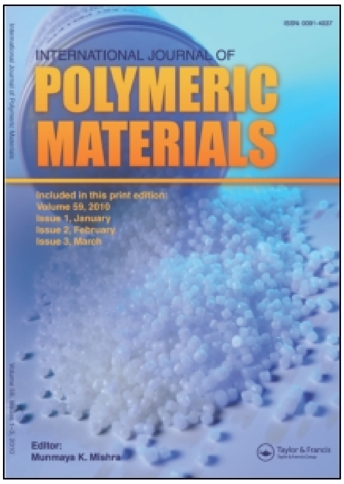

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Matrix Polycondensation: A New Route to Multicomponent Polymer System with Designed Properties

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Matrix Polycondensation: A New Route to Multicomponent Polymer System with Designed Properties

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The regularities of polyesterification in the presence of a filler as a heterogeneous matrix were considered. The filler introduced into the reaction system before polycondensation process influenced not only the reaction kinetics but also the resulting properties of polymer composites produced. The composites obtained by polymer synthesis in the presence of the filler have higher mechanical, thermal, frictional and electrical properties as compared with those of the composites prepared by mechanical filling.

KEY WORDS Matrix polycondensation, filler, graphite, mechanical properties.

INTRODUCTION

The term matrix reaction is usually used for polymerization processes taking place in another polymer. This can affect the reaction kinetics, structure and properties of the "daughter" polymer. While the matrix addition polymerization was studied extensively, the matrix polycondensation (step-growth polymerization) has attracted less attention. The majority of experimental data was obtained for the synthesis of aromatic polyamides.[1-3] Highashi *et al.*[1-3] have established that some flexible chain polymers introduced into the reaction system increase the molecular weights of rigid-rod aromatic polyamides obtained by the direct phosphorilation reaction from acids and diamines. These authors[3] have found that in the presence of poly(vinylpyrrolidone) as a matrix, it was possible to obtain high-molecular poly(*p*-phenylene terephtalamide) soluble in the organic solvent.

In our opinion, the matrix polycondensation is one of the best methods to design a multicomponent polymer system (miscible blends, molecular composites, composites, and etc.) with tailored or predesigned properties. However, the action of the matrix is not limited to dissolving the reaction system but the polymer can also act as the filler particles dispersed in the reaction medium. In this case it is possible to regulate the structure and the properties of the synthesized polymer by varying the content of the filler and its specific surface area.

In our previous work[4] we have discovered the heterogeneous matrix effect of the antifraction filler (graphite and molybdenum disulfide) in acceptor-catalytic polyesterification. It was established that the filler selectively adsorbed monomers and, as a consequence, influenced their reactivity. For instance, the reactivity of the aromatic hydroxyl groups after sorption was almost 3 times lower. However, the molecular weights of polymers obtained in the presence of 30 to 60% filler were more than two times higher as compared with those of the polymer obtained without the filler.

In the present study we consider the effect of the filler on the properties of polymer composites based on polyterephtalate of bis(4-oxo-3-chlorophenyl)-2,2′-propane and graphite.

MATERIALS AND METHODS

The substances and solvent were purified using standard methods. Polyterephtalate of bis(4-oxy-3-chlorophenyl)-2,2′-propane (dichlorodiane) was synthesized by acceptor-catalytic polyesterification in the presence of a filler amounting to 30–60% of the calculated weight of the filled polymer composite.[4]

It was established that the polyesterification process occurred under quasihomogeneous conditions.

The molecular weights of the polymers were determined by light scattering after separation of the filler by filtration followed by centrifugation of the composite solution in chloroform.

Microphotographs of the surface of the coatings based on the composites obtained by the polymer synthesis by mechanical means were made on a Hitachi scanning microscope.

The thermal, frictional, and mechanical properties, and electrical conductivity of the composites were measured by standard techniques.

RESULTS AND DISCUSSION

The properties of the investigated polymer composites, depend on many factors such as, the molecular weight of polymer, its structure, homogeneity of filler distribution within the polymer phase, orientation of polymer chains on the filler surface, interaction between filler particles and macromolecules, and etc.

The results presented in the Table I reveal a possibility to regulate the molecular weight of polymers by content of the filler introduced into the reaction system before the synthesis. We established[4] that this effect is caused by selective sorption of the polarized intermediate active complexes of the monomers on the filler surface.

Because of the matrix effect the growth of macromolecular chain occurs at the surface or in the region close to the surface of the heterogeneous matrix. For this

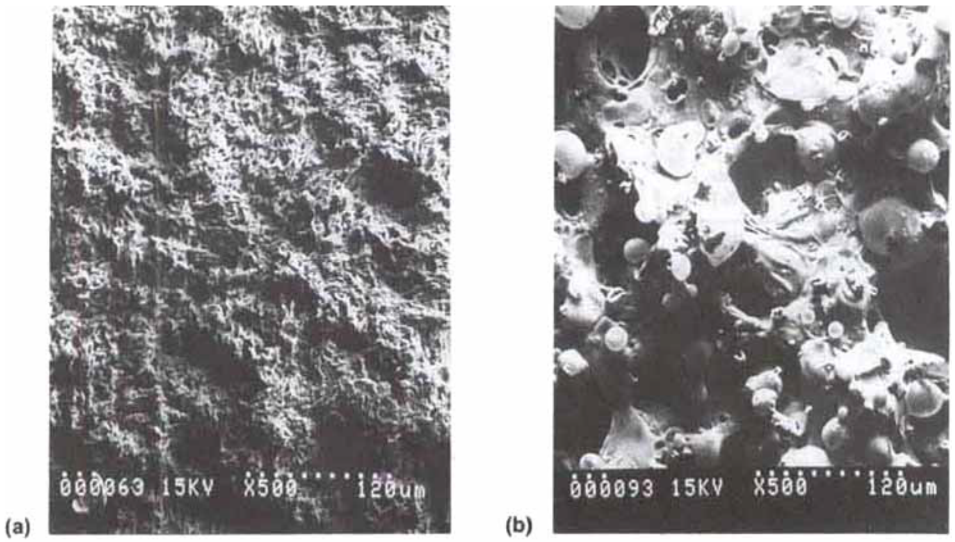

FIGURE 1 Microphotographs of surfaces of the coatings of a composite based on the dichlorodiane polyterephtalate and 30% graphite S-1: a) synthetic composite; b) mechanically filled composite.

