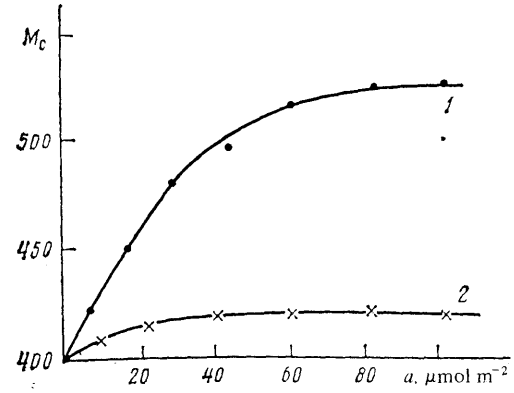


Figure 1. Dependence of M_c of the styrene–divinylbenzene (10 wt.%) copolymer, obtained in the presence of diamond containing surface NH_2 (curve *1*) and H (curve *2*) groups, on the concentration of the adsorbed ACVA initiator.[59]

Table 3 shows that the presence of fillers influences the density of the three-dimensional network [the molecular weight of the polymer between the nodes of the cross-linked structure (M_c)]: in all cases M_c for filled systems is greater than for the corresponding unfilled systems. This effect is manifested more strongly when fillers

containing the COOH and NH_2 surface groups are used. Furthermore, with increase in the amount of adsorbed initiator, the M_c of the copolymer formed increases only up to a specific initiator concentration (Fig. 1). Along the initial section of the curve, the dependence of M_c on the ACVA concentration is linear, which can apparently be explained by the dominant contribution of the surface to the termination of the polymer chain, which results in the formation of a defective three-dimensional network. On further increase in the amount of adsorbed initiator, a break in the curve is observed, which may be due to the initiation of the copolymerisation process by a much greater number of radicals, formed as a result of the thermal decomposition of the adsorbed initiators, and with their contribution to the formation of the polymer network of the copolymer. The final structure of the copolymer is determined by the overall effect of these factors acting in opposition.

2. Ionic polymerisation on the surfaces of disperse carbon substances

Studies have been published recently in which the ionic polymerisation of alkenes initiated by transition metal complexes fixed on the surfaces of fillers, including carbon fillers, was considered.[59-64] The presence on the carbon black surface of various oxygen-containing functional groups permits the fixation of $TiCl_4$ on the filler surfaces as a result of the formation of covalent bonds with the oxygen atoms:[60,61]

$$[C]_m(OH)_n \xrightarrow[-n\mathrm{HCl}]{n\mathrm{TiCl}_4} [C]_m(\mathrm{OTiCl_3})_n,$$

$$[C]_m(OH)_n \xrightarrow[-n\mathrm{HCl}]{n/2\,\mathrm{TiCl}_4} [C]_m(\mathrm{O_2{-}TiCl_2})_{n/2}.$$

Also possible is the addition of $TiCl_4$ to the carbonyl groups of the carbon black surface with formation of compounds having the composition (carbon black)—O.$TiCl_4$, which corresponds, according to Krasnobryzhii et al.,[61] to the "undissociated form of chemisorption" of $TiCl_4$. $TiCl_4$ adds to the graphite and diamond surfaces via a similar mechanism.[62-65]

Transition metal complexes fixed on the filler surface form the active centres for polymerisation. The characteristic features of the stereospecific polymerisation of ethylene initiated on the complexes of $TiCl_4$ with triethylaluminium have been determined.[62-65] In particular, the kinetics of this process under non-stationary conditions have been elucidated using graphite and diamond as fillers.[62] The much lower rate of polymerisation on graphite has been explained by the more pronounced reducing properties of its surface compared with the surface of diamond. In combination with the effect of alkyl groups, this gives rise to the possibility of the reduction of Ti(IV) ions to give a lower oxidation state, i.e. of their conversion into an inactive form.[66] The high rate of reaction on diamond is attributed to the formation of active complexes on interaction of the titanium chloride groups fixed on diamond with the triethylaluminium in the reaction medium.[62]

