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The Synthesis and Properties of Polymerisation-filled Polyalkenes

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The general principles of the polymerisation filling of polyalkenes and various other polymers have been examined. Physical and chemical methods for activating mineral and organic fillers, which lead to the production on their surface of active centres initiating polymerisation processes, have been discussed. The kinetic characteristics of the polymerisation of various monomers on a surface have been examined. The results of studies of the properties and various characteristic features of the structure of polymerisation-filled compositions have been described.
The bibliography contains 65 references.

CONTENTS

I. Introduction 117
II. Principles of the polymerisation filling of thermoplastics 117
III. The structure and properties of polymerisation-filled thermoplastics 122
IV. Conclusion 128

I. INTRODUCTION

The importance of filled polymers has increased sharply in recent years. This is due to two factors: firstly, the introduction of mineral and organic fillers into polymers gives materials with a new set of properties, and secondly, the presence of fillers leads to a decrease in the relative proportion of polymer in the final product, giving a saving in organic raw material or an increase in the production of the final product for the same amount of polymer. The rate of increase in the production of fillers for polymers in the developed capitalist countries is several times the rate of development of the production of polymeric materials[1-3]. Among the plastics produced at present, the greatest tonnage corresponds to polyalkenes (polyethylene, polypropylene), polyvinyl chloride, and polystyrene plastics. Thus the development of effective methods for introducing fillers into these polymers to obtain constructional materials for various purposes based on them is a task of practical importance.

The traditional method of obtaining filled thermoplastics involves the mechanical mixing of the polymer and the filler in powdered form or the combination of the components in a polymer melt. At the present time, practically all forms of filler in other countries are treated with special substances, or finishes, such as silanes and titanates[2], which give the surface of the filler improved adhesive properties with respect to the polymer. The aim of the finishing is to increase the degree of filling, and to improve the physicomechanical properties of the composites and their workability. The finishing of fillers is a multi-stage energy-consuming process. The expenditure on the preparation of the mixture compositions is 20-30% of the cost of the composite[3].

In spite of all the difficulty of introducing a filler into a polymer, considerable progress has been made in this field, and the world production of filled compositions is increasing steadily[1-3]. In 1975, a fundamentally new way of obtaining filled polymers was proposed, namely polymerisation filling, in which the polymer-filler composition is obtained by polymerising the corresponding monomer on the surface of an organic or inorganic filler, that is directly in the course of the synthesis of the polymers[5]. The polymerisation processes in this case can be initiated by complex catalysts, organometallic compounds, free radicals, or ions, fixed on the surface. As a result of the polymerisation of the monomer on the surface of the filler, the latter is covered by a layer of polymer, that is a polymeric capsule is in fact formed[4-6].

The method of polymerisation filling opens up extensive possibilities for the synthesis on filler surfaces of various polymers (homo- and copolymers, block copolymers, two different polymers, etc.).

Control of the kinetics of the process makes it possible to obtain polymer coverings of different thickness, that is compositions with practically any degree of filling (up to 95% of filler by volume). Thus control of the nature of the polymer matrix and the polymer-filler ratio makes it possible to create completely new composition materials which cannot be obtained by ordinary mixing methods.

Work on the synthesis and study of new types of polymer compositions, norplasts, is now being actively developed under the direction of N.S.Enikolopov in the Institute of Chemical Physics of the Academy of Sciences of the USSR and other research establishments in the Soviet Union. These studies are combined in a complex directed scientific and technical programme. A review of work on polymerisation filling using radical polymerisation was published recently[7]. The polymerisation of styrene on the surface of various materials has been studied[8-10].

In recent years, work on the development of a method for introducing fillers into polymers at the synthesis stage has also begun in other countries. Thus the firm of Dupont (USA) has published a series of studies on the polymerisation filling of super-high-molecular polyethylene by inorganic fillers[11].

The overall process of the production of a polymerisation-filled composite consists of three main stages: 1) the preparation of the filler, 2) the production of active centres on its surface, and 3) the polymerisation of the monomer on the surface. The present review examines methods for activating the surface of fillers, mainly using metal-complex and organometallic catalysts. The characteristic features of the kinetics of the polymerisation of monomers, mainly alkenes, on activated fillers, the structure of the materials formed, and their physicomechanical properties have been discussed.

II. PRINCIPLES OF THE POLYMERISATION FILLING OF THERMOPLASTICS

1. Methods for Activating the Surface of Fillers

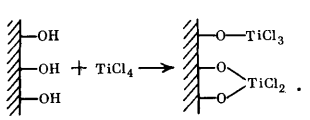
The activation of a filler involves the creation on its surface of active polymerisation centres; this can take place by an ion-coordination, radical, or ionic mechanism.

The preparation of a filler for polymerisation filling by ion-coordination polymerisation involves the removal, from its surface or from the bulk of the filler, of compounds which inhibit the polymerisation process. These compounds include H_2O, O_2, CO_2, CO, SO_2, NH_3, etc. A large number of hydroxide groups or a high acidity of the surface may also lead to retardation of the polymerisation process. In chemical technology, various methods have been developed for the thermal treatment and for the removal of oxygen from dispersed materials. For example, it is possible to use vacuum treatment, azeotropic drying, and sweeping with inert gases under different temperature conditions. From the viewpoint of the technology of removing inhibiting impurities, it is appropriate to use dispersed materials such as perlite, porous glass, Keramzit (light-weight aggregate), cement dust, etc., whose production involves high-temperature treatment. These fillers contain a minimum amount of moisture and hydroxide groups. Their subsequent treatment involves chiefly the removal of oxygen.

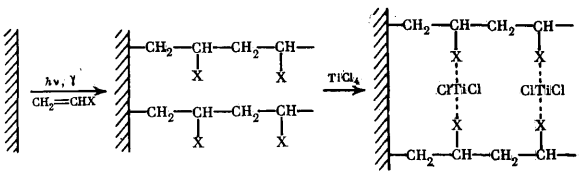
To carry out polymerisation filling by ion-coordination polymerisation, it is necessary to fix metal-complexes or organometallic catalysts on the surface of the filler. Methods have been developed[12,13] for fixing these catalysts, and the methods can be divided into two groups: physical and chemical. In the first case, precipitation (by different methods) of transition metal compounds leads to the formation of a solid phase of transition metal derivatives on the surface or in the pores of the filler. These processes may be accompanied by reduction or oxidation of the transition metal, and they do not require the presence of functional groups on the filler surface. A strong bond is formed between the solid phase of the transition metal compound ($TiCl_3$, VCl_3) and the filler, and this bond is not broken during polymerisation filling. The presence of the solid phase is particularly important for the production of stereoregular polymers such as polypropylene.

The physicomechanical properties of compositions based on polypropylene are determined to a large extent by the ratio of the isotactic and atactic fractions in the polymer. It is therefore necessary to obtain catalysts, fixed on the surface of the filler, which have not only a sufficiently high activity but also a high stereospecificity in the polymerisation of propylene. Of various methods for fixing titanium chlorides on the surface of fillers to act as highly stereospecific catalysts in the polymerisation of propylene, the most promising was found to be the reduction of $TiCl_4$ by organoaluminium compounds on the filler surface[14]. When this method is used, the $TiCl_3$ phase is formed on the surface of the fillers, including those which do not contain functional groups. It is possible to vary both the quantity of titanium fixed and the type of crystallographic modification[14]

Chemical methods of fixing are based on the reaction of transition metal compounds or organometallic compounds with reactive groups on the surface. The surface of an inorganic filler may carry hydroxide groups, whose surface density is easily controlled by thermal and chemical treatment[15-17]. The magnitude of the surface concentration of OH groups is reflected in the nature of the fixing of the catalytic systems. By appropriate reactions, OH groups can be converted into active polymerisation centres, for example:



Analogous processes take place in the case of compounds of other transition metals. If the surface has no reactive groups, it can be made functional by seeding the surface with small quanities (0.1–2%) of monomers with functional groups, using the published method[18]. These methods are convenient in the production of polymer–polymer compositions by the synthesis of one polymer on the surface of another.



