Polycondensation in the Presence of a Filler as a New Way To Create Polymer Multicomponent Systems with Prespecified Properties

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ABSTRACT: The matrix effect in polycondensation was first discovered and thoroughly studied using the example of acceptor-catalytic polyesterification. This effect is due to the influence of a filler on the reaction kinetics and the structure and properties of macromolecules produced. The filler (graphite or molybdenum disulfide), introduced into the reaction system during the growth of macromolecules, has been found to exhibit the properties of a heterogeneous matrix. Namely, it determines the kinetic parameters of the reaction, the molecular weight of the polymers, and the microstructure of the copolymers, as well as properties of composites produced thereby. A mechanism was proposed to explain the matrix effect observed.

Introduction

One of the promising ways for the creation of multicomponent polymer systems with prespecified properties is the synthesis of polymers in the presence of fillers. Development of a new approach to create new composites in the process of the synthesis is of great importance from the viewpoint of both economy and ecology, because introduction of fillers allows us to create technologies for production of composites which consume less power and raw materials and are less polluting. However, this problem can hardly be solved without thorough investigations into the fundamental regularities of polycondensation in the presence of fillers.

Though processes to manufacture filled systems are well studied,[1] there are practically no data about the effect of fillers on polycondensation kinetics and on the structure and properties of polymers produced.[2,3]

In this work, the effects of an antifriction filler (graphite and molybdenum disulfide) on the activity of monomers in low-temperature polycondensation, the molecular weights of polymers produced, the microstructure of copolymers, and the properties of composites thereof have been studied.

Experimental Section

Materials. The substances and solvents were purified using standard methods.[4] The content of water in the solvents, determined by coulometric titration in Fisher's reagent, did not exceed 0.005%. For fillers, graphite S-1, with a specific surface $S_{sp} = 14.0$ m^2/g, natural graphite "Taiginskii" ($S_{sp} = 9.5$ m^2/g), modified graphite TRG ($S_{sp} = 10.5$ and 22.0 m^2/g), and molybdenum disulfide ($S_{sp} = 7.2$ m^2/g) were used. After washing with chloroform and drying in a vacuum of 20 Pa for 4 h at 673 K, the content of the adsorbed water in the filler did not exceed 0.005%.

Polyterephthalate of bis[4-oxy-3-(chlorophenyl)]-2,2′-propane (dichlorodiane) was synthesized in the presence of these fillers by the acceptor-catalytic polyesterification method using the following technique. A filler amounting to 20–60% of the calculated weight of the filled polymer composite was loaded into a reaction vessel. To this were added the benzene solution of bisphenol (0.2 mol/dm^3) and terephthalic acid chloride (0.2 mol/dm^3). After dispersion of the reaction solution in an argon atmosphere, triethylamine (0.4 mol/dm^3) was added. The reaction mixture was then stirred intensively for 1.5 h at 303 K. After termination of the reaction, the composite obtained was precipitated into methanol, washed to remove excess triethylamine hydrochloride, and dried in a vacuum of 133 Pa until reaching constant weight.

Copolymers were synthesized under similar conditions by adding over a 15-min period a solution of the intermonomer (terephthalic acid dichloride) to the solution of comonomers (dichlorodiane and hexamethylene glycol) and tertiary amine.

The separation of the filler and polymer (copolymer) was carried out by filtration and centrifugation of the dilute solutions of composites in chloroform. It has been established that after additional washing of the filler with chloroform the polymers and monomers were eliminated completely. This has been examined by IR spectroscopy of the used chloroform after washing and by measurement of the weight of the filler before and after the reaction.

Measurements. Kinetic studies of the model reaction were carried out with an equimolar content of the reagents and tertiary amine according to the technique described.[5] Reaction in the samples were terminated by adding diethylamine in the ratio [OH]:[COCl]:[Et_2N] = 1:1:5. Under these conditions all intermediate reactive complexes interacted with diethylamine. Complexes containing acid chloride with tertiary amine (acyl ammonium complex) were transformed to yield amide groups and diethylamine hydrochloride; active hydrogen complexes of tertiary amine with hydroxyl groups were destroyed with diethylamine. In the sample, the degree of conversion of the reaction (from 4 to 70%) was determined from the value of the optical density of IR spectral peaks for the ester ($\lambda = 1740$ cm^{-1}) and amide ($\lambda = 1620$ cm^{-1}) groups, obtained after centrifugal separation of the filler. It has been established that model reagents can be extracted and separated from the filler completely by washing the samples with large volumes of chloroform. The errors in the determination of the observed reaction rate constant were from 4 to 6%.

