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Polymerisation Filling by the Method of Radical Polymerisation as a Procedure for the Preparation of Composite Materials

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Studies devoted to the polymerisation of monomers in the presence of dispersed fillers are surveyed. Attention is concentrated on systems where polymerisation accompanied by the formation of a chemical bond between the polymer matrix and the filler takes place. Procedures for polymerisation filling and the preparation of filled polymer compositions are described systematically and analysed; the characteristics and general features of radical polymerisation initiated from the surface of the solid phase, usually from the surfaces of dispersed inorganic fillers, are discussed. Cases of improvement of the physicochemical and operational properties of compositions resulting from the formation of the chemical bond between the polymer matrix and the filler are examined.
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I. INTRODUCTION

In recent years filled polymer compositions have been finding increasing applications in various branches of technology[1,2]. The introduction of solid dispersed or fibrous inorganic or organic substances into the polymer phase makes it possible not only to reduce significantly the cost of polymeric materials by employing cheap and readily available fillers but also this frequently leads to the strengthening of the materials, i.e. to an improvement of their physicochemical, mechanical, thermal, electrical, friction, and other properties. There is then a possibility of replacing expensive constructional plastics (polyamides and polyesters) by cheaper filled polymers[3-5].

Cheap and readily available mineral fillers constitute an increasing proportion of the overall volume of fillers employed and their assortment is being continuously increased[2,6,7]. Thus it is believed that the employment of fillers for plastics will have increased from 1.06×10^6 tonnes in 1975 to 15×10^6 tonnes in 2000, including the following substances (in million tonnes): carbonates (mainly chalk) from 0.7 to 9.0, asbestos from 0.18 to 1.7, aluminium hydroxide from 0.05 to 1.6, talc from 0.04 to 1.8, cellulose from 0.4 to 0.5, silicates from 0.025 to 0.5, and glass from 0.1 to 0.2.

We may note that the criterion of cost-effectiveness of filled compositions is not their absolute cost (the composition can be more expensive than the matrix polymer). It is in fact the difference in cost relative to the material replaced. For this reason, the most expensive fillers, which also have the greatest reinforcing effect, for example carbon fibre, are sometimes used in compositions based on fairly cheap polymers[8,9].

The most important factor which determines the strengthening effects of fillers in polymers is the adhesion of the polymers to the surfaces of the fillers[1,10,11], which depends on the adsorption and chemical linkages between the surface of the filler and the polymer matrix. The interaction of the polymer with the surface of the filler determines the nature of the deformation and breakdown of the filled polymer and many other properties. It is noteworthy that in the general case organic polymers are as a rule poorly compatible with inorganic fillers.

One of the ways of improving adhesion may be the employment of a third component (dressing agent) which forms an intermediate layer between the polymer matrix and the filler[1]. This approach can be conveniently employed in the stage involving the processing of the polymer by dressing the filler before mixing it with the polymer. In many cases expensive dressing agents with a complex structure must be used to achieve the necessary effect[12,13]. The mixing equipment and technology, which are in many instances specific to a particular polymer–filler combination, must be chosen taking into account the abrasive effect of the filler, which frequently becomes the key factor in the solution of the problem of preparation of filled compositions[7].

The mechanism of the strengthening effect of fillers in filled compositions has not so far been completely elucidated[14-17]. A common idea is that the difference between the moduli of elasticity of the polymer matrix and the filler is the cause of the "concentration" of the breaking stress at the interface between the polymer mass and the filler particle[18,19]. This phenomenon can be eliminated if the filler particle has been encapsulated in a polymer phase bound closely to it and having a modulus of elasticity close to that of the filler. It is believed[18] that such a capsule may consist of a polymer matrix linked by covalent bonds to the filler particle.

Together with the improvement of the physicomechanical and operational properties of the composition on formation of a chemical bond between the polymer matrix and the filler, the possibility of improving the rheological characteristics of the melt of the composition and its capacity for being worked has been noted in a number of studies[20].

The commonest methods ensuring the formation of a chemical bond between the polymer matrix and the filler consist in the introduction of the filler into the polymer and at the stage involving its processing, using dressing agents or functional groups on the surface of the filler and the polymer matrix[1]. However, the method of polymerisation filling, a realistic version of which has been recently proposed and applied by Enikolopov[21,22], is of greatest interest. Its essential feature reduces to the polymerisation of the monomer in the presence of a dispersed filler with a catalytic system deposited on its surface. In this case it is easy to ensure the encapsulation of the filler in a polymer "jacket".

The advantage of polymerisation filling as a procedure for the preparation of compositions consists in the ease of measuring out the amounts of the components and the elimination from the technological scheme of a series of

operations associated with the dressing of the filler and the homogenisation of the components.

Fairly numerous literature data concerning various procedures for polymerisation filling by radical polymerisation have been published recently; a number of specific features of the polymerisation of vinyl monomers, accompanied by the formation of a polymer bound chemically to the surface of the filler, have been discovered. However, there has been no systematic account of these data so far. The review of Kroker et al.[23] partly reflects the essential feature of the problem, but the intense development of this field in recent years makes it necessary to supplement significantly and analyse these data.

The aim of the present communication is to give a systematic account and to analyse the methods for polymerisation filling and the preparation of filled polymer compositions described in the literature. The general characteristics of radical polymerisation initiated from the surface of a solid phase, usually from the surfaces of dispersed inorganic fillers, are discussed.

II. PROCEDURES FOR THE POLYMERISATION FILLING OF POLYMERS BY THE METHOD OF RADICAL POLYMERISATION

The earliest communications concerning the possibility of preparing polymers bound chemically to the surfaces of mineral fillers directly in the polymerisation stage are associated with the initiation of the process by mechanochemical reactions. This possibility arises when fillers subjected to grinding and cleavage with the aid of a wide variety of apparatus for the comminution of solids are employed. The active centres formed on the surface of the filler under these conditions can initiate polymerisation.

One of the first communications on this field[24] dealt with the polymerisation of styrene, α-methylstyrene, butadiene, and chloroprene on grinding with silica in a ball mill in an atmosphere of nitrogen; the amount of non-extractable polymer was ~0.2–2%. Polymers grafted onto the surface of the filler have been obtained[25] as a result of the polymerisation of a number of monomers in the milling of titanium dioxide. Grafted polymers have been obtained[26] on vibration of monomeric specimens filled with Group III or VIII metal oxides. Vibration of dried sodium bentonite in the presence of methyl methacrylate[27] leads to polymerisation and the formation of a polymer bound chemically to the filler (yield up to 22%); a homopolymer is not then formed. On the other hand, when benzoyl peroxide was added to the reaction mixture, homopolymerisation took place.

It is striking that in the above communications no direct evidence is presented for the presence of covalent bonds between the macromolecules and the solid surface nor are any ideas concerning the mechanisms of the processes involving mechanochemical reactions described. Nevertheless Kroker et al.[23] assumed that the radicals formed on the solid surface as a result of the homolytic cleavage of chemical bonds by mechanical influences are responsible for the initiation of polymerisation. However, it has been shown in a number of studies by Kargin and Plate[28–31] and by Tsetlin[32,33] that radical-ions are the active centres which are formed on the surfaces of the solid particles during their comminution and initiate polymerisation.

A systematic study of the mechanochemical graft polymerisation on a wide variety of solid surfaces of different monomers[34–37] enabled the authors to establish a series of common features, on the basis of which a mechanism of the grafting process has been proposed[38]. Grafting was achieved in the course of the dispersion of coarsely disperse powders (calcium carbonate, barium sulphate, ionic single crystals of NaCl, LiF, and CaF_2, magnesium oxide, iron oxide, graphite, amorphous glasses, quartz, metals, and polymers) in a vibromill in the presence of the monomer in air or on powders and cleaved single crystals obtained in air or in argon with subsequent contact between the specimen and the monomer (styrene and methyl methacrylate).

The authors[34–38] reached the following conclusions. The degree of grafting depends quantitatively on the nature of the surface, but grafting does not exhibit specificity and occurs on the surfaces of solids with a wide variety of structures and chemical bonds. The formation of the homopolymer together with the grafted polymer is not due to polymerisation but is a consequence of the stripping off and dissolution of part of the layer of the grafted macromolecules formed. A proportion of the homopolymer can be formed as a result of the radiation effect of electron emission[39] and the influence of the latter can be manifested only when the filler is dispersed directly in the presence of the monomer. The aftereffect in the initiation of polymerisation persists for a long time, exceeding by several orders of magnitude the electron emission time.