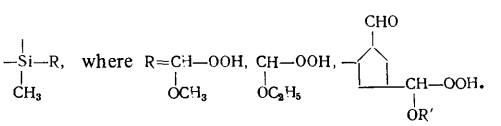
The use of mineral fillers containing catalytically active impurities is of interest. For example, heated kaolin is catalytically active in the polymerisation of ethylene, because of the presence of TiO_2.[11]

The subsequent reaction of transition metal compounds, fixed to the surface, with organometallic compounds (AlR_2Cl, LiR, AlR_3) leads to the formation of active centres, which bring about polymerisation on the surface in the gas phase or in liquid media.

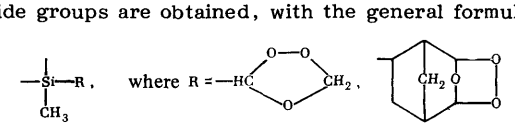
Organometallic compounds of the transition metals can be used for the polymerisation filling of polyethylene[19]. These catalysts have a high activity, and do not require additional activation in the polymerisation medium by an organoaluminium cocatalyst. The formation of the active component in these catalysts takes place by the reaction of the organometallic compound with the surface hydroxide groups of the filler. Compounds of the type $(E-O-)_x-MR_y$, where E = Si or Al, M is a transition metal, and R = C_3H_5, $CH_2C_6H_5$, BH_4, etc., are formed on the surface. Filled polyethylene can be obtained using one-component catalysts (for example $TiBz_4$) deposited on natural oxide fillers: asbestos, perlite, alumina, belite sludge, etc.[19]. A high catalytic activity is observed when organic and hydride compounds of zirconium are used.

The dependence of the quantity of catalyst fixed on the conditions under which the process is carried out has been studied[19,20,22]. In the chemical fixing of transition metal derivatives, the limiting quantity of fixed metal is restricted by the number of reactive functional groups on the surface, and for swollen perlite, for example, it amounts to 0.04–0.05% of the mass of perlite. With physical methods for the deposition and formation of the transition metal compound phase on the surface, the quantity of catalyst may be appreciably higher[20,21].

In polymerisation filling processes taking place by a radical mechanism, use is made of fillers which are peroxide group carriers (dialkyl, hydroperoxide) or fillers with groups on their surface capable of polymerisation[23-26]. Comparatively simple methods have been proposed for obtaining peroxide-containing mineral fillers with the general formula:



A mineral filler containing vinylmethylsilyl or norbornenylsilyl groups has been ozonised in alcohol or an organic acid. When the ozonisation is carried out in a hydrocarbon or a halogen derivative, peroxidised fillers with grafted ozonide peroxide groups are obtained, with the general formula



At increased temperatures, these mineral carriers initiate the process of heterogeneous radical polymerisation.

Active polymerisation centres can also be produced on the surface of inorganic fillers by various mechanical and physical treatments of the fillers. Thus the activating effect of thermal treatment and thermal vacuum treatment, and also mechanical grinding[27,28], are familiar in heterogeneous catalysis. The appearance of active centres when various oxides are heated may also be related, for example, to the formation of compounds of the Lewis acid type on the surface, and also to the production of coordinatively unsaturated metal atoms.

Irradiation using different forms of radiation can also be employed to initiate on a surface centres for the polymerisation of such monomers as vinyl chloride, vinyl acetate, acrylonitrile[29], and others, polymerising by a radical mechanism. In addition, these centres can react with organometallic compounds or metal-containing monomers, leading to the formation of ion-coordination centres[30].

2. Regular Kinetic Features of the Polymerisation Filling Process

The regular kinetic features of the polymerisation filling of polyalkenes are determined by the characteristic features of the polymerisation processes on the solid surfaces. Organometallic catalysts, particularly catalysts based on compounds of transition metals in a higher oxidation state, are unstable, and this is revealed in the appreciably non-stationary kinetics of the polymerisation of alkenes in their presence. The fixing of organometallic catalysts on a filler surface usually leads to appreciable stabilisation of their activity with time, and this makes it possible to increase the temperature range in which these catalysts can be used in polymerisation processes[20,21,31] and to increase their efficiency.

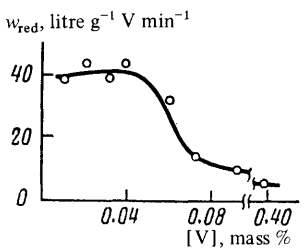


Figure 1. Dependence of the reduced rate of the gas-phase polymerisation of ethylene on the surface of perlite activated by VCl_4 and $Al(i\text{-}C_4H_9)_3$ on the quantity of vanadium fixed on the perlite surface; polymerisation temperature 87 °C, ethylene pressure 2.1 atm.[20]

Increase in the quantity of a transition metal (vanadium or titanium) fixed on a filler surface within the limits of the maximum possible number of reactive functional groups of the same type (for example up to ~6×10^{-6} mole M m^{-2} in the case of swollen perlite) is accompanied by a proportionate increase in the rate of polymerisation of ethylene; the specific activity of the catalyst remains constant (Fig.1). The similarity in the nature of the active centres produced with increase in the surface concentration of the catalyst to the limit given is also indicated by the fact that the observed rate constants of the deactivation of the active centres practically coincide (Table 1).[20,21]

With increase in the surface concentration of the fixed transition metal compound above the limit indicated, the formation of the solid catalyst phase begins, leading to a decrease in the specific catalytic activity of the system in the polymerisation of ethylene (see Fig.1). This is due on the one hand to a change in the nature of the active centres and on the other hand to a simultaneous decrease in the degree of utilisation of the transition metal in the polymerisation process.

Table 1. Kinetic characteristics of the gas-phase polymerisation of ethylene on the surface of inorganic fillers activated by VCl_4; cocatalyst $Al(i\text{-}C_4H_9)_3$.[21]

Catalytic system	[V], mass %	T, °C	w_{red}, litre min^{-1}g^{-1} V	E_{eff}, kcal mole^{-1}	k_d, min^{-1}
VCl_4/perlite	$7.1 \cdot 10^{-3}$	87	38	11.0	$1.8 \cdot 10^{-1}$
VCl_4/perlite	$3.6 \cdot 10^{-2}$	87	43	11.3	$1.5 \cdot 10^{-1}$
VCl_4/aluminosilicate	$8.5 \cdot 10^{-3}$	82	52	11.6	$4.8 \cdot 10^{-2}$
VCl_4/aluminosilicate	10^{-1}	82	16	11.8	$4.5 \cdot 10^{-2}$

Symbols: [V] is the quantity of fixed V, w_{red} the rate of polymerisation, related to the concentration of the monomer and the quantity of catalyst, E_{eff} the effective activation energy of the polymerisation of ethylene, and k_d the rate constant of the deactivation of the active centres in the initial section of the kinetic curve.