It has been established that varying the rotation rate of the stirrer from 300 to 2400 rpm did not affect the kinetic parameters of the reaction. This means that the process of polyesterification and the model reaction occur under quasi-homogeneous conditions in the kinetic range. Under these conditions, the reaction follows the regularities specific to third-order kinetic reactions (Figure 1).

The molecular weights of the polymers were determined by light scattering after separation of the filler by filtration followed by centrifugation of the 0.5% solution of the composite in chloroform. Following extraction of the filler and washing in chloroform (the best solvent for these polymers), no residual polymer was detected.

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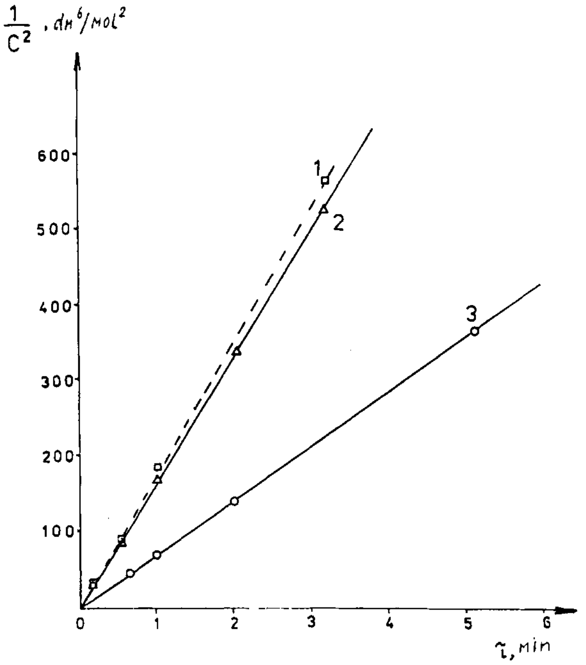


Figure 1. Anamorphosis of the kinetic curves of the reaction between benzoyl chloride and phenol in benzene (303 K, [OH]:[COCl]:[Et_3N] = 1:1:1): (1) without the filler, (2) in the presence of 80% graphite S-1.

The microheterogeneity coefficient K_m and the length of the copolymer blocks (n) were determined by ^1H NMR spectroscopy.[6] In a brief description of the method of calculation of K_m the copolymer reaction can be written as

$$A + C + B = ACBCBCACACABCBCA...$$

where A and B are the comonomers (hexamethylene glycol and dichlorodiphenylolpropane) and C is the intermonomer (terephthalic acid chloride). This method is based on the calculation of the relative content of the heterotriads and homotriads ACA, ACB, and BCB in the fragments, the molar fractions of the fragment sequence N_{ac} and N_{bc}, and the probabilities of the sequence of fragment AC after BC (P_{ba}) and BC after AC (P_{ab}). K_m is the sum of these probabilities. Thus

$$ACA = \frac{S_{aca}}{S_{aca} + S_{acb} + S_{bcb}};\ ACB = \frac{S_{acb}}{S_{aca} + S_{acb} + S_{bcb}};\ BCB = \frac{S_{bcb}}{S_{aca} + S_{acb} + S_{bcb}};\ N_{ac} = ACB/2 + ACA;\ N_{bc} = ACB/2 + BCB;\ P_{ab} = ACB/2N_{ac};\ P_{ba} = ACA/2N_{bc};\ K_m = P_{ab} + P_{ba};\ n_{ac} = 1/P_{ab} = 2N_{ac}/ACB;\ n_{bc} = 1/P_{ba} = 2N_{bc}/ACB$$

The accuracy of the K_m calculation depends on the ^1H NMR measurements. A 200-MHz Bruker NMR spectrometer was used. The calculated errors in K_m are from 1 to 3%.

To study the sorption process of monomers on the filler, a special method was developed for a quantitative assessment of the fraction of adsorbed molecules. It is based on the determination of the changes in the concentration of the monomers in the reacting solution after stirring with a filler. Then after the separation of the filler the concentrations of the monomers were determined by measuring the relative intensities in ^1H NMR spectra of the signals for the CH_3 protons in dichlorodiane and CH_2 protons in hexamethylene glycol.