The main conclusion reached in the series of the above studies[34–39] is that the mechanochemical initiation of polymerisation takes place via a free-radical mechanism. The role of the centre stimulating the initiation of polymerisation can be assumed also by the free (static) charges arising on comminution of the solid and persisting on the freshly formed surface for a very long time after electron emission has stopped.

Certain additional ideas about the mechanism of graft polymerisation or the mechanochemical method of initiation can be derived from recently published studies[40–42]. In a study of the polymerisation of styrene on the freshly formed surfaces of NaCl, KCl, and LiF [40,42] and shale of different origin[41], the authors concluded that the polymer is grafted to the negatively charged centres of the crystals[40,42] and on the charged defects of the surface of shale[41].

It is seen from the foregoing that, despite the growing interest in the mechanochemical initiation of graft polymerisation, the problem of the mechanisms of initiation and the formation of the grafted polymer has not been ultimately elucidated.

The mechanochemical method of activating the surfaces of solid inorganic substances for the initiation of graft polymerisation is not unique. Thus extremely effective initiation of polymerisation by molecular beams of crystallised substances has been achieved[28]. The possibility of the polymerisation of methyl methacrylate and styrene using the surface energies of specimens comprising the oxides SiO_2, BeO, and Al_2O_3, having atomically clean dehydrated surfaces, has been established[43]. Such an "unsaturated" surface of a solid inorganic substance, free from extraneous adsorption layers, exhibits a considerable reactivity by virtue of the large excess of free energy, which is the reason for the ease of the chemisorption of the monomer and the subsequent initiation of its polymerisation by the active surface centres (ionic or radical).[29] The polymerisation was carried out in a layer of monomer deposited on the surface either from solution or from the vapour phase. It has been suggested[43] that the polymerisation of methyl methacrylate is accomplished by the grafting of the polymer to the surface, judging from the amount of the non-extractable polymer (80–90%). However, in contrast to poly(methyl methacrylate), the grafting of polystyrene was not observed. We therefore believe that the presence of the non-extractable poly(methyl methacrylate) is most probably associated with the chemisorption of the polymer on the surfaces of the

oxides with formation of carboxylate ions of the type $(R-C(=O)-O)^- Me^+$ and not the formation of polymer–filler covalent bonds. Infrared spectroscopic studies revealed[43] the chemisorption of methyl methacrylate on both hydrated and atomically clean Al_2O_3 surfaces.

An interesting method for the activation of the surfaces of mineral fillers in order to achieve polymerisation filling has been proposed by Berg et al.[44], who reported the ability of styrene and ethyl vinyl ether to polymerise on the surface of SiO_2 (in the form of Aerosil) activated with the aid of plasma. The yield of polymers is then higher when the activation is carried out in an oxygen and not an argon plasma. The average molecular weight of the products was 4×10^3 and the main bulk of the polymer formed was grafted to SiO_2.

One of the first productive methods for the preparation of polymers grafted to the surfaces of fillers is based on the use of irradiation. Thus the preparation of grafted polystyrene and poly(methyl methacrylate) on the surfaces of a wide variety of mineral fillers subjected to preliminary γ-irradiation has been reported[45,46]. According to Dinh-Ngoc et al.[45], γ-irradiated fillers have reaction centres capable of existing for up to 20 days and distributed exclusively on the surface. The amounts of grafted polymer per unit area are approximately of the same order of magnitude for different fillers (Table 1); the homopolymer is hardly formed under these conditions.

Table 1. The results of the polymerisation[45] of styrene and methyl methacrylate on a filler surface subjected to preliminary irradiation.

Monomer	Filler	Yield of grafted polymer			s
		w_1	w_2	$10^4 w_3$	
Methyl methacrylate	Silica gel	0.06	0.57	12.7	450
Methyl methacrylate	Woelm	0.03	0.40	8.9	—
Methyl methacrylate	Sikron	0.0008	0.0035	5.8	6
Methyl methacrylate	$CaCO_3$	0.003	0.009	14.5	1.5
Styrene	Silica gel	0.05	0.19	4.1	—
Styrene	Calcite	0.00	0.0045	7.3	—

Notation: w_1 and w_2 are the yields on a non-irradiated surface and in postpolymerisation (grammes per gramme of filler), w_3 is the yield in postpolymerisation (g m^{-2}), and s the specific surface (m^2 per gramme of filler).

Polymerisation in the presence of fillers initiated directly by γ-irradiation has been investigated in a number of studies[46–63]. The reaction takes place in a layer of monomer adsorbed from the gas phase on the surface of the specimen of the mineral filler (silica gel and Aerosil). It has been suggested that surface silanol groups are responsible in this instance for the grafting of the polymer[47–49]. The polymerisation of vinyl acetate and acrylonitrile on the surfaces of inorganic fillers has been interpreted[47,48] as an inhibited reaction occurring under conditions where the concentration of a relatively ineffective inhibitor—surface hydroxy-groups involved in degenerate chain transfer—is high. It is assumed that the surface radicals $\gtrdot SiO^{\cdot}$ and $\gtrdot Si^{\cdot}$—arise under the influence of irradiation, which can lead to the formation of grafted polymers[50].

In contrast to an earlier study[51], it has been noted[52] that the polymerisation of vinyl acetate and acrylonitrile adsorbed from the vapour phase on the surface of Aerosil results in the formation, already in the initial stage, of a considerable amount (50%) of a polymer which is not grafted to the surface and the authors believe that this is caused by the formation in the system, as a result of the radiolysis of silanol groups, of low-molecular-weight radical species $H^{\cdot}$ and $OH^{\cdot}$, which are not bound chemically to the solid support. Radicals arising in chain transfer to the monomer can play a definite role in the formation of the grafted polymer[48], whereas the role of the radicals formed as a result of the direct absorption of the radiation energy by the adsorbed monomer is apparently not great[47,48].

A considerable influence of adsorption–desorption processes on the formation of the polymer phase on a solid support in such systems has been noted[53]. The amount of styrene adsorbed on silica gel has been varied[54] from the value corresponding to less than a monolayer up to the level of uniform adsorption. It has been shown that the rate of graft polymerisation and the molecular weight distribution (MWD) (Fig. 1) of the polymer formed vary with the amount of adsorbed styrene; the maximum effectiveness of the grafting has bee achieved under the conditions of monolayer adsorption.

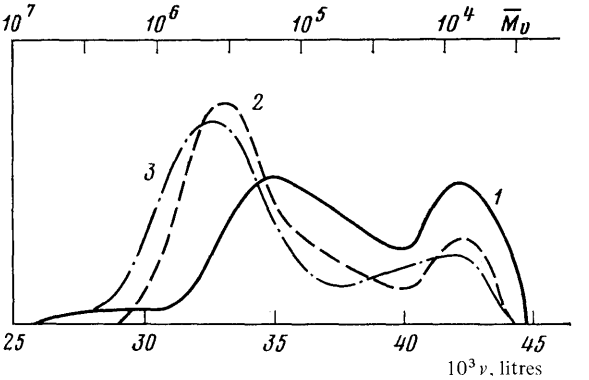


Figure 1. The molecular-weight distribution (MWD) of polystyrene grafted to silica gel and obtained in 1 h at a dose rate of 1×10^6 rad h^{-1} for different amounts of the monomer adsorbed on the filler; number of monolayers; *1*) 0.5; *2*) 1; *3*) 3 (v is the volume of eluent).[54]

A considerable change in the kinetic parameters of the polymerisation of vinyl acetate adsorbed on Aerosil relative to the liquid-phase polymerisation has been observed[55]: the rate constants for chain propagation and bimolecular termination decrease by 1–1.5 and 5 orders of magnitude respectively.

Believing that surface silanol groups are responsible for grafting, Japanese investigators[46,49,54,56–62] have adopted a different point of view concerning the mechanism of radiation-induced graft polymerisation. When the study of the polymerisation of styrene and methyl methacrylate in the presence of silica gel and Aerosil established that both grafted polymer and the homopolymer are formed simultaneously via both ionic and radical mechanisms over the entire range of dose rates. This conclusion is based on the analysis of GPC (gel permeation chromatography) peaks

which in the case of both the grafted polymer and homopolymers are bimodal, and also in the study of the influence of the dose rate and reaction temperature[57,60] and the presence of the inhibitors of radical and ionic reactions[61,62] on the nature of the GPC peaks. Analysis of the results of the polymerisation of styrene in the presence of various fillers (Aerosil and silica gel) led to the conclusion that the impurities and microporosity do not influence the reaction mechanism[59].