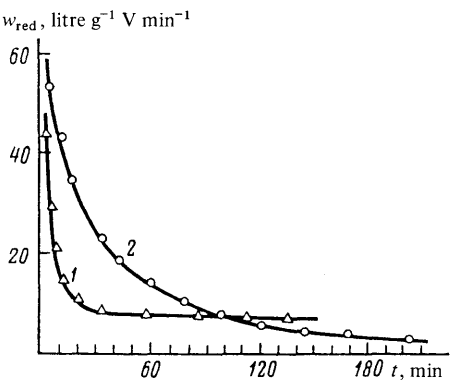


Figure 2. Kinetic curves for the gas-phase polymerisation of ethylene on the system VCl_4/perlite (5.9×10^{-6} g-atom V m^{-2} perlite) (1) and VCl_4/aluminosilicate (8.8×10^{-6} g-atom V m^{-2} aluminosilicate) (2); cocatalyst $Al(i\text{-}C_4H_9)_3$; molar ratio Al/V = 9.2, polymerisation temperature 87 °C, ethylene pressure 2.1 atm.[20]

The mineral materials used as polymer fillers generally have a complex chemical composition. For example, fillers based on SiO_2 or Al_2O_3 contain traces of the oxides of a number of other metals, and this should naturally influence the catalytic properties of the systems formed when catalysts for polymerisation processes are attached to these fillers. As shown in Fig.2, in the gas-phase polymerisation of ethylene

on VCl_4 fixed on perlite and on an aluminosilicate, at similar surface concentrations of vanadium, other conditions of the process being equal, the maximum specific rates of polymerisation have similar values. The stabilities of the catalytic systems formed on perlite and on an aluminosilicate differ considerably, however. For perlite, after an initial non-stationary region, the rate of polymerisation remains constant for a long time, and the kinetics of polymerisation can be described assuming the existence of two types of centre, one of which is deactivated by a first-order reaction, while the second is stable. When an aluminosilicate is used as a filler, the active centres in the initial range are deactivated much more slowly (see also Table 1), the stationary state in general is not reached, and the deactivation law is more complex[20,21].

The increased stability of fixed metal-complex catalysts compared with colloidally dispersed catalysts makes it possible to synthesise polymerisation-filled polyethylene at higher temperatures than usual, up to at least 100 °C.[21] The effective activation energy of the polymerisation of ethylene on the surface of fillers activated by titanium and vanadium compounds is 11.0–11.8 kcal $mole^{-1}$ for both the gaseous and the suspension methods of carrying out the process. As shown by a published analysis[21], the decrease in the rate of polymerisation with time, observed in the processes studied, is not related to diffusion restrictions in the transport of the monomer through the polymer covering to the active surface of the filler, but is due to chemical factors. The transformations leading to the deactivation of the active centres are generally reactions of first order with respect to the active centres. Bimolecular disappearance of the active centres fixed on a surface is seldom observed in the polymerisation of alkenes.

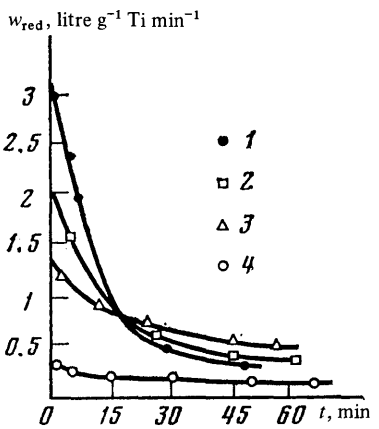


Figure 3. Kinetic curves for the polymerisation of propylene in the liquid monomer for different methods of producing the catalyst on the perlite surface (cocatalyst concentration $[(C_2H_5)_2AlCl] = 4 \times 10^{-3}$ M, polymerisation temperature 70 °C); *1*) β-$TiCl_3$ (reduction of $TiCl_4$ on perlite treated with $(C_2H_5)_2$.AlCl, at 20 °C, 1.5 mass % Ti); *2*) $TiCl_3$ (reduction of $TiCl_4$ on perlite from the complex $TiCl_4$–$(C_2H_5)_2AlCl$, at −45 °C, 2.4 mass % Ti); *3*) $TiCl_3$ (obtained from catalyst 1 by subsequently heating to 180 °C, 1.5 mass % Ti); *4*) $TiCl_3$ (reduction of $TiCl_4(C_2H_5)_2AlCl$ at 180 °C without treatment with $(C_2H_5)_2AlCl$, 1 mass % Ti).[14]

For the polymerisation of propylene on filler surfaces, fixed phase catalysts based on MCl_3 (M = Ti, V) are used[14]. Studies have shown that the level of activity achieved, and the nature of the kinetic curves, depend on the conditions of the formation of the catalyst on the surface of a given filler and on the conditions of the propylene polymerisation process. This is effectively illustrated by the data given in Fig. 3.

The activity of catalysts for the polymerisation filling of polypropylene for a number of fillers studied was found to be higher than that of finely dispersed crystalline titanium trichloride[14].

As in the polymerisation of ethylene, the nature of the filler has a significant influence on the catalytic properties shown by the resulting fixed systems in the propylene polymerisation process[14,32]. The results obtained using graphite as filler are particularly noteworthy[32]. The catalyst $TiCl_3$, deposited on graphite, has a higher activity than $TiCl_3$ deposited on other fillers such as perlite, talc, and chalk (Fig. 4). The polypropylene formed in this case has molecular mass of 1.5×10^6. The introduction of hydrogen into the reaction zone makes it possible to control the molecular mass over a wide range without change in the rate of polymerisation, and this makes it possible to obtain extruded and cast forms of filled polypropylene.

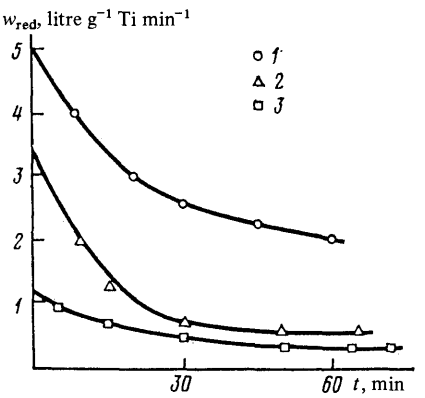


Figure 4. Influence of the nature of the filler on the kinetics of the polymerisation of propylene in the liquid monomer (fixed $TiCl_3$–$Al(C_2H_5)_3$ catalyst, where $[Al(C_2H_5)_3] = 4 \times 10^{-3}$ M, polymerisation temperature 70 °C); *1*) graphite, [Ti] = 0.14 mass %; *2*) perlite, [Ti] = 0.24 mass %; *3*) $TiCl_3.0.33AlCl_3$ (finely dispersed)[32].

The specific activity of a catalyst, based on vanadium and deposited on a filler, in the polymerisation of propylene, as in the case of a catalyst fixed on polymeric catalysts, depends on the surface concentration of the vanadium compound on the filler[33], and this dependence is extreme in character.

Metal-complex catalysts, modified by electron-donating additives and fixed on a surface, can be used to initiate the polymerisation of not only alkenes but also derivatives of vinyl monomers (for example vinyl chloride), whose polymerisation usually takes place by a radical mechanism with the aid of peroxide initiators. This type of polymerisation of vinyl chloride has been carried out[20] using fixed catalysts based on vanadium and titanium chlorides; tri-isobutylaluminium was used as cocatalyst, and diethyl ether was

used as an electron-donating additive. As in the polymerisation of alkenes, the fixing of the catalysts on the surface of the fillers leads to a sharp increase in the efficiency of the polymerisation of vinyl chloride.

The polymerisation of vinyl chloride at first takes place in non-stationary fashion; subsequently, a practically constant rate is established for a long period[20]. The initial non-stationary sections of the kinetic curves, irrespective of the surface concentration of the catalyst, the molar ratio Al/V, and the polymerisation temperature, become complete straight lines on coordinates $1/w-t$. This indicates that the disappearance of the active centres is bimolecular in the polymerisation of vinyl chloride on metal-complex catalysts fixed on a surface, in contrast to the polymerisation of alkenes, where, as shown above, the transformation of the active centres almost always takes place according to the law governing reactions of first order with respect to the active centres. The ratio of the rate constants of the bimolecular disappearance of the active centres and propagation (k_t/k_p) is $(2-3) \times 10^3$, which is characteristic, in principle, of radical polymerisation. The activation energy of polymerisation, determined from the initial reaction rate, is 5.8 kcal mole^{-1}, which is also similar in magnitude to the activation energy of growth in the polymerisation of vinyl chloride by a radical mechanism. On going to the stationary part of the curve, the activation energy of the polymerisation increases considerably (to 11 kcal mole^{-1}), that is to a value characteristic of the ion-coordination polymerisation of vinyl monomers. The polymer formed in the early stages of the polymerisation of vinyl chloride in the production of a polymer covering on the filler particles is characterised by a unimodal molecular-mass distribution (MMD). With further increase in the quantity of polymer in the composite, a second maximum appears on the polydispersion curves in the range of higher molecular masses, and the proportion of the high-molecular-weight polymer increases considerably with time.