The study of the polymerisation of propene on stereospecific Ziegler–Natta catalysts, obtained by the alternate deposition of $TiCl_4$ and $(C_2H_5)AlCl_3$ on different carriers, established that the activity of the catalyst on graphite is several times greater than on perlite, talc, tuff, and other fillers.[67,68] The high activity and stereospecificity of the catalysts fixed on the graphite surface are determined both by the layered structure of graphite and by its electron-donating properties, which influence the structure of the polymerisation active centres.[67]

Further detailed studies on the kinetics and other features of the polymerisation of olefins on carbon fillers should give rise to the possibility of regulating the amount of the polymer formed on their surface in order to impart the required physicomechanical properties to the compositions.

Apart from the fixation of transition metal complexes, other methods for the modification of the surfaces of carbon black and graphite, used in the ionic polymerisation of monomers of different nature, are also known. It is known[69,70] that the inclusion compounds of alkali metals in graphite, having the general formula MC_n, are active catalysts of anionic polymerisation. It has been suggested that metal cations are inserted between the graphite layers, which then acquire a negative charge and ability to initiate polymerisation. The negative charge on the carbon network of graphite and hence the initiating activity depend significantly on the nature of the alkali metal and increase in the sequence Li < Na < K.[71,72] Polymerisation can occur both on the surfaces of the graphite layers and between the carbon networks. In the former case, chain propagation takes place following the adsorption of the monomer on the catalyst surface and in the latter after the insertion of the monomer between the graphite networks in the anion–graphite bonds.[72]

The possibility of using variable composition potassium–carbon black compounds as the catalyst of the anionic polymerisation of vinyl monomers has been studied.[77] It has been suggested that the polymerisation of monomers with strongly electro-negative groups may be initiated by radical-ions of the type R–$\dot{C}$H–$\overline{C}H_2$ arising as a result of electron transfer from the conductivity band of the catalyst to the monomer molecule adsorbed on its surface.

The direct propagation of ionic chains on the carbon black surface becomes possible as a result of a preliminary treatment which leads to the replacement of some of the hydrogen atoms, forming part of the polyaromatic structure, by lithium atoms.[16] Butyllithium, forming part of the composition of a complex with tetramethylenediamine, has been used for such "metallation" of the carbon black.[73-76]

An interesting way of obtaining graft polymers on the carbon black surface involves the initiation of the polymerisation by alkali metal and ammonium carboxylates.[78-80] It has been observed that, in the polymerisation of propiolactone, accompanied by ring opening and initiated by the COOM groups on the carbon black surface, the efficacy of the grafting diminishes with increase in the degree of conversion of the monomer.[78,79] This effect has been attributed to chain transfer to the monomer and the formation of the homopolymer. The reactivity of the COOM groups on carbon black depends on the nature of the alkali metal and increases in the sequence Li < Na < K < Rb < Cs.

Studies dealing with the modification of the carbon black surface by polymers formed via a cationic mechanism have been published recently.[81-85] A study has been made of the cationic polymerisation of α-methylstyrene, isobutyl vinyl ether, indene, and *N*-vinyl-2-pyrrolidinone on a carbon black surface.[83,84] It has been suggested that the polymerisation is initiated by the surface carboxy-groups of the carbon black.[81] In the polymerisation of *N*-vinylcarbazole on carbon black,[85] the polymerisation active centres are formed as a result of electron transfer from the monomer to the carbon black and the recombination of the radical-cation formed with the surface of the carbon black. The monomer cations fixed on the surface in this way function as the polymerisation active centres. The rate of polymerisation is directly proportional to the monomer concentration and the amount of the carbon black.