Microphotographs of the surface of the films and coatings based on these polymer composites were made using a Hitachi scanning microscope. The frictional properties were measured in a torsion friction machine (p = 0.1 MPa, v = 1 m/s).

The electrical conductivities of the samples of the composites produced were measured by standard methods.

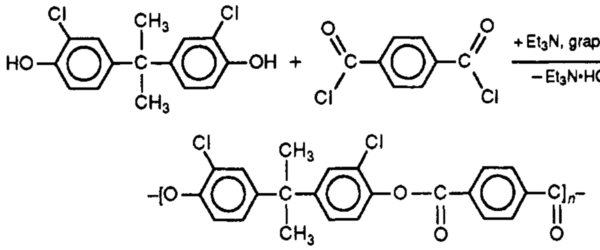
Results and Discussion

Table I
Effect of Filler on the Molecular Weight of Dichlorodiane Polyterephthalate (Benzene, Et_3N, 303 K)

filler (%)	specific surface S_{sp}, m^2/g	[η], 100 mL/g (in tetrachloroethane)	mol wt of polymer,[a] $\bar{M}_W \times 10^{-3}$
no filler		0.68	30
graphite "Taiginskii" (30.0)	9.5	0.87	53
graphite S-1 (30.0)	14.0	0.92	60
graphite S-1 (60.0)	14.0	1.15	70

[a] Weight-average molecular weights ($\bar{M}_W$) of polymers were measured by the method of light scattering in chloroform.

For the acceptor-catalytic polyesterification of terephthalic acid dichloride with bis[4-oxy-3-(chlorophenyl)]-2,2′-propane (dichlorodiane) carried out at 303 K in benzene with an equimolar content of the reagents and triethylamine (reaction 1), the molecular weight of the polymers synthesized in the presence of 30% and 60% graphite with different values of specific surface has been established to be much higher than that of the polymer produced without fillers (see Table I).



(1)

The effect observed is caused by reduced contributions of the side processes, which resulted in the termination of polymer chain growth. An example is the interaction between the acid chloride and adventitious water in solvent. Thus a primary hypothesis for the observed effect is likely to be due to the sorption of this water on the graphite.

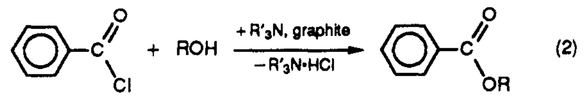
However, the results of the investigation of the sorption of water from benzene on graphite give evidence that this process is not the cause of an increase of the molecular weight of the polymer. Keeping the reaction solution at a humidity of 0.005% in the presence of 30% of graphite S-1 for 2 h results in no sorption of water by the filler (the content of water was determined by titration in Fisher's reagent).

A second hypothesis involves the effect of a heterogeneous matrix, which is related to the sorption of monomers and the polymer formed and, as a consequence, to the condensation of the reagents on the filler surface. Due to this process the growth of the macromolecular chain occurs on the filler surface or in its vicinity.

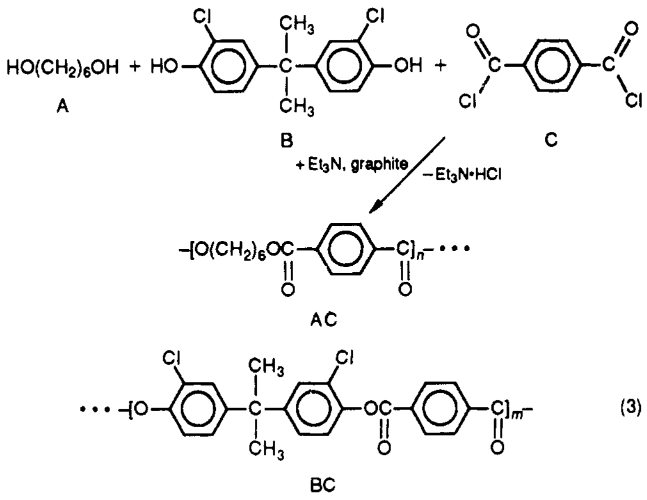
To test this supposition, we studied the influence of a filler on the kinetics of the model reactions between benzoyl chloride, phenol, and n-butanol (reaction 2) as well as on the microstructure of copolymers of terephthalic acid dichloride, hexamethylene glycol, and dichlorodiane, which are synthesized under the conditions of acceptor-catalytic copolyesterification (reaction 3).