The appearance of the bimodal molecular-mass distribution during the process, and the change to stationary polymerisation, might be related in principle to the hetero-phase character of the polymerisation of vinyl chloride in the mass. The second mode, characterising the high-molecular-weight fraction of the polymer, appears, however, even in the initial non-stationary stage of the process, and the ratio of the rate constants k_t and k_p remains constant with time. The observed characteristic features of the kinetics of the polymerisation of vinyl chloride on metal-complex catalysts fixed on filler surfaces can apparently be attributed to the presence of two types of active centre for polymerisation—radical and ion-coordination.

Thus the kinetic studies carried out have established that the catalytic and initiating power of transition metal complexes or organometallic compounds, fixed on a filler surface, is greater than that of the analogous non-fixed systems. This makes it possible to decrease the consumption of catalysts or to obtain a given degree of filling in a short time. Naturally, in the synthesis of highly filled and superhighly filled compositions, the consumption of catalyst per unit weight of the polymer increases. The general regular kinetic features of polymerisation filling are similar to those of the polymerisation of the analogous monomers. The specific features of reactions on a surface, however, raise the question of the reactivity of the associates of the active centres and the transition metal clusters in these systems.

3. Technological Aspects of Polymerisation Filling

Technological studies of the production of polymerisation-filled polyethylene have now been carried out[6,34-36]. Various general questions can be considered. The composition of the material (the degree of filling ϕ) formed in the polymerisation is given by the simple expression[12]

$$\varphi = \frac{P \cdot 100}{\int_0^t w_t dt + P}$$

where P is the quantity of filler introduced into the reaction vessel, and

$$\int_0^t w_t dt —$$

the quantity of polymer formed in the reactor in time t. Thus the degree of filling is determined by the quantity of added filler and the rate and time of polymerisation. The productivity of a continuous reaction vessel g with respect to the overall product will be given by

$$g = \frac{\alpha(P')\bar{y} + P'}{V}$$

where V is the volume of the reactor, P' the quantity of filler added to the reactor in unit time, $\alpha(P')$ the quantity of catalyst on the filler surface, and $\bar{y}$ the specific yield of polymer per unit of catalyst in unit time.

The addition of the filler to the reaction vessel increases the yield of the overall product, and a given concentration of the suspension (Π_p) is reached for a shorter average residence time τ_{av} of the particles in the reaction vessel.

$$\tau_{av} = \frac{\Pi_p}{g} = \frac{\Pi_p \cdot V}{\alpha(P')\bar{y} + P'} .$$

A significant feature is that the productivity of the reactor with respect to the overall product can increase in polymerisation filling without an increase in the heat liberated in the system. If the productivity of the reactor is limited by the limiting concentration of the suspension, it can be seen from the given relationships that this limit is reached in a shorter time when the filler is added to the reactor.

The technological process of polymerisation filling can be carried out under conditions of both gas-phase and suspension polymerisation, and also by polymerisation in the mass of the monomer. The stage of activation of the filler—the fixing of the catalyst or the polymerisation initiator on the filler particles—can also be carried out from the vapour phase of the catalyst in a vacuum or in a stream of an inert gas carrier, or from solution in an organic solvent. Thus the addition of the filler to the polymer at the stage of its synthesis can be organised technologically in such a way that it is entirely gas-phase, entirely suspension, or a mixed version. Necessary requirements for obtaining a product of good quality in all conditions are uniform deposition of the catalyst on all the particles of the filler, and the suppression of the processes of agglomeration of the filler at the stage of catalyst fixing and polymerisation. The latter is important not only from the viewpoint of obtaining the necessary physicomechanical properties of the final material but also to ensure stability of operation of the polymerisation reactor under continuous conditions. The apparatus design for the processes of polymerisation filling is practically the same for the polymer synthesis process. Thus the synthesis of pilot-plant batches of polyethylene–kaolin compositions has been carried out using a technological line for the preparation of high-density polyethylene in the Gur'ev chemical plant[34,36]. A basic diagram of the technological line is shown in Fig. 5. The polymerisation was carried out at 70–80 °C to give 80–70 mass % of polyethylene relative to the added kaolin. The principal parameters of the technological process are given in Table 2.

Analysis of the results of the industrial synthesis of filled polymers has shown that the use of continuous mixing flow reactors has a number of important technological and economic advantages (easy transportation of the suspension, effective removal of the heat of the reaction, the possibility of using existing technological units, etc.). In this case, however, at the outlet from the reaction vessel there will be a certain proportion of particles on which a polymer covering has not been able to form, because of the short residence time in the reactor. The experimental data indicate that the presence of particles not covered by polymer has a significant influence on the quality of the composition, leading to a deterioration in its properties and making processing difficult. This unsatisfactory feature can be eliminated by introducing a grader into the technological line[37]. A mathematical analysis of the possibility of using continuous mixing reactors with pulse introduction of the original reagents and removal of the polymerisation product has been carried out[38]. The analysis showed that this reactor makes it possible to guarantee a given value of the minimum covering of the filler particles by the polymer.

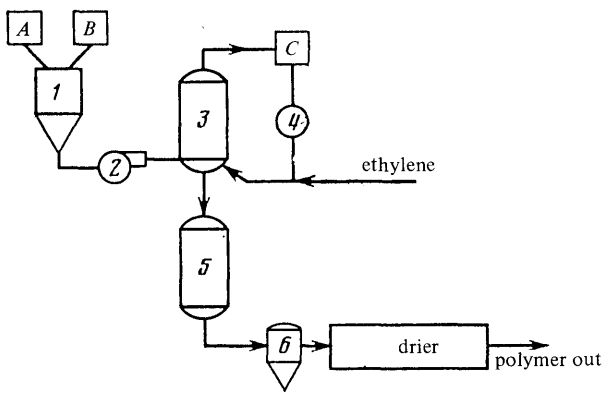


Figure 5. Basic technological scheme for producing a polyethylene–kaolin composition: *1*) vessel for depositing the catalyst on the kaolin surface; *2*) centrifugal pump; *3*) reactor; *4*) gas blower; *5*) product collector; *6*) centrifuge; *A*,*B*) equipment for metering the components of the catalyst; *C*) cooler[34].

Table 2. Parameters of the technological process[34].

T, °C	τ, h	$P_{C_2H_4}$, kg cm^{-2}	$Q_{C_2H_4}$, kg	c_{H_2}, vol.%
72—80	4.0	2.4—3.2	900	—
70—82	2.0	3.0	550	—
76—78	3.5	2.1—4.0	900	1.2—1.7
73—79	3.0	2.2—3.2	750	6.8

Symbols: τ is the average polymerisation time, $P_{C_2H_4}$ the ethylene pressure in the reactor, $Q_{C_2H_4}$ the quantity of ethylene absorbed, and c_{H_2} the hydrogen concentration in the gas mixture.

The principles of the technological process for the synthesis of porous plastics in the gas phase have been examined[39]. Studies of the kinetic parameters of the process and the removal of heat showed that the gas-phase synthesis of a polyethylene–perlite composition can be carried out under stable conditions.

III. THE STRUCTURE AND PROPERTIES OF POLYMERISATION-FILLED THERMOPLASTICS

1. Some Characteristic Features of the Structure of Polymerisation-Filled Polyalkenes

One of the principal factors determining the properties of filled polymer systems is the nature of the adhesion interaction between the surface of the filler and the polymer. Thus in the production of composite materials the problem is to achieve a strong bond between the polymer matrix and the filler. It is for this purpose, that is to improve the adhesion of the polymer to the filler, that modifying treatment of the fillers and matrix polymers is carried out. There is an extensive literature on the study of the structure and properties of the boundary layers at the surface of separation between the polymer and filler phases, since in the final analysis these determine the principal properties of composite materials[40]. An important contribution to the development of ideas in this field has been made by the work of Lipatov and co-workers[41].