It has been noted in all the studies that the yield of the homopolymer always exceeds that of the grafted polymer but the molecular weight of the grafted polymer is higher (Fig.2) than that of the homopolymer. The grafted polymer, formed via a radical mechanism, has a higher molecular weight than the polymer formed via an ionic mechanism. It has been noted that in the presence of fillers (Aerosil, silica gel, and alumina) the rate of polymerisation is higher than in their absence. It has been suggested that this acceleration is associated with the excitation of the monomer molecules or of the growing chain by energy transfer from the filler[55,58].

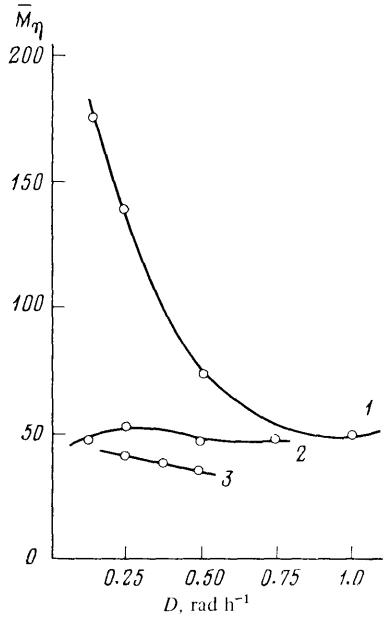


Figure 2. Dependence of M_η for polystyrene on the irradiation dose D: *1*) polystyrene grafted to silica gel; *2*) homopolymer; *3*) polymer obtained in the absence of the filler[56].

From a practical point of view, it is not without interest that on γ-irradiation a mixture of silica gel and styrene forms a greater amount of grafted polymer than in the grafting of styrene on silica gel subjected to preliminary irradiation[63].

The photochemical vapour-phase graft polymerisation of acrylonitrile, methyl methacrylate, and styrene on Aerosil with a peroxide coating, obtained using t-butyl hydroperoxide under conditions described by Poletukha[65], has been achieved[64]. Acrylonitrile has also been polymerised on Aerosil with a chlorosilylated coating[66] and on Aerosil with adsorbed quinones[67]. Analysis of infrared spectroscopic and gravimetric data led the authors of[64,66] to the conclusion that, when the modified silica is acted upon by ultraviolet light, the peroxide and chlorosilylated coatings decompose photochemically with formation of the corresponding radicals:

$$\equiv Si{-}O{-}O{-}C_4H_9 \xrightarrow{h\nu} \equiv Si{-}O^{\cdot} + C_4H_9O^{\cdot} ;$$

$$\equiv SiCl \xrightarrow{h\nu} \equiv Si^{\cdot} + Cl^{\cdot} .$$

It has been shown[68] that the quinone adsorbed on Aerosil is reduced by ultraviolet light as a result of the phototransfer of hydrogen atoms from the surface hydroxyls with formation of the radicals $\equiv SiO^{\cdot}$, which are also believed to be formed[68] in the photodehydration of the silanol groups of silica. The surface radicals $\equiv SiO^{\cdot}$ and $Si^{\cdot}$ initiate the graft polymerisation of monomers, particularly acrylonitrile:

$$\equiv Si{-}O^{\cdot} + n\,CH_2{=}\underset{\underset{CN}{|}}{CH} \rightarrow \equiv Si{-}O{-}(-CH_2{-}\underset{\underset{CN}{|}}{CH}{-})_n{-} ,$$

$$\equiv Si^{\cdot} + n\,CH_2{=}\underset{\underset{CN}{|}}{CH} \rightarrow \equiv Si{-}(-CH_2{-}\underset{\underset{CN}{|}}{CH}{-})_n{-} .$$

According to extraction data, the content of the homopolymer in the overall amount of polyacrylonitrile does not exceed 20%.[67]

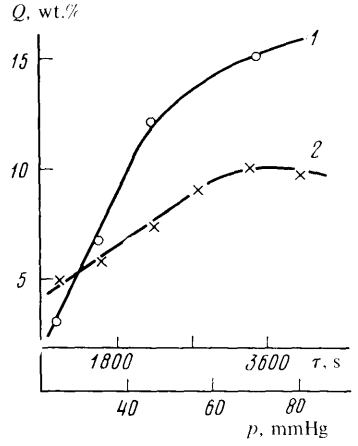


Figure 3. Dependence of the yield Q of the grafted polyacrylonitrile (at a monomer vapour pressure of 80 mmHg) on the time τ (curve *1*) and on the vapour pressure of the monomer p (curve *2*); irradiation for 45 min at 25 °C.[67]

The radical mechanism of the graft polymerisation of acrylonitrile on Aerosil is also indicated by the reaction order with respect to the intensity of the irradiating light (0.5) and by the inhibition of the reaction by oxygen[67,69]. The authors[67,69] investigated certain features of the mechanism of the photochemical vapour-phase graft polymerisation of acrylonitrile on Aerosil with quinone and peroxide coatings. It was established that, in contrast to the gas-phase radiation-chemical graft polymerisation, the yield of the polymer after prolonged ultraviolet light irradiation reaches a maximum value (Fig.3). This finding as well as data obtained in the study of the effect of the acrylonitrile vapour pressure on the rate of polymerisation (Fig.3) and the

observed[69] negative temperature coefficient of the reaction have shown that the rate of graft polymerisation of acrylonitrile on Aerosil is determined by the concentration of the monomer in the sorption layer and not in the vapour phase, i.e. the process proceeds via a sorption mechanism.

It is noteworthy that postpolymerisation is not observed in the system investigated, which shows that the radicals $\geq SiO^{\cdot}$ are rapidly deactivated under the experimental conditions. The absence of an aftereffect served as a basis for the hypothesis[33] that the initiation of the radiation-chemical graft polymerisation, where postpolymerisation takes place, is due to other radicals, whose nature has not been established. It has been noted[69] that the Aerosil surface has no specific catalytic effect on the polymerisation taking place in the test systems, because the activation energy for the given process is close to the value for the photochemical polymerisation of acrylonitrile in bulk.

Table 2. The influence of the nature of the monomer, the inorganic compound, and the initiator on the yield of the grafted polymer[70].

No.	Filler	s, m^2 per gramme of filler	Initiator	Polymer	Yield of polymer		α, %
					m_1	m_2	
1	Al_2O_3	93.80	APS	PAN	20.0	13.0	69.0
2	Al_2O_3	93.80	BP	PAN	0	0	0
3	Al_2O_3	93.80	APS	PAA	55.4	53.6	97.0
4	Al_2O_3	93.80	BP	PAA	10.7	8.0	73.0
5	Al_2O_3	93.80	APS	PMAA	30.0	26.4	87.6
6	Al_2O_3	119.00	APS	PAN	26.3	17.9	72.2
7	Al_2O_3	145.00	APS	PAN	43.4	38.4	88.5
8	$CaCO_3$	0.12	APS	PMAA	15.6	15.1	97.0
9	$CaCO_3$	0.12	APS	PAA	33.6	33.5	99.0
10	TiO_2	3.50	APS	PAN	22.8	3.5	15.4
11	TiO_2	3.50	APS	PMMA	12.4	1.0	8.8
12	ZnO	2.40	APS	PMMA	9.6	0.8	8.1
13	Al	0.12	APS	PAA	8.3	3.7	44.2
14	Al	0.12	BP	PMMA	27.0	2.7	10.0
15	Al	0.12	BP	PVA	12.8	2.9	22.3

Notation: APS = ammonium persulphate; BP = benzoyl peroxide; PAN = polyacrylonitrile; PAA = poly(acrylic acid); PMAA = poly(methacrylic acid); PMMA = poly(methyl methacrylate); PVA = poly(vinyl acetate); m_1 and m_2 = amount of polymer formed and the amount of polymer after extraction (% of weight of substrate); α = fraction of grafted polymer in the overall yield of polymer.