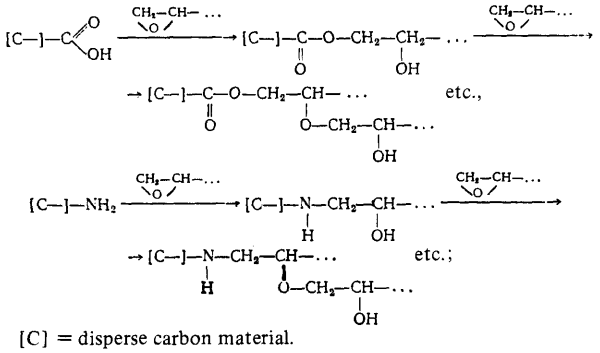
The cationic polymerisation of styrene on the surface of carbon black containing the $CO^+ClO_4^-$ functional groups has been studied.[86] The overall yield of the graft polymer increases linearly with increasing polymerisation time and reaches 85% at 313 K. The grafted $CO^+ClO_4^-$ groups are also capable of initiating the polymerisation of vinylpyridines and cyclic monomers.

3. Polyaddition and polycondensation on the surfaces of disperse carbon materials

The presence of reactive functional groups, especially COOH or NH_2, on the surfaces of carbon materials leads to the possibility of obtaining graft polymers by methods involving the polyaddition of oligomers and their polycondensation with the corresponding groups.

Modern ideas about the interaction of polymers with fillers are to a large extend based on the study of the adsorption of polymers and oligomers from solutions.[56] Thus, in the investigation of the adsorption interaction of the ED-20 epoxide resin on the phenol-formaldehyde Novolac resin with the surfaces of diamond, carbon black, and graphite powders, containing the H, Cl, COOH, or NH_2 groups, established that the degree of adsorption of the oligomers increases in the sequence H < Cl < COOH < NH_2.[87,88] This has been attributed to the differences between the energies of the sorption interactions of the oligomers with the surface. The hardening of the epoxide and phenolformaldehyde resins in the presence of disperse carbon materials without the introduction of a hardening agent into the system is induced by the participation of the surface groups of the carbon substances in this process.[9,89,90]

An IR spectroscopic study has led to the hypothesis[87,88] that the interaction of the epoxide resin with the COOH and NH_2 groups proceeds via the mechanisms



[C] = disperse carbon material.

There have been numerous studies in which the formation of three-dimensional polymer networks in the presence of disperse fillers was considered,[9,30,31] but at the present time the influence of the nature of the filler on the formation of network polymers and their structure still remains little investigated.[90]

The questions of the molecular interaction of the polymer–filler surface and of the mechanism of the influence of the filler on the polymer at comparatively large distances from its surface, greatly exceeding the radius of action of intermolecular forces (up to 150 to 200 μm), are also controversial.[91]

In order to ensure a strong adhesion bond between the polymer and the filler, both the chemistry of the surface of the filler[90,91] and the structure of the interfacial oligomeric adsorption layer[64,91,92] are very important. Depending on the nature of the oligomer and the filler, either rigid or elastic networks can be formed near the surface, which is also determined by the distance of the polymer layer formed from the surface.[90,91]

It is known[54,92] that the influence of the filler on the formation reactions of network polymers can be characterised by two opposed effects:

(1) By the chemisorption interaction between the macromolecules on the surface and also by the formation of strong physical adsorption bonds between them, which tends to reduce the degree of swelling of the compositions.

(2) By the termination of the reactions involving the growth of the macromolecules on the filler surface with formation of a defective network, which increases the degree of swelling of the filled network polymers.

In each specific case, the contributions of these processes acting in opposition are different and the final properties of the composition are determined by their overall effect.

Table 4. Dependence of the density of the polymer network (M_c) and the Huggins constant (χ) of the ED-20 epoxide resin, hardened in the presence of disperse diamond, graphite, and carbon black containing NH_2 groups, on the concentration of the filler.[88,89]

Filler	Filler concentration, wt.%	M_c^* at		χ at	
		298 K	333 K	298 K	333 K
Diamond	10	112	342	1.09	0.80
	30	103	—	1.10	—
	50	95	315	1.11	0.84
	90	82	300	1.14	0.84
Graphite	10	92	330	1.10	0.82
	30	88	—	1.10	—
	50	84	311	1.17	0.83
	90	71	292	1.26	0.85
Carbon black	10	216	424	0.85	0.44
	30	169	—	0.86	—
	50	146	391	0.92	0.46
	90	109	373	0.94	0.50

* M_c = 323 in the absence of the filler at 333 K.