As noted above, in the polymerisation introduction of a filler into a polymer, the centres initiating polymerisation are situated on the surface of the filler particles, and the polymer crystallises directly on the surface or in the pores of the carrier. In a composite material, a chemical bond may be formed between the macromolecules and the surface of the filler[42], or an effective adsorption interaction may be established between them, and this determines the nature of the packing of the macromolecules in the surface layer and the characteristic features of the structure of the boundary layer, and has a significant influence on the physicomechanical properties of the final material.

As a result of polymerisation on the surface, the particles of the filler are covered by a layer of polymer of controlled thickness. Studies carried out by scanning electron microscopy and X-ray spectroscopy[43,44] have shown that the polymer coverings formed under the optimum technological conditions for carrying out the process are uniformly distributed over the surface of the particles, and are compact and continuous. This makes it possible to obtain a fairly homogeneous distribution of the particles of the filler in the polymer matrix in the final composite material.

To increase the area of contact between the filler and the polymer matrix, attempts are usually made to decrease the size of the filler particles, down to fractions of a micron. The processes of agglomeration of the finely dispersed particles of the filler, which always take place, are different for the polymerisation method of introducing the filler and for the mechanical mixing of the prepared components. Thus the optimum dimensions of the particles of the original filler for achieving the required properties of a composite material are determined by the conditions of the process and the nature of the catalytic systems or their components. Thus organometallic compounds and transition metal derivatives may bring about agglomeration or deagglomeration of the particles of the filler during the synthesis of the composite[11].

In polymerisation on the surface of filler particles, the polymer is also formed within the pores, micro-cracks, and defects, so that there is a considerable increase in the area of contact between the filler and the polymer matrix and an increase in the strength of their mechanical interaction.

This is confirmed by scanning electron microscopy, which has been used to study the surface produced by the breakdown of composite specimens[45]. According to the data obtained[45-48], the polymer layer produced during polymerisation on the surface of a filler has an increased density.

It has been shown[45,46] that for identical degrees of filling, composites based on polymerisation-filled polyethylene have a lower coefficient of linear expansion than composites based on mechanical mixtures. This is apparently due to the more compact packing of the macromolecules in the intermediate layer at the polymer–filler boundary in the polymerisation-filled materials. The existence of a compact layer of polyethylene round the particles of filler in norplastics has been demonstrated by other workers[47,48].

X-Ray structural analysis[49] has shown that as a result of the cooperative growth of macromolecules on the surface of fillers, in a number of cases, orientation phenomena are observed in the resulting polymer layer, and the direction of orientation of the molecules corresponds to the normal to the filler surface. These orientation phenomena may be fairly clearly defined. Thus for polypropylene obtained on the surface of organic and inorganic fillers, the extent of the orientation corresponds to that of a polypropylene fibre elongated by a factor of 4–5. The observed orientation phenomena influence the density of packing of the macromolecules in the surface layer and the properties of the boundary layer as a whole.

Calorimetry and X-ray structural analysis indicate that materials based on polyethylene filled during synthesis have a degree of crystallinity which is on the average 10% greater than that of mechanical mixtures with similar compositions and identical characteristics of the polymer matrix[45,46].

These characteristic features of the structure of composite materials based on norplastics are apparently helping to ensure the improvement of the properties of composites relative to mechanical mixtures.

2. Compositions Based on Polyethylene

The use of catalytic systems based on the surface of fillers leads to the formation of high- or superhigh-molecular-weight polymers in the polymerisation process. Polymerisation filling is therefore used to synthesise composites based on a high-molecular-weight polyethylene matrix. Methods have been developed for synthesising polyethylene–kaolin compositions[34,36]. The kaolin was activated using catalysts based on titanium or vanadium in the presence of organoaluminium compounds. Polyethylene–kaolin compositions with a polymer molecular mass of $(1.3-5) \times 10^6$ and containing 30–50 mass % kaolin have good physicomechanical properties. These compositions have no fluidity, and articles are produced by sintering, hot pressing, or extrusion. Superhigh-molecular-weight polyethylene has recently been attracting increasing interest as a material with unique properties, and also as a substitute for Fluoroplast. Polymerisation-filled superhigh-molecular-weight polyethylene has a higher wear-resistance and a higher modulus of elasticity than these polymers. Since it is unlikely that alternative methods for obtaining filled compositions based on superhigh-molecular-weight polyethylene by methods involving mixing will be found, the development of the technology for the synthesis of these compositions by polymerisation filling is an important direction of development in this field.

The molecular mass of the polymer matrix in compositions based on polyethylene (PE) is controlled by the usual methods, by adding hydrogen or other chain transfer agents to the system. Thus in the polymerisation filling of polyethylene by kaolin activated by complex vanadium catalysts, the introduction of 15 vol.% hydrogen leads to a decrease in the molecular mass (MM) of the polyethylene matrix from $(2-3) \times 10^6$ to $(1.2-1.6) \times 10^4$.[50] The fluidity index of a molten polyethylene–kaolin composition with a degree of filling of 30 mass % increases from zero (in the absence of H_2) to 10 when $Al(i\text{-}C_4H_9)_3$ is used as cocatalyst. Thus polymerisation filling using an additive which controls the MM of polyethylene gives composites which can be worked by extrusion.

With decrease in the molecular mass of PE, its degree of crystallinity increases, leading to an increase in the rigidity of the polymer and the composition as a whole, to an increase in the modulus of elasticity and the yield point on elongation, and to a decrease in the relative elongation at the yield point[51].

The extent of the decrease in various physicomechanical characteristics with decrease in the molecular mass of the polymer matrix of a composition depends on the nature of the surface of the filler and on its dispersion composition. For various fillers, compositions have been developed which can be worked by casting and extrusion, and articles with good physicomechanical properties have been obtained ($\sigma_t = 25$ MPa), $\varepsilon = 50-400\%$).

Polymerisation has been used[50] to obtain composites with different concentrations of kaolin over a wide range of MM of the polymer matrix (from 3000000 to 125000). When superhigh-molecular-weight polyethylene with MM $> 10^6$ was used as the matrix, the introduction of a filler into the composition in concentrations up to 50 mass % did not lead to any loss of plasticity by the material. The composite deformation curves show high values of the deformational-strength characteristics. For polyethylene–kaolin compositions containing 0, 30, and 50 mass % filler, the limiting tensile strength (σ_t) is 46, 44, and 23 MPa, ε_t decreases from 260 to 240 and 150%, and the modulus E_t increases from 900 to 1900 and 1900 and 2900 MPa respectively. The filling of low-molecular-weight PE leads to the loss of plasticity by the composite at degrees of filling lower than those for superhigh-molecular-weight PE.

Table 3. Properties of heat-insulating materials obtained from norplastics containing swollen perlite and polyethylene[12].

Material	c_p, mass %	σ_c, MPa	σ_b, MPa	m, kg m^{-3}	λ, kcal m^{-1} s^{-1} K^{-1}
Norplastic perlite–PE	10—12	5—9	3	120—150	0.03—0.04
Perlite–phenol-formaldehyde resin*	70	3—5	3	120—150	0.03—0.05

Symbols: c_p is the polymer concentration, σ_c the compressive strength, σ_b the bending strength, m the volume mass, and λ the thermal conductivity coefficient.

*The properties of a heat-insulating material based on perlite and produced in industry at present are given for comparison.

Polymerisation filling can be used not only to obtain finished composites with a given concentration of filler but also to modify the surface of a filler. This is achieved by producing thin polymer coverings during polymerisation on the particles of the filler, and the process can be regarded as a form of finishing of the surface, using macromolecular chains.