The graft polymerisation of a series of monomers has been achieved[70] under the influence of initiators preadsorbed on the surfaces of mineral fillers (Al_2O_3, TiO_2, $CaCO_3$, and Al). The polymerisation was carried out in a layer of monomer deposited from the liquid phase onto the surface of the filler. It has been observed (Table 2) that the effectiveness of the grafting depends to a large extent on the nature of the substrate, its specific surface, and the nature of the modifying polymer and the polymerisation initiator. When an initiator (benzoyl peroxide) soluble in monomers was used, the effectiveness of grafting was lower in all the experiments. Other conditions being equal, the effectiveness of grafting is higher for polymers insoluble in their own monomers (Table 2, Nos.1, 3, 5, and 10). It is believed[70] that this can be associated with the fact that, in the case of a monomer dissolving its own polymer (methyl methacrylate), the possibility of chain transfer via the monomer is greater. In many instances an extremum has been observed in the relation between the degree of conversion of the monomer and the amount of initiator (Fig.4) due to the fact that the initiator participates in the reaction not only in the initiation stage but also in the chain termination occurring both on the growing macroradicals and on the primary radicals. It has been suggested[70] that the graft polymerisation proceeds in this instance via a mechanism involving chain transfer from the initiator radicals, which has been examined in detail[71].

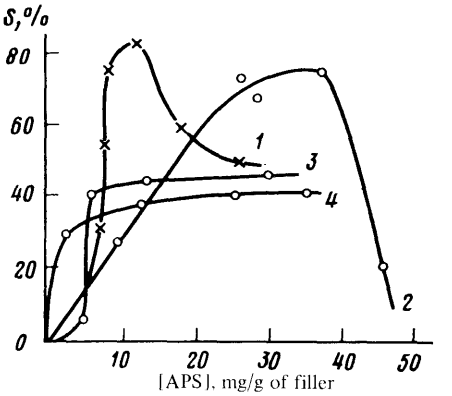


Figure 4. Dependence of the degree of conversion S of the monomer on the concentration of the ammonium persulphate (APS) initiator for the systems TiO_2–PAN (curve *1*), Al_2O_3–PMAA (curve *2*), Al_2O_3–PMAA (curve *3*), and Al_2O_3–PAM[PAN?] (curve *4*) at 60 °C (curves *1*, *2*, and *4*) and 70° (curve *3*) and for reaction times of 2.5 h (curve *1*), 4 h (curve *2*), and 5 h (curves *3* and *4*).[70]

Table 3. The content of polyacrylonitrile on the surfaces of mineral specimens[73].

Filler	g	Yield of polymer	
		m_1	m_2
Natural Sarigyukhsk bentonite	—	150	—
Sarigyukhsk bentonite in Na-form	0.32	200	144
Natural glauconite	—	3	—
Glauconite in Na-form	0.07	8.2	—
Glauconite in Na-form	0.09	11.2	7.5
Argillaceous-hydroxide adsorbent from Obolsk clay	—	31	—
Alkali-acid activated Al	0.11	28	23
Natural kaolin	0	0	—
Kaolin in Na-form	traces	1.6	1.2
KSK-2 *silica gel in* Na-form	0.02	1.2	0.7
Industrial KSK-2 silica gel	0	0	—

Notation: m_1 and m_2 = amount of polymer formed and amount of polymer after extraction (% of weight of filler); g = amount of Fe^{2+} absorbed by the filler (mequiv.g^{-1}).

A simple method has been proposed[72–74] for the preparation of grafted polymers on transition metal ion-modified (via an ion-exchange reaction) aluminosilicates and silica gel, which serve as components of oxidation-reduction systems initiating polymerisation in solutions and emulsions. In particular, it has been shown that acrylonitrile vinyl acetate, 4-vinylpyridine and acrylamide polymerise on the surfaces of a

series of $Fe^{2\pm}$ and $Cr^{3\pm}$ containing aluminosilicates in the presence of peroxy-compounds, part of the polymers being grafted to the solid surface (Table 3).

Graft polymerisation on chemically unmodified fillers in the presence of initiators has been described in a communication[75] dealing with a study where grafted copolymers used as pigments were obtained by dispersing a carbonaceous material (soot, coke, or graphite) in an aqueous medium together with the vinyl monomer (vinyl halides, styrene derivatives, unsaturated carboxylic acids, and dienes) in the presence of an oxidation-reduction initiating system.

It has been reported[76] that carbon fibres subjected to an oxidising treatment are capable of undergoing copolymerisation with methyl, ethyl, and n-butyl acrylates initiated by benzoyl peroxides. The rate of graft copolymerisation increases with increase of the degree of oxidation of the surfaces of the fibres and their monomer concentration.

An interesting method of initiating the graft polymerisation of vinyl monomers on the surface of glass has been described[77,78]. Reactive trichlorosilyl and trichloromethyl groups, which initiate the graft polymerisation of vinyl monomers in the presence of $Ni(CO)_6$ and $Mo(CO)_6$ respectively, were introduced onto the surface of glass beads by modifying the surface hydroxy-groups. The grafted polymer chains on the surface of the glass usually form a uniform monomolecular layer.

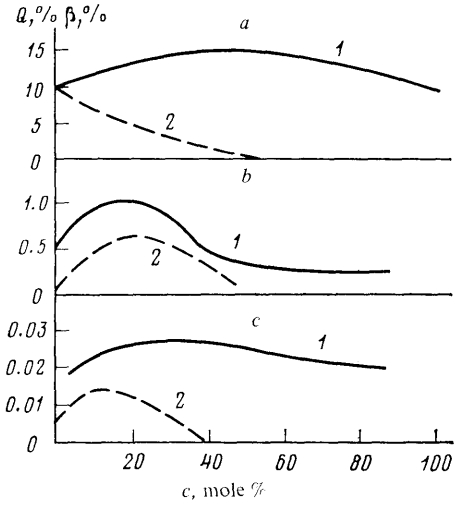
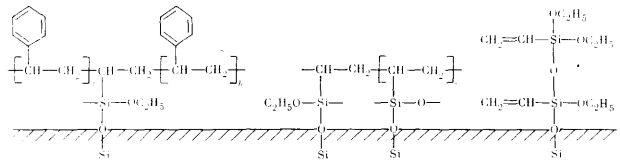


Figure 5. The influence of the composition of the monomer mixture on the yield Q of the grafted polymer (curve *1*) and the content of styrene units β in the grafted polymer (curve *2*): *a*) silica gel; *b*) broken brick; *c*) glass beads[79] (*c* is the content of triethoxyvinylsilane in the monomer mixture).

The polymerisation of binary monomeric triethoxyvinylsilane–styrene and triethoxyvinylsilane–methyl methacrylate systems on silica gel, quartz, glass beads, and brick dust has been investigated[79] with the reaction initiated by benzoyl peroxide or γ-radiation. In order to solve the problem of the sequence in which the copolymerisation and surface grafting reactions occur, a study was made of the influence of the composition of the monomer mixture on the yield of the grafted polymer, the content of the styrene and methyl methacrylate units in the grafted polymer, and the composition of the polymer. It was established (Fig.5), that, whereas the total amount of the grafted polymer does not depend greatly on the composition of the monomer mixture, the content of styrene and methyl methacrylate units in it is a maximum only in the mixture enriched in the corresponding monomer. The content of triethoxyvinylsilane in the grafted polymer is in all cases higher than in the monomer mixture.

On the grounds that the copolymerisation constants calculated from these data, namely r_1 (styrene) = 0.06 and r_2 (triethoxyvinylsilane) = 4.2, differ significantly from the literature values r_1 = 26 and r_2 = 0 (the corresponding values for methyl methacrylate are respectively r_1 = 37 and r_2 = 0), a conclusion has been reached[79] concerning the mechanism of the formation of the grafted copolymers. In the first place triethoxyvinylsilane condenses with the surface silanol groups and part of the triethoxyvinylsilane can polymerise with the partial opening of the double bond and another part gives rise to grafted polyethoxyvinylsilane as a result of the polycondensation of the ethoxy-groups. Next, some of the grafted triethoxyvinylsilane molecules undergo vinyl copolymerisation with the monomer under the influence of benzoyl peroxide or γ-radiation. It is of interest that the authors[79] were unable to separate the grafted polymer from the filler by dissolving the latter in hydrofluoric acid. They believe that this is due to the fact that the grafted copolymer closely shields the surface of the filler and hinders the access of HF to the latter.