The study of the structure of three-dimensional polymer networks has shown[88,89] that, with increase in the degree of filling of the resins, M_c diminishes (Table 4). This effect is associated with the increase in the total number of the surface COOH and NH_2 groups, functioning as centres for grafting and for the hardening of the resin on the surface, and leads to a diminution of M_c. The increase in the Huggins constant with the degree of filling can be explained, according to Burban et al.[93] and Lipatov et al.,[94] by the fact that the increase in the amount of filler diminishes the thermodynamic stability of the polymer–solvent system.

Fig. 2 shows that the degree of sorption of acetone vapour by the epoxide resin, hardening in the presence of carbon black (30% filling), depends significantly on the chemistry of its surface and increases in the sequence NH_2 < COOH < initial specimen < Cl < H.[88] The values of M_c for the corresponding compositions, amounting to 169, 182, 201, 221, and 254, increase in the same sequence. The phenomena indicated are apparently associated with the different kinds of interactions (chemical and physical with different energies)[93,95,96] of the epoxy-groups of the oligomers with the functional groups on the carbon black surface.

The values of M_c measured on the specimens swollen in solvent vapour at an elevated temperature (Table 5) characterise in the main the chemical nodes of the three-dimensional polymer network.[95,96]

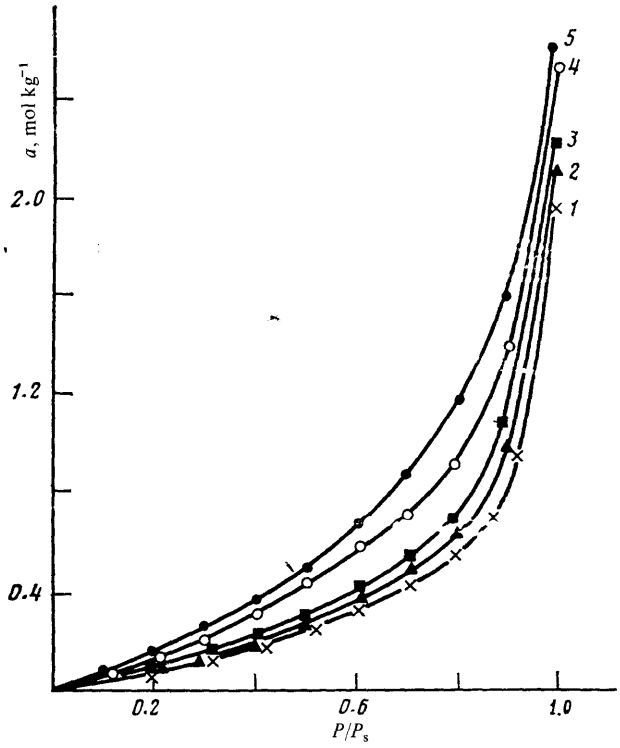


Figure 2. Isotherms of the sorption of acetone vapour by the ED-20 epoxide resin hardened in the presence of carbon black (30 wt.%) containing different surface groups at 298 K:[95] *1*, NH_2; *2*, COOH; *3*, initial carbon black; *4*, Cl; *5*, H.

Thus the structure of the polymer networks, formed when the epoxide and phenol formaldehyde resins are hardened on the surfaces of disperse carbon materials, depend significantly both on the chemistry of the surface and the structure of the fillers and on the total number of the chemical and physical cross links. Comprehensive investigation of the structure of three-dimensional polymers at different temperatures has made possible certain reliable conclusions about different interactions leading to the formation of the network structures.

The nature of the adsorption interaction of the oligomers and the structure of the polymer networks, formed when the epoxide and phenolformaldehyde resins are hardened on the surfaces of disperse carbon fillers, undoubtedly influence the properties of the polymeric materials obtained.

The increase in the glass point T_g of the network polymer in the presence of an active surface is due to the strong physical or chemical interaction of the polymer molecules with the solid phase, which limits the mobility of sections of the polymer chain, this being equivalent to the formation of an additional number of cross links.[91,92] In particular, the glass point of the composition is influenced by the state of the filler surface:[90,97-99] if the filler is subjected to the surface antiadhesion treatment, which eliminates the possibility of chemical interaction, then the T_g of the composition based on epoxide polymers does not increase and remains almost the same as for the unfilled resins.