These polymerisation-modified fillers or norplastic "concentrates" can be used as independent superhigh-filled composition materials containing up to 80–95 mass % of a mineral component, for example for the production of heat-insulating materials (Table 3).[12]

In addition, norplastic "concentrates" can be introduced as modified fillers by mixing with a prepared industrial polymer of similar character; in particular, this represents one possible way of obtaining cast and extruded composite products[43,45,52–56]. The use of norplastic "concentrates" is promising, since it makes it possible to obtain materials having better physicomechanical properties than mechanical mixtures with analogous composition. For polyethylene composites, these differences are revealed particularly clearly in the values of the specific impact ductility: this property is 1.5–2 times greater for composites based on polymerisation-modified fillers than for mechanical mixtures[43,56].

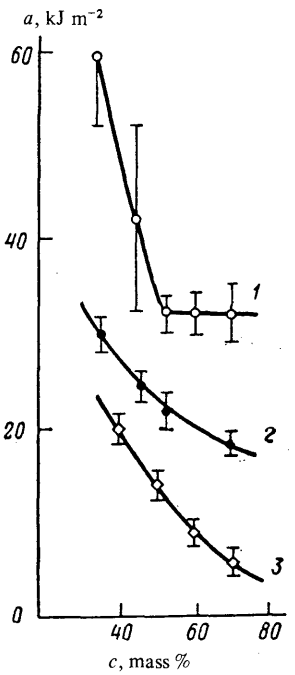


Figure 6. Dependence of the specific impact ductility (a) on the tuff concentration (c) for compositions based on HDPE and tuff (average particle size of the tuff 8.6 μm): *1*) HDPE–norplastic concentrate; *2*) HDPE–tuff–SHMPE mechanical mixture; *3*) HDPE–tuff mechanical mixture[56].

Fig.6 gives the dependence of the specific impact ductility for composites based on high-density polyethylene (HDPE) and a norplastic concentrate containing 87.5 mass % tuff and 12.5 mass % superhigh-molecular-weight polyethylene (SHMPE) on the concentration of tuff in the composite[56]. For comparison, data are given for mechanical mixtures of the matrix polymer and tuff and for mechanical mixtures with the addition of SHMPE in the same quantities as were added in the form of the norplastic "concentrate" to the composites based on norplastics. Results showing differences of a similar scale have also been obtained for composites based on other fillers[43].

The dependence of the tensile strength and the static bending strength on the degree of filling in the composites studied is extremal in character[45,56], and the optimum value lies in the range corresponding to 30–50 mass % filler, depending on the nature of the filler. Fig.7 gives comparative data on the dependence of the maximum tensile strength on the degree of filling for composites with the same composition as in Fig.6. Fig.7 shows that the strength of the composites based on norplastics is much greater than that of the materials obtained by mixing. The use of polymerisation filling also leads to an increase in the rigidity of the resulting material, compared with mechanical mixtures[43].

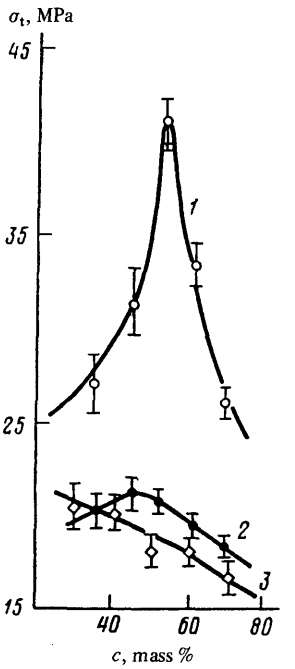


Figure 7. Dependence of the maximum tensile strength (σ_t) on the concentration of filler for compositions based on HDPE and tuff: *1,2,3*) see caption to Fig.6; rate of deformation $\bar{\nu}_\varepsilon = 1.04 \times 10^{-1}$ min^{-1}, σ_t for HDPE = 21.3 ± 1.4 MPa.[56]

Increase to a definite limit in the thickness of the polymer covering which is formed on the particles of the filler and which consists of superhigh-molecular-weight PE leads to an improvement in the strength properties and rigidity of materials based on norplastic "concentrates" for a given concentration of the mineral filler (Fig.8). Fig.8 shows that for the compositions studied, this limit corresponds to ~30 mass % PE in the "concentrate" or ~9 mass % in the composite, for a perlite concentration of 30%. The addition of SHMPE in the same quantities to mechanical mixtures of the matrix polymer and the filler also leads to an increase in the strength of the material, but the properties of the composites obtained in this way are considerably inferior to those of the composites based on norplastics.

3. Compositions Based on Polypropylene

The use of polymerisation filling to introduce fillers into polypropylene (PP) has given new materials with an unusual set of physical and mechanical properties. The structure of polypropylene formed on the surface of a filler is determined to a large extent by the nature of the filler and by the conditions under which the catalyst is prepared and the process is carried out[14,32]. An interesting feature is that the use of graphite as a filler gives the highest degree of isotactic character in PP (up to 94–96%).

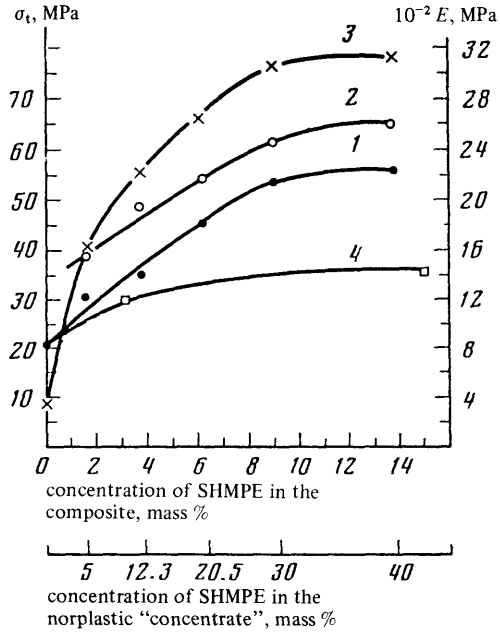


Figure 8. Influence of the concentration of SHMPE in a norplastic concentrate based on SHMPE and swollen perlite on the tensile strength (*1*), the static bending strength (*2*), and the tensile modulus of elasticity (*3*) for compositions based on HDPE and a norplastic "concentrate"; concentration of swollen perlite in all compositions 30 mass %; $\bar{v}_\varepsilon$ = 0.87 min^{-1}; *4*) change in tensile strength for HDPE–perlite–SHMPE mechnical mixtures[43].

The study of the electrical conductivity of polypropylene–graphite compositions has shown that polymerisation filling provides a new and promising method for obtaining heat-conducting and electrically conducting compositions[57–59]. Comparison of the specific resistance of composites obtained by polymerisation filled and mechanical mixtures of polypropylene and graphite shows that for the same degrees of filling, the mechanical mixture has a much lower conductivity (Fig. 9). The conductivity differences are particularly marked (by a factor of 10^7) at low concentrations of the filler $c \leq 8$ vol.%. To obtain by mechanical mixing a composition with the same conductivity, it is necessary to add 30 vol.% graphite, and this leads to a decrease in the tensile strength and compressive strength by factors of 1.5. Composites based on PP and graphite have a high uniformity, as indicated by the linear dependence of σ on the length and thickness of the specimen. In the temperature range 4.2–300 K, the values of σ for polymerisation-filled compositions are independent of temperature (for composites containing 8–61 vol.% graphite)[57] (Fig. 10). For these compositions, a conductivity constant with time was observed for graphite concentrations $c \geq 8$ vol.%, whereas for the compositions obtained by mixing this was observed only at $c \geq 20$ vol.%.

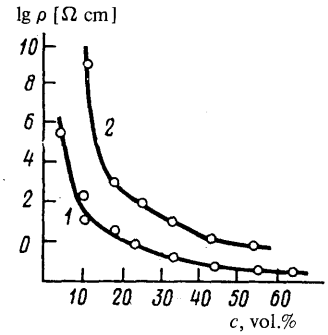


Figure 9. Dependence of the bulk specific electrical resistance (ρ) of compositions based on polypropylene and graphite on the graphite concentration: *1*) polymerisation filling, *2*) mechanical mixture of polypropylene and graphite[57].