Methacryloylmethyltriethoxyvinylsilane mixed with a monomeric dye has been polymerised[80] after impregnating fibres with the mixture (to achieve a more stable colour and more hydrophobic properties of the fibres. Conditions ensuring the quantitative grafting of the polymer have been determined. However, the quoted yield of the grafted polymer is apparently too high; this can be postulated bearing in mind the extremely low solubility of copolymers containing methacryloylmethyltriethoxysilane units[81] and their branching as a result of chain transfer to the methyl group of methacryloylmethyltriethoxysilane[82] and hence the difficulty of the separation of the grafted and ungrafted copolymers by the extraction method.

When 2,3-epoxypropyl methacrylate is polymerised on contact with a large area of a glass surface[83], the epoxy-groups are cleaved quantitatively, which leads to the formation of at least three different products. One of these, 2,3-dihydroxypropyl methacrylate, forms a polymer chemically bound to the glass in the course of the polymerisation process.

The possibility of obtaining graft polymers in polymerisation in the presence of inorganic fillers with the process initiated by free-radical initiators containing functional groups (carboxy-groups, etc.) has been described[84,85]. It is suggested that the functional groups of the initiator ensure the grafting of the polymer to the surface of the filler in the reaction with the surface silanol groups.

Organic peroxides have been used as initiators of this kind: t-butylperoxymaleic acid, peroxysuccinic acid, and their salts as well as a series of common organic and

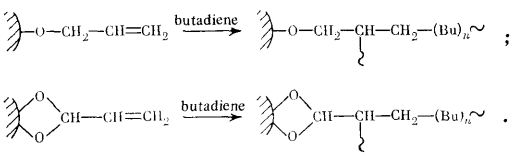
inorganic peroxides in combination with a reductant containing a carboxy-group, in the free state and in the form of the salt (malonic, oxalic, L-ascorbic, thioglycolic, and other acids and their salts). In order to obtain the maximum yield of the grafted polymer, the peroxide was added in an amount corresponding to 0.1–2.0 parts by weight to 100 parts by weight of the dispersion in water, ketones, ethers, and alcohols, while the reductant was added in an amount corresponding to 0.2–2.0 parts by weight for one part by weight of the peroxide. A wide variety of inorganic and organic solids in the form of a powder, fibre, film, sheets, etc. have been used as supports: metals and their oxides, sulphur, nitrogen, carbon, silicon, boron and chlorine compounds, the salts of various acids, hydroxides, and inorganic pigments.

It has been noted[84,85] that coating of the support with a mixture of grafted and ungrafted polymer in an amount corresponding to 3–50 parts per weight, about half of which corresponds to the polymer bound chemically to the filler, is in most cases the optimum procedure from the standpoint of the uniform coverage of the filler particles by the polymer and a satisfactory capacity of the product for being worked by pressing, extrusion, and casting under pressure. The specimens have a high bending strength. Thus a specimen made up of compressed filings coated with the product of the polymerisation of a mixture of ethyl acrylate, methyl methacrylate, and *N*-(hydroxymethyl)acrylamide in an aqueous suspension in the presence of benzoyl peroxide and oxalic acid had a bending strength of 840 kg cm^{-2}.

A procedure[85] for a uniform stable encapsulation of the filler in a polymer jacket which is bound chemically to it is noteworthy; the reaction is performed in a liquid medium containing the filler, the vinyl monomer, and the polymerisation initiator under conditions such that at least one reactant, giving rise to radicals, contains in its molecule a substituted or unsubstituted amino-group. Such a reactant can be both the monomer (mainly amino-derivatives of acrylates and methyl and ethyl methacrylates or monomers with nitrogen-containing heterocycles) and the initiator, for example the salt 2,2-azobis(2-amidinopropane) hydrochloride, as well as the peroxide–amine redox system usually employed as the radical polymerisation initiator. In most cases a high yield of the grafted polymer has been noted (80–90%). The composition produced has a high ultimate bending strength. Thus the ultimate bending strength of the specimen obtained by pressing grass charcoal coated with poly(methyl methacrylate) in an amount of 0.09 g per gram of filler was 383 kg cm^{-2}.

Publications concerning the polymerisation of monomers on the surfaces of fillers with grafted groups capable of polymerisation have appeared only recently. A method of binding the polymer to a silicon-containing support has been described[86]. The silicon-containing material in the form of individual particles is treated initially with an inorganic acid to increase the content of OH groups on its surface and then with an unsaturated silane (alkenyltrialkoxysilane or alkenyltrichlorosilane), after which the product is copolymerised with an unsaturated monomer having the general formula RCH = CHR', where R and R' = H, C_1–C_{10} alkyl or alkenyl, phenyl, amide group, or trichlorosilyl. These products are subjected to an additional treatment in order to introduce ion-exchange or chelate groups and are used to fill chromatographic columns.

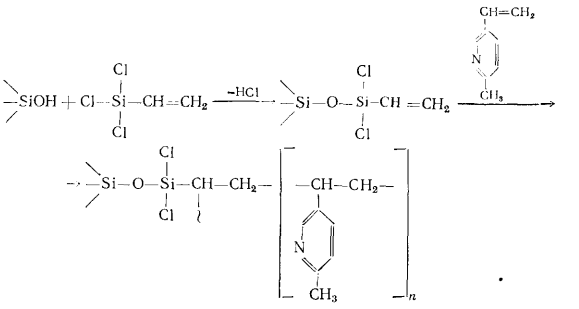
It has been shown[87,88] that unsaturated ethers and acetals, formed on interaction of the silanol groups of silica gel with allyl alcohol or acrolein respectively, copolymerise with butadiene in the presence of benzoyl peroxide:



The degree of conversion of butadiene is between 10 and 100%. An increased initial rate of polymerisation was noted when silica gel with unsaturated surface acetal groups was used. It is suggested that this finding is associated with the formation of additional radical centres owing to the thermal abstraction of hydrogen atoms from the allylic carbon atoms of the acetal group. The same workers[89] modified a silica filler with acrylonitrile and *N*-vinylpyridine. The use of such modified silica for copolymerisation with butadiene leads to an increase of the moduli of rupture and the resistance of the compositions to rupture.

The polymerisation of various monomers of the vinyl series, adsorbed from the gas phase on the surface of silica gel containing vinyl groups, has been investigated[90]. The reaction was initiated by adsorbed azobisisobutyronitrile at 60 °C. Up to 40 wt.% of the polymer bound chemically to silica gel is formed together with the homopolymer. It was found that the reaction order with respect to the initiator is 0.47, while that with respect to the monomer varies from 1 to 2.3. The reaction is of first order with respect to the monomer in polymolecular adsorption of the monomer, while higher reaction orders are obtained for degrees of adsorption corresponding to less than the monolayer coverage. The experimental data can be accounted for in terms of a kinetic reaction mechanism including as one of the elementary stages the grafting of the polymer to the surface by chain transfer and chain termination reactions on the free sections of silica gel with participation of both vinyl and silanol groups. The authors[90] believe that, as a consequence of the low concentration of the monomer in the gas phase and also the short lifetime of the surface radicals, the grafting of the polymer to the filler via the direct reaction of the monomer with the macromolecules growing on the surface is unlikely. The authors believe that the involvement in the copolymerisation of the vinyl groups grafted to the surface is insignificant by virtue of their low concentration on the surface and reduced reactivity caused by the resonance stabilisation due to the silicon atom.

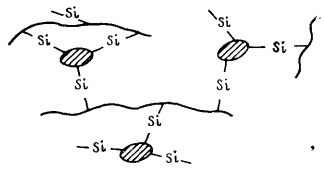
New mineral absorbents have been obtained[91] by the chemical grafting of certain monomers (vinylpyridines and *N*-vinylpyrrolidinone). For this purpose, a study was made of the graft copolymerisation of 2-methyl-5-vinylpyridine on vinyl-silica gel (silica gel with vinyl groups deposited on its surface by treatment with trichlorovinylsilane):



The process was carried out in the temperature range 70–80 °C and the initiator (diniz) and monomer concentrations were varied from 0.015 to 0.045 *N* and from 0.3 to 1.5 *N*

respectively. It was established that the yield of the grafted polymer increases with temperature, the initiator and monomer concentrations, and the amount of trichlorovinylsilane taken for surface treatment, but does not exceed ~12%. The kinetic features of the copolymerisation of monomers with a vinyl-substituted surface were discovered for the first time in systems of this kind. The reaction rate constants at 60°, 70°, and 80 °C are respectively 0.034, 0.128, and 0.376 litre$^{1/2}$ mol$^{-1/2}$ h^{-1}; the process activation energy is 25.9 kcal mol^{-1}. With the aid of computer search programmes, the authors[91] showed that the kinetics of the copolymerisation process can be described with the aid of the equation for ideal radical polymerisation.