First, we have established that in the absence of a filler the reactivity of phenol in benzene at 303 K is 200 times higher than that of n-butanol in the reaction with benzoyl chloride in the presence of an equimolar content of triethylamine. The kinetic investigation was carried out by the method described in the Experimental Section.

Copolymers produced under similar conditions with an equimolar content of reagents and a gradual introduction of the intermonomer (terephthalic acid dichloride) have a block structure with the microheterogeneity factor K_m



where ROH = C_4H_9OH, PhOH; R'_3N = Et_3N, Py



= 0.23. It is known from the literature[6] that the value of K_m characterizes the degree of ordering in the copolymers and is the sum of the probabilities of the dispositions of units in the chain. When $K_m = 1.0$, the distribution of units is random; if $K_m \ll 1.0$, it testifies to a block structure of the copolymer.

According to the results obtained, it has been established that the filler influences both the kinetics of reaction 2 and the microstructure of the copolymers (reaction 3). Some results are given in Table II. These data reveal that introduction of 80% graphite with a specific surface of 14 m^2/g increases the reaction rate of benzoyl chloride with n-butanol by a factor of 1.5, while in the case of the reaction with phenol under similar conditions the reaction rate decreases by about 3.

Reducing the differences in the activities of the phenolic and alcoholic OH groups in acceptor-catalytic copolyesterification in the presence of fillers leads to a decrease in the number of units in the blocks of copolymers (the number of the aromatic units decreases from 11 to 5, the number of aliphatic groups decreases from 7 to 3). As a consequence, the values of the microheterogeneity factor K_m^F are 2.5 times higher for copolymers produced in the presence of graphite.

The dependence of the matrix effect on the specific surface of the filler is clearly displayed by the reaction carried out in the presence of graphite with a specific surface of 22.0 m^2/g. In this case even 20% of the filler reduces the relative activity of phenol groups and increases K_m^F of the copolymer. Thus, 30% of the filler induces the same effect as does the 80% graphite with a 9.5 m^2/g surfaces area (Table II).

The results obtained allowed us to establish a linear dependence between K_m^F of the copolymers and the specific surface of the filler (Figure 2). An increase in the specific surface of the filler results in the formation of copolymers with shorter blocks. It should be noted that this linear dependence was obtained when different fillers (synthetic graphite S-1, natural graphite Taiginskii, molybdenum disulfide) were used.

Figure 3 shows the results of the study on the effect of the content of graphite with the same specific surface (S_{sp} = 14.0 m^2/g) on the activity of phenolic OH groups and the coefficients of microheterogeneity K_m^F for the copolymers synthesized. As the filler content increases from 20 to 80%, the relative activity of phenolic groups decreases and the value of K_m^F for the copolymer increases.

Thus, the experimental dependencies provide an opportunity to produce copolymers of defined structures using the corresponding amount of a filler having a definite value of specific surface area.

The results obtained allow us to affirm that we have first discovered the matrix effect of polycondensation

Table II
Effect of the Filler's Nature on the Kinetics of Model Reaction 2 and the Microstructure of the Copolymers (Benzene, Et_3N, 303 K)

filler (S_{sp}, m^2/g)	amount, %	$K_m^F/K_m = \lambda$	$n_{ac}^F + n_{bc}^F$ [a]	$k_0^F/k_0 = \chi$ C$_4$H$_9$OH	$k_0^F/k_0 = \chi$ C$_6$H$_5$OH
MoS_2 (7.2)	20	1.00	7,3 + 10,8		
	80	1.70	4,1 + 6,7		
graphite	20	1.00	7,4 + 10,9	1.00	1.00
“Taiginskii”	80	1.74	4,0 + 6,6	1.27	0.54
(9.5)					
graphite	20	1.00	7,2 + 10,5	1.00	1.00
TRG-10	30	1.10	7,0 + 10,3	1.06	0.96
(10.5)					
graphite	20	1.00	7,3 + 10,8	1.00	1.00
S-1 (14.0)	40	1.26	5,7 + 9,0		0.93
	80	2.30	3,1 + 5,0	1.40	0.36
graphite	20	1.35	6,5 + 9,8	1.22	0.70
TGR-10	30	1.74	4,0 + 6,6	1.31	0.54
(22.0)					

[a] $n_{ac} + n_{bc}$ = 7,3 + 10,8. The numbers of aliphatic and aromatic units in the blocks of copolymer obtained without graphite.