It has been established[93] that the T_g of the epoxide and phenol-formaldehyde resins hardened in the presence of carbon materials increase significantly with increase in the content of the solid phase from 10 to 90% (Table 5). With increase in the polarity of the surface functional groups of the carbon materials, the glass point of the resin also increases.[88]

Table 5. Dependence of the glass points (T_g, K) of compositions based on epoxide and phenolformaldehyde resins on the degree of their filling by disperse carbon materials containing COOH and NH_2 surface groups.[93]

Resin	Degree of filling, wt.%	Diamond		Graphite		Carbon black	
		—COOH	—NH_2	—COOH	—NH_2	—COOH	—NH_2
ED-20*	10	435	434	435	436	433	434
	30	438	440	441	443	436	438
	50	443	447	446	449	441	445
	70	451	453	453	454	446	452
	90	454	458	458	459	452	456
FFS**	10	426	428	438	437	422	425
	30	433	436	445	446	428	430
	50	439	442	452	453	433	434
	70	446	447	458	459	443	442
	90	453	454	464	466	446	447

* T_g = 431 K in the absence of the filler.
** T_g = 460 K in the absence of the filler.

The improvement in the adhesion interaction at the polymer–solid interface and an increase in the strength of the material are important practical tasks in the creation of polymer compositions.

The question of the dependence of the mechanical properties of vitreous polymers on the concentration of chemical and physical nodes of polymer networks has been fairly adequately reflected in the literature.[100-103] The introduction of relatively small amounts of active fillers into polymers, including network polymers, increases the mechanical strength of the compositions as a consequence of the formation of additional cross links and the limitation of the mobility of segments of the macromolecules.[104]

For low and moderate degrees of filling of the epoxide and phenolformaldehyde resins, the ultimate compressive strength of the compositions increases with increase in the amount of carbon substances containing the COOH and NH_2 surface groups.[87,88,93] This phenomenon can evidently be attributed both to an increase in the density of the three-dimensional polymer network, formed in the presence of the filler, and to the formation on its surface of a more rigid boundary layer.[97] On the other hand, the decrease in the strength of the compositions in the region of high degrees of filling is apparently induced by the increase in the residual stresses at the polymer–solid surface interface and the increase in the defectiveness of the polymer network.[105,106]

The state of the filler surfaces also influences significantly the mechanical strength of the composition, since the adhesion bond between the polymer and the solid phase and the orientation and fixation of the oligomers on the surfaces of the particles depend on it.[91] The reinforcing effect of carbon fillers containing various surface groups increases in the sequence H < Cl < initial powder < COOH < NH_2. This is apparently associated with the increase in the same sequence in the density of the polymer networks formed as a result of the hardening of the epoxide and phenolformaldehyde resins on the surfaces of disperse carbon materials.

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The above analysis of the studies on the synthesis of polymers in the presence of disperse carbon materials shows that the chemistry of the filler surfaces influences significantly the process kinetics, the degree of grafting, and the molecular weight of the polymers formed and also the density of the three-dimensional networks of the polymers formed in the three-dimensional polymerisation and polycondensation of filled monomers and oligomers.

The physicochemical properties (glass points and degradation temperatures) and the mechanical properties (compressive strength) of the polymers obtained in the presence of carbon black, graphite, and diamond also depend on the chemistry of the filler surfaces. For the same type of surface functional groups, the polymerisation kinetics, the degree of grafting, and the structure and properties of the polymers formed on the graphite, carbon black, and diamond surfaces are influenced appreciably by the structure of the skeleton of the disperse carbon materials.

It is notable that ionic polymerisation and polycondensation processes on the surfaces of carbon materials with homofunctional groups have been inadequately investigated. Studies on the elementary stages of the free-radical polymerisation process on the surfaces of carbon materials containing surface groups of different kinds and having different structures of the skeleton require further development.

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