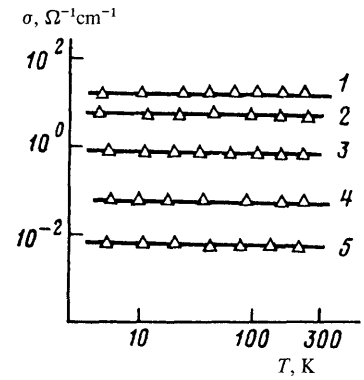


Figure 10. Temperature dependence of the conductivity of polymerisation-filled composites based on polypropylene and graphite for different volume concentrations of graphite: *1*) 0.61, *2*) 0.4, *3*) 0.35, *4*) 0.1, *5*) 0.08.[57]

The materials obtained show another remarkable property, namely their retention of plasticity and mechanical strength after repeated cooling and heating cycles from 300 K to 4.2 K. A scanning electron microscope study of the surface of pressed specimens of norplastics based on polypropylene and graphite showed that the norplastic (for identical original graphite particle sizes) contains graphite particles of smaller dimensions, uniformly distributed in the polymer matrix, compared with the mechanical mixtures, and the distance between the particles of the filler is much smaller in the norplastic.

These composites based on polypropylene and graphite are promising for applications in many branches of technology, as elements in electric-heating assemblies, coverings for screens in radio-electronic apparatus, strain gauges at low temperatures, highly stable resistors, antistatic coverings, and electric filters[60].

The strength properties of norplastics based on PP with a degree of filling of 30–40% are similar to those of non-filled isotactic polypropylene[32]. The presence of an atactic polypropylene fraction in the composite (up to 10–15%) has a plasticising influence and improves the deformational properties of the compositions.

Isotactic polypropylene has a low resistance to cold. To improve this property, rubber is added to polypropylene, or copolymerisation with ethylene is carried out. The use of polymerisation to introduce fillers into PP has made it possible to produce, on the basis of filled polypropylene, materials having a high resistance to cold (brittleness temperature between −35 °C and −45 °C) and a high impact strength (up to 18 kJ m^{-2}) at a concentration of filler (tuff, kaolin) of 40–50 mass %.[5]

4. The Thermo-Oxidative Degradation and Stabilisation of Norplastics

The kinetics of the thermo-oxidative degradation of polymerisation-filled polyethylene and mixed compositions at temperatures of 160–200 °C and oxygen pressures of 24×10^3–27×10^3 Pa have been studied[61]. Inhibitors were introduced into the powdered composite from a solution in ethanol or toluene, after which the powder was dried in a vacuum. The principal rapid method used to estimate the effect of the inhibitors was a volumetric method involving the measurement of the absorption of oxygen by the specimen on heating under static conditions. As with polyethylene, irrespective of the nature of the filler, the introduction of the inhibitor leads to a significant increase (by a factor of 3–7) in the induction period, and a decrease (by a factor of 1.5–3) in the rate of oxidation of the composite. The greatest increase in the induction period and decrease in the rate of oxidation were observed at concentrations of Irganox 1010 corresponding to 0.1–0.15% of the total mass of PE in the composite. The best results for composites containing any filler, however, were obtained using a synergic mixture of Irganox 1010 and Irganox PS 802. When fillers containing metallic components are used, and with specimens used at high temperatures in contact with a metal surface, it is necessary to add metal deactivators to the inhibitor mixture.

5. Compositions Based on Other Polymers

Among other thermoplastics, the polymerisation filling of polyvinyl chloride (PVC) is of greatest interest. The grafting of PVC macromolecules to the surface of fillers during radical polymerisation makes it possible to obtain "concentrates" which when mixed with PVC give a composite with much better properties than compositions based on non-modified fillers[42]. Both the technological properties and the strength characteristics are improved. In addition, the chemical grafting of PVC to the surface of fillers may be an important factor in obtaining composites with long-term strength.

Problems related to the radical mechanism of polymerisation initiated on the surface of a solid phase and to the characteristic features of radical copolymerisation taking place on the surface of solid particles have been examined[25,26]. The studies established that it is possible to vary widely the characteristics of the graft polymers: the molecular mass, the density of grafting, and the ratio of the grafted and non-grafted polymers in relation to the parameters and methods of polymerisation. When there are no reactions of chain transfer, it is possible to obtain polymerisation-filled compositions in which practically all the macromolecules are grafted to the surface of the dispersed filler. As a consequence of the formation of the chemical bond between the polymer and the filler, these polymerisation-filled polymers have higher wear-resistance, creep-resistance, and strength properties, compared with polymers filled by traditional methods. The industrial production of polymers filled by polymerisation under radical-polymerisation conditions can be carried out in existing equipment used for polymer synthesis[7].

The development of methods for the polymerisation filling of reactive carbo-chain polymers is also important. These include polymers obtained by the homo-polymerisation of propadiene and acetylene derivatives, and their copolymerisation with alkenes. Propadiene polymerises in the presence of metal-complex catalysts[62] based on vanadium, titanium, nickel, and rhodium. The use of transition metal salts as catalysts makes it possible to use polar solvents such as water and alcohol for the polymerisation of propadiene. In the presence of a catalyst based on rhodium acetylacetonate carbonyl in a medium of ethanol, the polymerisation is non-stationary (Fig. 11). After an induction period, the reaction rate increases and reaches a maximum value, after which almost complete deactivation of the catalyst takes place. The deposition of this catalyst on the surface of swollen perlite leads to an increase in the activity and stability of the catalyst. The rate of the polymerisation of propadiene is higher when the deposited catalyst is used, and remains unchanged for a long time. The increase in the stability of the catalyst deposited on the filler surface is due to a decrease in the rate of the reactions involving the disappearance of the active centres taking place in the solutions.

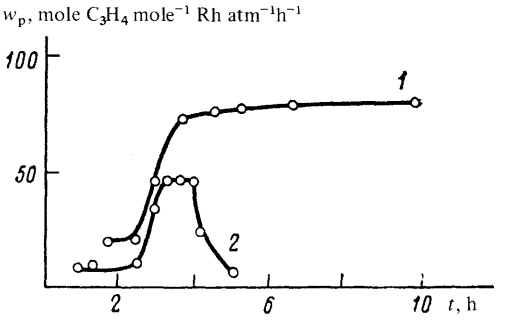


Figure 11. Change with time in the rate of polymerisation of propadiene on $Rh(AcAc)(CO)_2$ fixed on perlite (*1*) and $Rh(acac)(CO)_2$ in C_2H_5OH (*2*).[62]

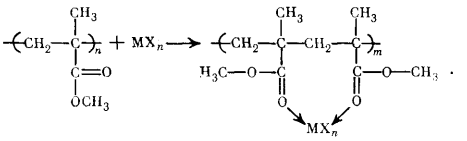
Similar kinetics are observed in the polymerisation of phenylacetylene in the presence of $MoCl_5$ fixed on kaolin, talc, and aluminium and magnesium oxides[63]. The fixing of $MoCl_5$ on mineral carriers leads to an increase in the lifetime of the catalyst and to an increase in the degree of transformation of phenylacetylene. The nature of the mineral carrier influences the stereospecificity of the catalyst and the molecular mass of the polymer.

The products obtained by the polymerisation filling of propadiene and acetylene derivatives can subsequently be cross-linked by various methods.

6. Polymer–Polymer Compositions

The immobilisation of metal-complex catalysts on carbochain polymers makes it possible, by using a polymer carrier as filler, to synthesise polymer–polymer compositions (PPC) at the stage of the polymerisation or copolymerisation of alkenes, and this represents a further development of the method of polymerisation filling[64]. The polymeric fillers used include polyvinyl chloride, polyvinyl acetate, polymethyl methacrylate (PMMA), polyformaldehyde, cellulose, and other polymers.