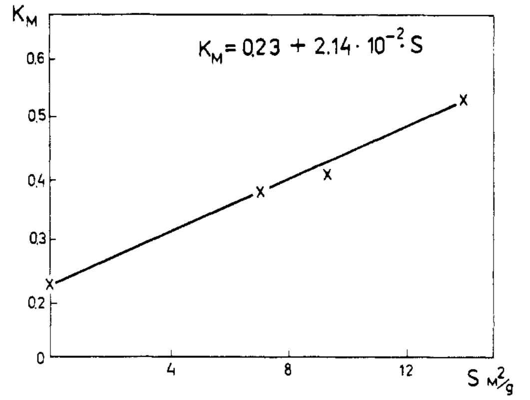


Figure 2. Effect of the value of the specific surface of a filler on the values of microheterogeneity coefficient K_m of the copolymers obtained in benzene in the presence of 80% filler (catalyst, triethylamine; 303 K).

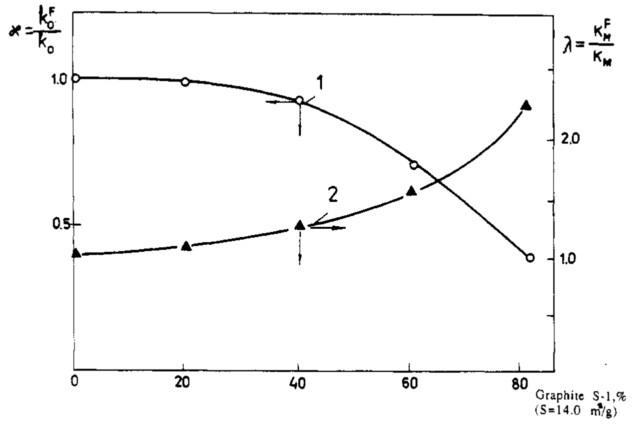


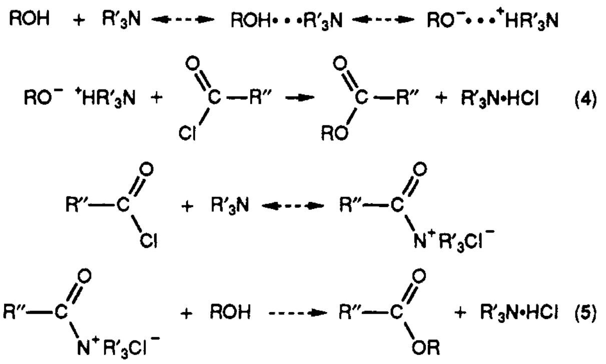
Figure 3. Effect of the content of graphite S-1 on the kinetics of model reaction 2 (curve 1) and on the microstructure of the copolymers (curve 2) (benzene, Et_3N, 303 K).

caused by the influence of fillers on both the reaction kinetics and the microstructure of the macromolecules produced.

It is necessary to emphasize that the term matrix reactions denote a chemical transformation of monomers or oligomers to macromolecules which is controlled by the structure chemical information contained in the matrix (of a chemically inert component in the reaction medium).[7] Such a role of the matrix has previously been considered to be only played by macromolecules such as biological macromolecules, biopolymers in living systems, and polymer matrices in organic syntheses and in the polymerization processes.

In our opinion, the polymer formation reactions in the presence of fillers should also be referred to those terms, provided the filler exhibits matrix properties such as a selective sorption of monomers and an influence on the kinetics of the process and on the structure of the growing macromolecular chain.

We propose the following mechanism for the matrix effect discovered. The filler particles dispersed within the reaction medium selectively adsorb such molecular dipoles as a polarized H complex of a tertiary amine with phenol produced under the general basic catalysis (reaction 4) or an acyl ammonium complex produced in the case of the nucleophilic mechanism (reaction 5).[8]



$$\mathrm{ROH} + \mathrm{R'_3N} \longleftrightarrow \mathrm{ROH\cdots R'_3N} \longleftrightarrow \mathrm{RO^-\cdots{}^+HR'_3N}$$

$$\mathrm{RO^-\ {}^+HR'_3N} + \mathrm{R''C(=O)Cl} \longrightarrow \mathrm{R''C(=O)OR} + \mathrm{R'_3N{\cdot}HCl} \qquad (4)$$

$$\mathrm{R''C(=O)Cl} + \mathrm{R'_3N} \longleftrightarrow \mathrm{R''C(=O)N^+R'_3Cl^-}$$

$$\mathrm{R''C(=O)N^+R'_3Cl^-} + \mathrm{ROH} \dashrightarrow \mathrm{R''C(=O)OR} + \mathrm{R'_3N{\cdot}HCl} \qquad (5)$$