Clay has been used in polymerisation filling[92]. After its treatment with (γ-methacryloyloxypropyl)trimethoxysilane followed by copolymerisation with styrene at 80 °C in the presence of azobisisobutyronitrile, the yield of the grafted polymer was 4.1–8.4% of the weight of the composition. The polymer consists of a gel which swells in benzene. Since the analogous copolymer obtained without a filler is soluble in benzene, it has been suggested that cross-linking via the following scheme takes place in the course of the graft copolymerisation:

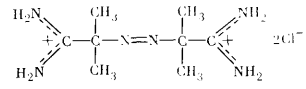


It has been noted that the analogous finished copolymer reacts less effectively with clay and does not form a gel, which has been explained by the reduced reactivity of the methoxysilane groups in the copolymer. These results agree with the features noted[79] in the copolymerisation of a binary monomer mixture in the presence of a filler where the active monomer is first attached to the surface and then the surface copolymerised with the second monomer.

The use of methacryloyloxymethyltriethoxysilane for the modification of Aerosil[93] makes it possible to obtain polymer compositions in which a considerable proportion (up to 23%) of poly(butyl methacrylate) is bound chemically to the surface of the filler. This results in a significant increase (by a factor greater than 4) of the tensile strength of the film based on the composition obtained relative to the composition based on unmodified Aerosil. It was established that the influence of the filler surface on the polymerisation kinetics is observed only when there is a possibility of the physical or chemical interaction of the monomer with the solid surface. The presence of the free comonomer of methacryloyloxymethyltriethoxysilane comonomer in an amount equal to that introduced together with the modified Aerosil did not affect the rate of the process.

The physicochemical and thermomechanical properties of certain polymerisation-filled systems have been investigated[94]. It has been noted that, as a result of the cross-linking of the poly(methyl methacrylate) macromolecules in the polymerisation of the monomer on allyl-substituted silica, the polymer becomes more rigid, which is reflected in its thermomechanical properties. The glass point of such a filled polymer is higher than that of the pure polymer by 12° and 19° respectively in the presence of 2.5 and 5 wt.% of allylsilica.

One of the new trends in the chemical modification of fillers is activation of the filler surface by initiating systems with subsequent polymerisation of the monomers on such a filler, serving as a carrier of active centres, and the formation of a chemically bound polymer. In this connection one should note studies[95,96] on the attachment of 2,2-azobisisobutyramidine hydrochloride to the surface of the filler (kaolin and bentonite) via an ion-exchange reaction and the initiation of the emulsion polymerisation of vinyl monomers by such systems.



(I)

According to Dekking's results[95], the attachment of the initiator to the surface entails an increase of the rate constant for its decomposition; the values of $10^4 k_{decomp}$ (s^{-1}) for compound (I) in a free form and attached to the filler surface are given below:

t, °C	(I)	(I)-kaolin	(I)-bentonite
60	0.358	0.666	—
70	1.41	2.17	3.33
80	5.01	9.91	10.13

The enthalpy and entropy of activation for the decomposition of the immobilised initiator have been determined (32.048 kcal mol^{-1} and +18.16 e.u. for kaolin and 30.227 kcal mol^{-1} and +13.20 e.u. for bentonite), their values being almost independent of the immobilisation of the initiator on the surface.

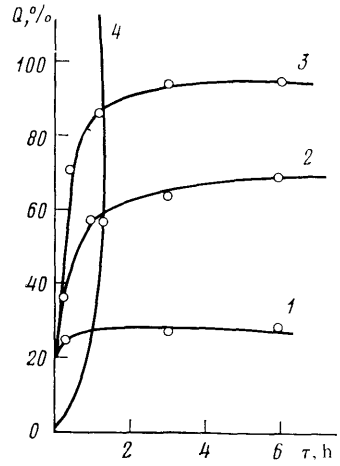
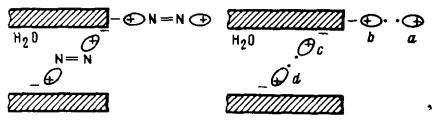


Figure 6. The yield of polymers Q in the emulsion polymerisation of methyl methacrylate initiated by the initiator–bentonite system (curves *1–3*) and by the initiator (curve *4*): *1*) grafted polymer; *2*) homopolymer; *3*) and *4*) overall yield of polymers[95].

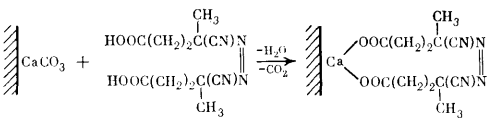
On immobilisation, the molecules of the initiator can behave in an ion-exchange reaction as monofunctional compounds, when they are located on the outer surface of the filler plates, and as bifunctional compounds when they are located between the plates and form monolayers of dications:



Determination of the ion-exchange capacity showed that in the case of bentonite ~80% of the initiator molecules are present on the surface in the form of dications and ~20% in the form of monocations. Radicals of types *b*, *c*, and *d* lead to the formation of polymers grafted to the filler, while radicals of type *a* lead to the homopolymer.

It was observed that the rate of formation of the homopolymer in the emulsion polymerisation of methyl methacrylate is approximatley twice as high as that of the grafted polymer (Fig.6), which can be explained by the difficulty with which the monomer approaches radicals of types *c* and *d*. The rate of formation of the homopolymer by a radical of type *a* is then six times higher than the rate of homopolymerisation of methyl methacrylate under analogous conditions but in the absence of the filler; the author[96] finds it difficult to account for this finding.

The influence of the grafting of the initiator to the particles of the solid filler on the rate of its thermal decomposition and its initiating activity in the polymerisation of vinyl monomers has been examined in a recently published communication[97]. The initiator was 4-azobis-4-cyanopentanoic acid (ACA) and the filler was calcium carbonate (chalk), their interaction resulting in the chemical grafting of the initiator to the surface of the chalk particles:



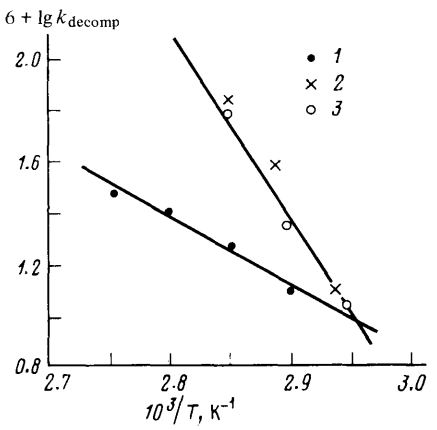
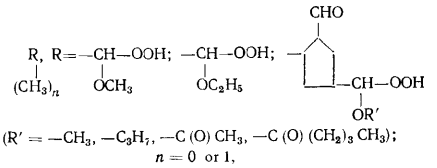


Figure 7. Temperature dependence of k_{decomp} for grafted ACA (curve *1*), ACA (curve *2*), and the calcium salt of ACA (curve *3*).[97]

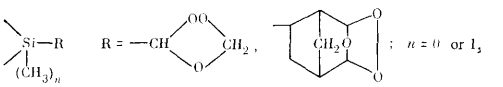
It has been established that the kinetic parameters of the thermal decomposition of the initiator change significantly in the chemical grafting of initiators to the surfaces of fillers. Thus the grafting of ACA to the solid phase lowers $k^{80°}_{decomp}$ (from 6.8×10^{-5} to 2.1×10^{-5} s^{-1}) and E^{a}_{decomp} (from 123.9 to 53.1 kJ mol^{-1}) (Fig.7). A sharp decrease of the rate of polymerisation of methyl methacrylate has been noted in the case where the initiator was grafted to the surface of the solid phase. The authors[97] explained these effects by the limited diffusional mobility of the radicals linked to the solid phase, which leads to the rapid recombination of the primary radicals, and also by topochemical factors due to the localisation of the initiation, propagation, and termination reactions at the surface of the particles. It has been shown that 3% conversion of methyl methacrylate into the polymer is sufficient to cover the entire surface of the chalk with a polymer "coating".