The fixing of MX_n to the surface of such polymers as polymethyl methacrylate or polyvinyl acetate can be represented as follows:



The process is accompanied by a displacement of the carbonyl group stretching frequency from 1740 cm^{-1} to 1650 cm^{-1}.[64] The fixing of MX_n to polyvinyl acetate takes place similarly. The mechanism of the interaction of MX_n with cellulose is more complex, and leads to cross-linking of the cellulose molecules.

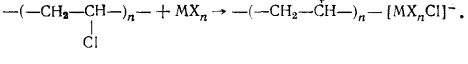
Table 4. Physicomechanical properties of PE–PMMA polymer–polymer compositions and the original components (upper values—data for the synthetic PPC, lower values—data for the mechanical PPC).[64]

Parameter	PMMA*/PE	[PMMA], vol.%			
		4	7	14	29
ρ, kg m^{-3}	1.190 / 0.948	0.959 / 0.962	0.968 / 0.965	0.983 / 0.965	1.019 / 1.017
σ_y, kg mm^{-2}	5.0 / 2.50	3.20 / 2.70	3.15 / 1.20	3.50 / 1.15	—
ε, %	2—3 / 370	250 / 80	210 / 70	180 / 45	—
T_g, K	383 / 203	217 / —	224 / 224	224 / 224	225 / 224

Symbols: ρ is the density, σ_y is the yield point, ε the elongation at rupture, and T_g the temperature of glass formation.

*This column gives the corresponding values of the parameters of the original components of the polymer composition.

Of particular interest is the fixing of MX_n on the surface of polymeric carriers containing a mobile halogen atom: copolymers of PVC, polyvinylidene chloride (PVDC), polytetrafluoroethylene (PTFE), copolymers of styrene with α-bromostyrene, etc. In these cases, the fixing involves the formation of ionic products:



The synthesis of PPC based on polymers activated by these methods is carried out by ordinary polymerisation methods. The physicomechanical properties of synthetic and mechanical PE–PMMA and PE–PVC compositions are compared in Tables 4 and 5. Increase in the volume fraction of PMMA in the composition with PE is accompanied by a decrease in the relative elongation and an increase in the yield point of the compositions. The synthetic PPC have much better physicomechanical properties than the corresponding mechanical compositions. The difference is particularly marked at high values of ϕ.

Table 5. Various properties of PE–PVC polymer–polymer compositions and the original components (upper values—data for the synthetic PPC, lower values—data for the mechanical PPC).[64]

Parameter	PE*/PVC	PE/PVC, mass %				
		83/17	77/23	70/30	56/44	45/55
σ_t, MPa	30.1 / 42.0	22.0 / 24.2	16.2 / 14.4	21.3 / 5.0	20.3 / —**	16.8 / —
ε, %	40.0 / 23.0	80.0 / 8.5	30.0 / 5.0	20.0 / —	62.5 / —	13.0 / —
r, kN m^{-1}	52 / 30	19 / 3.0	30 / 3.5	17 / 3.5	25 / —	31 / —

Symbols: σ_t is the limiting tensile strength, ε the relative elongation, and r the tear-resistance.

*Corresponding values of the parameters of the original components of the composition.
**Brittle specimens; the properties could not be determined.

In PPC obtained by mechanical mixing, the intermediate layer is formed by the mutual diffusion of the polymers. In the synthetic PPC, the production of the intermediate layers involves not only physical but also chemical interactions.

According to a model[64] in which there are no interactions at the boundary of separation between the phases, the following relationship should be observed between the yield point of polyethylene (σ_0), σ_{PPC}, and the volume fraction of polyethylene ϕ:

$$\sigma_{PPC}/\sigma_0 = 1 - \varphi^{2/3}.$$

Fig. 12 shows that in mechanical PPC based on polyvinyl chloride and polyethylene, there is satisfactory agreement between the experimental data and the theoretical relationship. This relationship is not observed for the synthetic compositions, indicating the existence of specific interactions between PE and PVC. One factor responsible for chemical interaction between the two polymers may be the grafting of polymer chains during the synthesis of the PPC. The presence of grafted chains in synthetic PE–PMMA and PE–PVC compositions has been established by physicochemical and extraction methods[64]. Mechanical PPC may undergo complete breakdown into the original components. The concentration of grafted polymer chains in the synthetic PPC depends on the type and volume fraction of the polymers. For example, with increase in the volume fraction of the vinyl polymer, the degree of grafting increases in the PE–PMMA system, and decreases in the PVC–PE system[64]. The mutual grafting of chains during the synthesis of polymer–polymer compositions may take place at the initiation stage, at the growth stage by the copolymerisation of unsaturated units,

and by reactions involving chain transfer at the surface of the basic polymer.

The formation of the intermediate layer may be influenced by the physical interweaving of the linear macromolecules with the open network of the surface. An X-ray diffraction study of synthetic polymer–polymer compositions based on PMMA–PE and PVC–PE has revealed changes in the values of the interplanar distances in the structures of synthetic compositions[65]. This indicates a reaction between the PE and the other polymers in synthetic compositions at the molecular level.

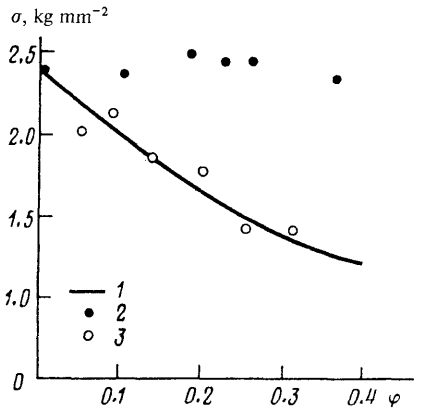


Figure 12. Dependence of the yield point of PPC based on PE and PVC on the volume fraction of the latter: *1*) theoretical curve; *2*) mehcnical PPC; *3*) synthetic PPC.[64]

Thus the synthetic method for preparing PPC makes it possible, at the stage of the synthesis of the polyalkene component, to increase the compatibility of the components as a result of the characteristic treatment of the surface, and to some extent to restrict or suppress the negative effects characteristic of mechanical methods for prepared PPC. This method can be used to obtain composition materials based on polymers which are not readily compatible under ordinary conditions.

IV. CONCLUSION

Examination of studies carried out up to the present, and the results obtained, shows that the method of polymerisation filling extends considerably the possibilities for creating composite materials for different purposes, including constructional purposes, on the basis of the filled polymers.

This is determined by many factors, including the wide synthetic possibilities of the method, the possibility of controlling over a wide range the composition of the products with the achievement of exceptional uniformity of the distribution of the particles of the fillers in the polymer matrix, the possibility of fine control of the structure of the compositions, and the improvement of the adhesion interaction at the surface of separation between the filler and the polymer phases, either as a result of chemical bonding between the macromolecules and the surface of the filler or as a result of the development of an effective adsorption interaction between them. Essentially, Enikolopov and his school have developed a new branch of macromolecular chemistry, involving the study of the specific features of the kinetics of polymerisation on solid surfaces, the characteristic features of the structure of the polymeric layer formed on the surface of fillers during polymerisation, the characteristic features of the physicomechanical properties of composites, and the working of these materials.

A number of promising ways of using the polymerisation filling of thermoplastics have now been established: the synthesis of highly-filled compositions based on superhigh-molecular-weight polyethylene, the synthesis of "concentrates" containing ~10% of the polymer matrix, and the synthesis of highly conducting and cold-resistant compositions based on polypropylene. New phenomena requiring further intensive study have been observed. The production of a composite material with given properties naturally requires the solution of complex problems both in the synthesis of the polymers and in the physics and mechanics of the compositions. Specific fields of application of polymerisation-filled materials and realistic possibilities for the development of industrial processes for their production have already been pointed out, however.

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