In the first case, the electron density on the oxygen atom of the phenoxide ion decreases during sorption. As a consequence, nucleophilic reactivity decreases, and this results in a decrease of the values of the observed rate constant k_0 for the reaction between benzoyl chloride and phenol. In the second case, the same effect reduces the electron density on the carbonyl carbon atom; i.e., the reactivity of the acyl ammonium complex increases.

The growth of the macromolecular chain occurs at the surface or in the region close to the surface of the heterogeneous matrix due to the selective sorption of monomers. This is the major difference between the heterogeneous matrix polycondensation and radical polymerization in the presence of a filler. In the latter case no matrix effects are observed because growth of the macromolecular chain occurs throughout the reaction volume. Owing to the mechanism of radical polymerization, only one end of the macromolecular chain is attached to the surface of the filler.[1]

The polycondensation matrix effect determines the reaction kinetics and the copolymer microstructure. Due to the increase of the reagent concentrations at the filler surface, the contribution of the side reactions is reduced, because the ratio between the reagents and water in the solvent in the vicinity of the filler surface is higher than that in the reaction volume. This effect promotes the production of polymers with higher molecular weights.

Table III
Effect of the Nature of Solvent and Tertiary Amine on the Kinetics of Reaction 2 and the Microstructure of the Copolymers (Graphite S-1, 80%, 303 K)

tertiary amine	solvent (μ, D)	$K_m^F/K_m = \lambda$	$(n_{ac}^F + n_{bc}^F)/(n_{ac} + n_{bc})$	$k_0^F/k_0 = \chi$	
				C_4H_9OH	C_6H_5OH
triethylamine	benzene (0)	2.30	(3,1 + 5,0)/(7,3 + 10,8)	1.40	0.36
pK_a = 10.9	dichloroethane (1.75)	1.30	(4,5 + 8,3)/(6,5 + 9,1)	1.00	0.77
pyridine	benzene	1.15	(1,9 + 1,7)/(2,2 + 1,9)	1.24	0.98
pK_a = 5.2	dichloroethane	1.10	(2,0 + 1,7)/(2,1 + 1,9)	1.23	1.00

The conclusion about the selective sorption of the charged particles is confirmed by the study of kinetics of the model reaction and the microstructure of the copolymers which are synthesized in dichloroethane. The molecules of the latter solvent are dipoles with the dipole moments $\mu = 1.75$ D (Table III). In this solvent the kinetic and structural matrix effects are displayed much more weakly than in nonpolar benzene (μ = 0 D). The attenuation of the matrix effect is probably connected with the fact that the molecules of the polar solvent are sorbed on the filler as well. This process suppresses the sorption of the polarized complexes of the starting monomers.

The character of the matrix effect is determined by the chemical nature not only of the solvent but of the tertiary amine as well. We have found that in the presence of pyridine, which has weaker basic properties, no matrix effect exists (Table III). This is determined by the predominance of the mechanism of nucleophilic catalysis involving the formation of an acyl ammonium complex. In the presence of a filler, the sorption occurs and the reactivity of this complex increases, but no changes in the reactivity of the aromatic OH groups takes place, because there are no H complexes of diols with pyridine in the reaction system in this case.

According to the results of the direct study on the sorption of dichlorodiane and its equimolar mixture with triethylamine on graphite in a benzene solution with concentration of 0.2 mol/dm^3, in the presence of tertiary amine the fraction of sorbed bisphenol increases 3-fold compared with the sorption of a free bisphenol. This fact also confirms the conclusion about a predominant sorption of the H complex rather than that of a free diol. It has been established by ^{1}H NMR spectroscopy that, in the simultaneous presence of bisphenol, hexamethylene glycol, and triethylamine, the concentration of free residual glycol was much higher than that of free bisphenol. But, without of tertiary amine, it has been observed that an equal amount of free bisphenol and glycol are absorbed. This is caused by the higher value of the equilibrium constant of the bisphenol's H-complex formation[8] as compared with that of the glycol H complex.