A simple method has been proposed recently[98] for the preparation of peroxidised mineral fillers, containing peroxy-groups with the general formula



which are capable of initiating polymerisation.

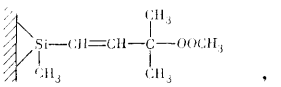
The method consists in the ozonisation of the mineral filler containing the grafted vinylmethylvinyl or norbornenylsilyl groups at temperatures between −20° and +20 °C in alcohol or in organic acid. When the ozonisation process is carried out in a hydrocarbon or its halogeno-derivative[99] at temperatures between −40° and +20 °C, peroxidised fillers with grafted ozonide peroxy-groups having the general formula



are obtained.

It has been shown[100] that the compounds produced when the temperature is raised may serve as a source of radicals bound to the filler, incapable of initiating the polymerisation of vinyl monomers, and giving rise to grafted polymers.

The same workers[101] investigated the characteristics of the polymerisation of styrene on the Aerosil A-175 filler with grafted dialkylperoxy-groups having the structure



The method of preparation of such fillers has been described[102].

An increased order of the reaction with respect to the monomer (1.68) was observed. The order of the reaction with respect to the initiator depends on the surface concentration of the latter and varies from 0.48 to 0.65 with increase of the density of the peroxy-groups on the surface of Aerosil (the concentration of active oxygen in the filler varies from 0.35 to 0.75 wt.%). The polystyrene formed consists of a polymer both grafted to the surface of Aerosil and the ungrafted homopolymer extractable with hot benzene. It has been established that the fraction of the polymer grafted to the surface of the filler depends on the polymerisation conditions and increases with increase of the temperature of the reaction, its duration, and the concentration of the peroxy-groups on the surface of Aerosil (Table 4 and Fig.8). When the monomer concentration is raised from 1.14 to 6.90 M, the yield of the grafted polymer increases from 0.38 to 2.75 g per gramme of Aerosil. The ratio of the amount of grafted polymer to that of the homopolymer increases with increasing surface concentration of peroxy-groups (Table 4) and the degree of conversation (Fig.8). It has been shown that k_{decomp} and E^{a}_{decomp} for the peroxide are independent of its concentration on the surface.

III. CHARACTERISTICS OF POLYMERISATION INITIATED FROM THE SURFACE OF A SOLID PHASE

The above analysis of the comparatively few studies on polymerisation filling, which have not always been combined in a single approach, indicates an endeavour to develop a method of preparation of composite materials which would permit the polymerisation of monomers (in bulk, in solution, or in an emulsion) in the presence of fillers with subsequent isolation of the finished composition using the familiar methods for the extraction of polymers from the reaction medium.

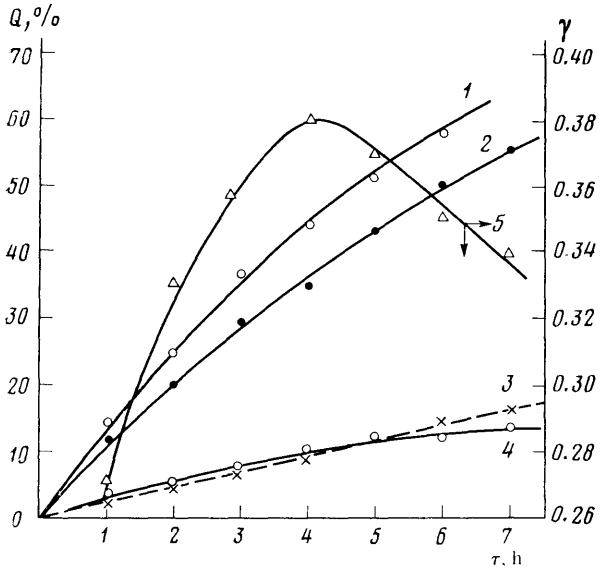


Figure 8. Dependence of the yield Q of polystyrene on the polymerisation time: *1*) overall product; *2*) homopolymer with allowance for the thermopolymer; *3*) thermopolymer; *4*) grafted polymer; *5*) ratio of the amounts of the grafted polymer and homopolymer γ (in the absence of thermopolymer); [M] = 2.02 M; [I] = 8.8×10^{-3} M; concentration of active oxygen on the filler surface 0.62 wt.%; 120 °C.[101]

The bond between the polymer and the surface of the filler arises directly during polymerisation and is due either to the effect of physical factors on the surface of the filler (γ- or ultraviolet irradiation, comminution and cleavage, or an increased temperature), inducing the formation of radicals which initiate the grafting of the polymer formed, or the copolymerisation of the vinyl monomers with monomers containing functional groups capable of chemical interaction with the surface functional groups of the filler (in the course of the copolymerisation or after its completion). Finally, there is a possibility of a third variant, where the polymerisation filling is achieved using fillers subjected to a preliminary modification by the grafting to the surfaces of polyfunctional monomers capable of copolymerisation or polyfunctional initiators capable of forming free radicals under the conditions of the polymerisation reaction.

There is no doubt that each method is distinguished by its specific features both from the standpoint of kinetic deviations from ideal radical polymerisation and from the standpoint of optimum yields of the grafted polymer, its characteristics, and the possibilities for the practical application of the methods. Unfortunately the amount of data concerning the amount of polymeric products bound to the surfaces of fillers and also information about the relative amounts of the grafted polymer and the homopolymer, the molecular weight characteristics of the polymers, and the properties of the compositions obtained are frequently insufficient for the analysis of the advantages of a particular method of polymerisation filling described in the literature quoted. Furthermore, in many instances there is no complete certainty that the solvent has been chosen correctly for the elimination of the homopolymer adsorbed on the surface. In this respect mention should be made of a study[52] where it was shown in relation to poly(vinyl acetate) that the probability of the dissolution of the polymer chain on the surface depends not only on the "quality" of the solvent in relation to the given polymer but also on the energy of the interaction of the solvent with the adsorption centres on the surface. In other words a "good" solvent in relation to the given polymer may prove to be a "poor" displacing agent and the polymer will not dissolve in it, which leads to unduly high results in the determination of the yield of the grafted polymer.

Table 4. Dependence of the rate of polymerisation of styrene v and the yield of graft polymer Q on the conditions in the reaction initiated by a dialkyl peroxide grafted to the surface of Aerosil {chlorobenzene, [M] = 2.02 M [101]}.

t, °C	10^3[I], M	$10^5 v$, mol litre^{-1} s^{-1}	Q, g/g of aerosil	γ, %
		c_{O_2} = 0.35 wt.%		
120	11.4	8.65	0.28	20.5
120	7.4	7.07	0.63	20.1
120	4.9	5.96	0.51	19.9
120	2.4	5.98	—	—
		c_{O_2} = 0.62 wt.%		
100	17.5	2.24	0.20	24.4
100	13.1	1.75	0.20	26.4
100	8.8	1.32	0.23	18.5
110	17.5	4.95	0.25	20.1
110	13.1	3.98	0.45	29.2
110	10.1	3.34	0.40	22.8
120	17.5	17.23	0.42	24.7
120	13.1	12.40	0.55	30.1
120	8.8	9.17	0.56	25.1
120	4.4	7.07	0.54	11.7
120	0.9	3.78	—	—
		c_{O_2} = 0.75 wt.%		
120	21.2	12.17	0.80	49.2
120	15.9	10.66	0.95	33.6
120	10.6	9.90	0.78	25.7
120	5.3	8.74	—	—
120*	10.6	9.60	—	—

Notation: c_{O_2} = content of active oxygen in Aerosil with grafted peroxy-groups; [I] = initiator concentration.

*In ethylbenzene.

Nevertheless, it is seen from the data presented that many characteristics of the graft polymerisation initiated by γ-irradiation (effective polymerisation only in a thin adsorption layer, influence of adsorption-desorption

processes on the formation of the graft polymer, and complexity of apparatus) are responsible for the limited applications of the given method. Mechanochemical initiation of graft polymerisation, which is frequently simple from the technological standpoint, does not ensure the attainment of the maximum possible coverages of the surface of the filler by the polymer layer, because the polymer is not grafted in a continuous coating but in the form of isolated spherical drops[103]. Photochemical initiation eliminates the disadvantages of other methods of polymerisation filling such as the formation of appreciable amounts of homopolymers and the degradation of the grafted layer. However, this method is not free from disadvantages characteristic of the method of initiation of graft polymerisation by γ-irradiation.