We have established that the chemical structure of the acid chlorides does not significantly affect the matrix effect. The reactivity of the acid chloride groups of sebacic acid dichloride increases 1.5 times in its reaction with n-butanol in benzene at 303 K in the presence of 80% graphite S-1, as is in the case of benzoyl chloride. It should be supposed that in both cases the nucleophilic mechanism of catalysis prevails, which is present in the production of the acyl ammonium complex. The reactivity grows proportionately to the content of the filler in the reaction system in the sorption on graphite.

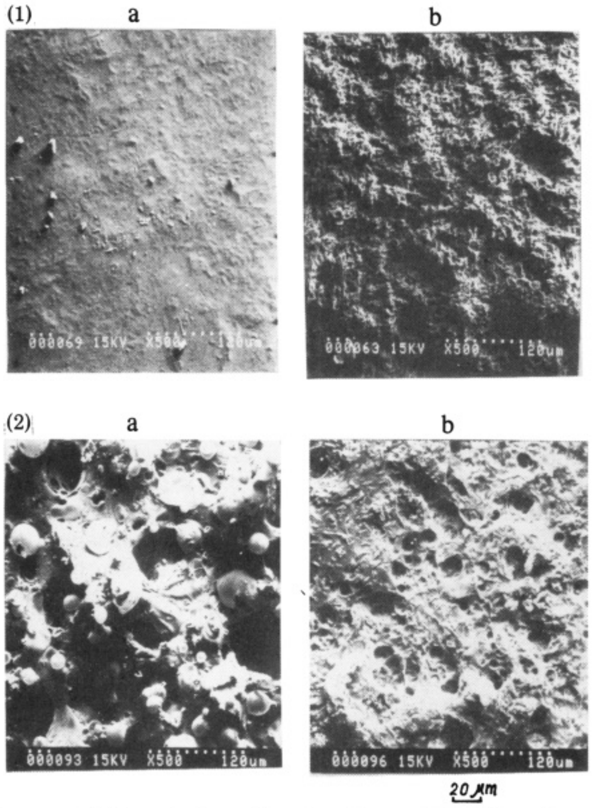


Figure 4. Microphotographs of surfaces of the films (1) and coatings (2) of a composite based on the dichlorodiane polyterephthalate and 30% graphite S-1: (a) mechanical stirring; (b) stirring in the synthesis.

Preliminary electron scanning microscopy data on the composites produced by synthesis and by mechanical stirring confirm the assumption of the predominant growth of macromolecules on the filler surface. This results in a more homogeneous distribution of the filler in the synthetic composites.

As is seen on the microphotographs of the coatings and films, in the case of the synthetic composite of dichlorodiane polyterephthalate with 30% graphite S-1, the distribution of graphite particles within the polymer is homogeneous (Figure 4.1b and 4.2b). The surface of the mechanical composite is more enriched with polymer and exhibits inhomogeneous distribution of the graphite particles (Figure 4.1a and 4.2a). The mechanical composite disintegrates because of adhesive destruction of the polymer–filler bonds, while the synthetic composite fractures because of cohesive destruction of the polymer phase itself.

One of the practical advantages of the polymer synthesis in the presence of the filler exhibiting the properties of a heterogeneous matrix is the advanced thermomechanical, thermal, mechanical, and antifriction properties of such systems compared with the properties of the similar composites prepared by mechanical stirring. It should be noted that the suspension based on a synthetic composite is advantageous from the technological viewpoint since it retains its stability for 1 day and more, while the suspension produced by mechanical stirring of the components becomes laminated in 2–5 min due to the precipitation of graphite particles.

We have studied the friction properties of the samples of a coating produced by deposition from solution on a metal substrate and by compression molding of composites at 553 K and 60 MPa. Figure 5a shows the friction properties of coatings based on the polyterephthalate of dichlordiane and 30% graphite S-1. The results demonstrate that friction of the synthetic composites (curve 2) displays a much more stable character. The frictional coefficient of the synthetic composite is 3 times lower than that of the mechanically filled systems. The improvement of the friction properties of the synthetic composite in our opinion is also related to a more dense packing of the molecules of the polymer on the filler surface.

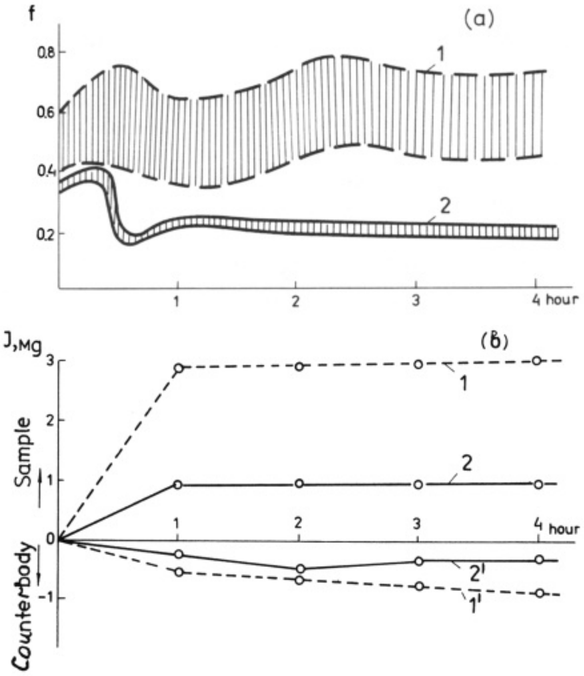


Figure 5. Results of friction tests of the coatings based on the polymer composite of dichlorodiane polyterephthalate with 30% graphite S-1: (a) the friction curves; (b) the wear curves. (1,1′) Mechanical stirring. (2,2′) Synthetic stirring.

Table IV
Physicomechanical Properties of Composites Based on Dichlorodiane Polyterephthalate and 30% Graphite S-1 Which Is Obtained Directly in the Synthesis and by Mechanical Stirring

		thermolysis			
method of obtaining composites	T_{soft}, K	[CO] $\times 10^3$, mol/unit·mol	[CO$_2$] $\times 10^3$, mol/unit·mol	specific impact strength, kJ/m^2	specific electroconductivity χ, 10^{-13} Ω^{-1} m^{-1}
mechanical stirring	493	9	63	45	1
stirring in synthesis	533	1	2	118	500

As is seen from Figure 5b, for the coating based on the composite produced by mechanical stirring (curve 1), the value of wear is 3 times greater than that of the synthetic composite (curve 2). During the friction of the synthetic composite, wear of the steel counterbody is reduced and a transport film of antifriction plastic appears. In the friction of the composite produced by mechanical stirring, no friction film appears and the counterbody wear keeps growing. In the latter case inhomogeneity of the coating brings about an increase in the wear of both the coating and counterbody.

The other advantage of synthetic composites is their increased heat resistance (Table IV). According to the results of the thermomechanical tests, the softening temperature of the mechanically mixed composites is 40 K lower than that of the synthetic composites.

The chromatographic study of the gaseous products of thermal destruction of synthetic and mechanical composites in vacuum at 623 K showed that the former ones possess higher thermal stability. The amounts of carbon monoxide and dioxide evolved from a mechanically stirred composite as thermal degradation products of the ester group are, respectively, 10 and 30 times higher than those of the synthetic composite (Table IV).

Results of the physicomechanical tests of the composites also give evidence of the advantages of synthetic filling. In particular, the value of the specific impact strength of a synthetic sample is 2.5 times higher than that of a mechanically stirred one.

It should be noted that the specific electrical conductivity of the synthetic composites is 500 times higher than that of the mechanical-stirred system due to a more homogeneous distribution of a filler in the first case (Table IV). This could lead to dielectric materials with prespecified electric properties.

Thus we have first established that in polycondensation processes a filler introduced into the reaction system at the stage of growth of the macromolecular chain exhibits the properties of the heterogeneous matrix; namely, it influences the reaction kinetics, the structure of the polymers synthesized, and the properties of the composites produced thereby.

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Registry No. A, 629-11-8; B, 79-98-1; C, 100-20-9; BC (copolymer), 25685-97-6; BC (SRU), 25839-75-2; ABC (copolymer), 38334-02-0; benzoyl chloride, 98-88-4; phenol, 108-95-2; *n*-butanol, 71-36-3; graphite, 7782-42-5; molybdenum, 1317-33-5; sebacic acid dichloride, 111-19-3; triethylamine, 121-44-8; benzene, 71-43-2; dichloroethane, 1300-21-6; pyridine, 110-86-1.