The method of the oxidation-reduction initiation of graft polymerisation is superior to the other procedures by virtue of its simplicity. Since many inorganic substances have ion-exchange properties and can be modified by transition metal ions, this method is fairly promising. The method of synthesising a surface-grafted polymer by the copolymerisation of monomers with a surface containing unsaturated bonds is one of the simple and effective methods of obtaining polymerisation-filled polymers.

The procedure based on the simultaneous polymerisation and grafting via the functional groups of the monomer is promising; this method eliminates the stage involving the preliminary treatment of the filler although it does not ensure the regulation of the density of the growth centres for macromolecules on the surface and is associated with an excess consumption of the active monomer and the formation of the copolymer not linked to the surface. The method based on the initiation of the reaction by agents capable of reacting with the surface via the functional groups of the initiator in the course of polymerisation is not free from these disadvantages either.

The method of polymerisation filling of polymers by filler-initiators is one of the interesting and new procedures for the preparation of composite materials, because it makes it possible to regulate fairly flexibly the process kinetics and the properties of the monomer layer bound to the filler particle by varying the density of the peroxy-groups on the surface and the polymerisation conditions; the stage in which a measured amount of the initiator is introduced is then significantly facilitated. The methods of synthesis of such fillers which have been described are suitable for technological application and the initiators themselves are universal for the polymerisation of many vinyl monomers. The realisation of the advantages of a particular method should apparently depend on the particular problems.

Whatever the nature of different methods of graft polymerisation may seem to be at first sight, in most studies a deviation of the kinetics from the ideal picture for radical polymerisation has been noted[79,90,95-97,101,104-106]. The presence of the filler in the reaction zone exerts a great influence on all the stages of the radical polymerisation regardless of the modification of its surface. In the first place the surface of the filler can influence the rate of decomposition of the peroxide initiator. Thus the acceleration of the decomposition of cumenyl hydroperoxide adsorbed on the surface of refractory titanium compounds (titanium carbide, nitride, carbonitride, and oxycarbonitride as well as the oxides TiO_2 and TiO) has been noted[108]. The decomposition of benzoyl peroxide and azobisisobutyronitrile is influenced only by TiC and TiO_2 respectively. The acceleration of the decomposition of benzoyl peroxide and cyclohexyl peroxydicarbonate has been attributed to the basic nature of the asbestos zeolite[109]. On the other hand Aerosil which has acid properties, does not affect the rate of decomposition of azobisisobutyronitrile[107].

Chemical grafting of peroxy-compounds on the surface of the filler or their fixation in the surface zone leads to a decrease of the mobility of the peroxide molecules and the radicals arising from them and to the formation (in the case of polyfunctional initiators) of strained and less stable cyclic structures. This can result in a significant decrease of E_d for the decomposition reaction[97] and an increase of the rate of decomposition of initiators[95,96].

The fixation of the initiator on the surface hinders the diffusional separation of the radical pair, increasing the probability of the "cage" effect, which is responsible for the decrease of the initiation efficiency, as noted in some investigations[97,108]. For example, when the molecules of 4-azobis-4-cyanopentanoic acid are attached via both ends to the surface of chalk, there is virtually no diffusional separation of the radical pair and the initiation efficiency is low[97].

The localisation of the initiator at the solid surface–liquid interface narrows the initiation reaction zone, increasing simultaneously the concentration of peroxy-groups in this zone. The probability of the recombination of the primary radicals in the surface layer and of the involvement of such radicals in the termination of the growing chains is therefore increased.

Account must be taken of the fact that the efficiency of the initiation of graft polymerisation depends on the concentration of the monomer in the initiation zone, i.e. near the surface. An increase of the monomer concentration in this zone increases the probability of the conversion of primary radicals into growing radicals. The specific features of the surface zone, namely the small difference between the concentrations of the monomer and initiator in this zone, necessitate allowance for the consumption of the monomer in the surface zone during the initiation reaction[110]. This may be the cause of the increase of the reaction order with respect to the monomer noted in a number of instances[101].

Apart from the diffusion-dependent limitations associated with the escape of the radicals from the surface, there can also be difficulties in the transport of monomer molecules to the active centres on the surface. The role of diffusional control increases as the grafted polymer accumulates on the filler surface whereupon the reaction centres are partly shielded by the macromolecules formed. The access of monomer molecules to the polymer phase bound to the surface, formed in the process, becomes hindered and this can then lower the rate of graft polymerisation with increasing degree of conversion[97,101,111]. At the same time, the escape from the surface zone of primary radicals which are not bound to the surface and which are capable of initiating homogeneous polymerisation, occurring simultaneously with the graft polymerisation, is less hindered. The rate of homopolymerisation can therefore be as a rule higher than the rate of graft polymerisation[95,96,101,111]. It is to be expected that the difference between the rates of graft polymerisation and homopolymerisation will be more appreciable when a "poor" solvent is used, in which the transport of the monomer molecules and radicals through the polymer layers grafted to the filler surface is difficult.

Under the conditions of both chemical and adsorption interaction of the monomer with the active surface at low degrees of polymerisation, mesomeric and inductive effects[112-116] as well as orientation effects[93,117] can make a large contribution to the reactivity of the growing radicals. In most cases the changes in the reaction rate constants are in fact accounted for by such factors.

The specific features of radical polymerisation initiated from the surface of the solid phase may consist not only in the diffusional control of the initiation and propagation reactions but also in an increase of the role of the diffusional

control of the chain termination reaction. The restriction of the mobility of macroradicals on their fixation to the surface leads to a sharp fall of the constant k_0.[55] It is therefore of interest to draw an analogy with studies[118,119] devoted to the gel effect in the polymerisation of many monomers. The authors of these investigations attribute the onset of self-acceleration to structure formation in the reaction systems. The polymerisation systems which we have examined and which contain initially an active solid phase constitute even in the first stages of the process a structural network which hinders termination. At the same time the direct involvement of fillers in the chain termination reaction has been stated in a number of investigations[48,69,90,120].

The deviations of the heterogeneous process considered from ideal radical polymerisation, noted in the above studies, indicates the failure of the assumptions of the stationary or quasi-stationary nature of the processes initiated from the surface of the solid phase. It is important to note that polymerisation on the surface frequently entails specific changes in the structure of the polymer chain formed, which affects the properties of the product. A study[121] where it was shown that the radiation-induced polymerisation of acrylonitrile and methacrylonitrile, pre-adsorbed in the form of monomolecular layers on sodium and calcium montmorillonites, leads to the formation of grafted polymers with a cyclic structure is striking in this respect[121]. Such cyclisation proved to be possible as a result of the favourable orientation of neighbouring macromolecules.

A number of studies[122,123] have shown that the method of graft copolymerisation in a mixture of the vapours of monomeric compounds, containing at least one component which is adsorbed selectively on specific functional groups of the support, can be used for the matrix synthesis of copolymer chains with a regular distribution of monomer units specified by the support. The possibility of additional chemical transformations of the monomers under the influence of the surface on which they are fixed has been noted[124]: when polyacrylonitrile grafted to Aerosil was heated *in vacuo* at 200 °C, the amine structure isomerised to the enamine structure as a result of the interaction of the nitrile groups of the polymer and the surface silanol groups with formation of additional polymer–filler chemical bonds.

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The data presented in this review on the physicomechanical, rheological, and other properties of the compositions obtained by the method of polymerisation filling confirm yet again the fact that the formation of a chemical bond between the polymer and the filler tends to improve significantly the properties of the filled compositions as a whole[80,84,85,89,92,93,125–127].

Thus the results of the studies examined in this review demonstrate the likely usefulness of polymerisation filling by radical polymerisation as a method of preparation of filled compositions, the fairly wide variety of the methods investigated, and also the specificity of the reactions involved, whose mechanism has not been ultimately elucidated in a number of instances. The continuation of such studies would therefore be of great interest not only from the standpoint of the optimisation of the filling methods but also as a significant contribution to the study of reactions occurring on solid surfaces. Furthermore, a more detailed investigation of the technological properties of the compositions obtained and their comparison with the properties of polymers filled by the usual methods are necessary.

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