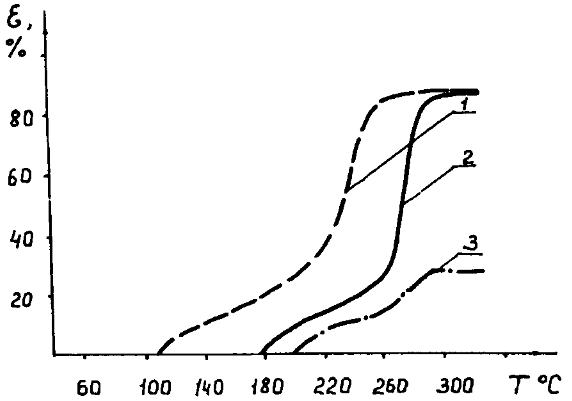

FIGURE 2 Data of thermomechanical tests of the composites: 1—mechanically filled composite; 2, 3—synthetic composites with 30% and 60% graphite S-1, respectively.

reason the matrix effect provides an opportunity to produce polymers with higher molecular weights.

The microphotographs of the coatings based on i) synthetic composites and ii) mechanically filled composites indicate a more homogeneous distribution of the filler particles in the first case (Figure 1a). The coatings based on the mechanical composite are more enriched with polymer spherical particles formed during the deposition of the polymer composite solution on the metal plate. This means that in the mechanically filled composite the interaction between polymer molecules themselves is stronger than the polymer-filled interaction.

For this reason the mechanical composite disintegrates because of adhesive destruction of the bonds between polymer and filler, while the synthetic composite fractures because of the cohesive destruction of the polymer phase.

TABLE I

Effect of a filler on the molecular weight of dichlorodiane polyterephtalate (benzene, Et_3N, 30°)

Filler, (%)	Specific surface, S_{sp}, m^2/g	$[\eta]$, 100 mL/g (tetrachloroethane, 25°)	Molecular weight, $\bar{M}_w \cdot 10^3$
No filler	—	0.68	30
Grpahite "Taiginskii" (30)	9.5	0.87	53
Graphite S-1 (30)	14.0	0.92	60
Graphite S-1 (60)	14.0	1.15	70

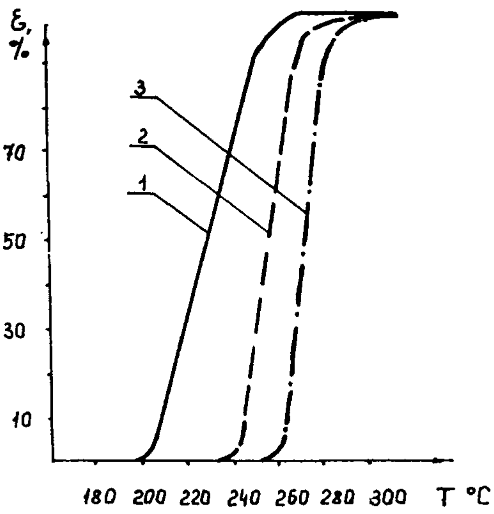

FIGURE 3 Data of thermomechanical tests of polymers (Table I) obtained without graphite (curve 1) and in the presence of 30% (curve 2) and 60% graphite S-1 (curve 3).

The results of thermomechanical tests reveal an increased heat resistance of synthetic composites (Figure 2). The softening temperature of the synthetic composite with 30% of graphite is 70° higher as compared with the mechanically filled system. For synthetic composite with 60% of graphite this value increases up to 90°. One of the reasons could be an increased molecular weight of polymers in the synthetic composites (Table I).

Polymers obtained in the presence of graphite have an increased heat resistance (Figure 3). However, the difference in the softening temperatures is lower (40°). The greater difference in softening temperatures of the composites could be explained by a more intense interaction between polymer molecules and filler particles in the synthetic composite.

The thermomechanical tests of the synthetic and mechanical composites with 30% of graphite S-1 and polymers with the same molecular weights (50,000) confirm the conclusion about more intense interaction between polymer and filler in the

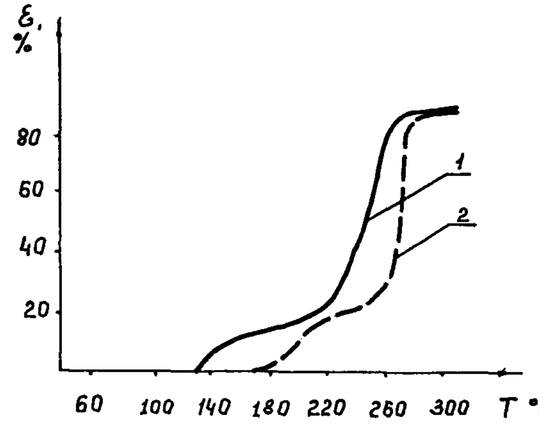

FIGURE 4 Thermomechanical curves of the composites based on polyterephtalate of dichlorodiane ($M_w = 5 \cdot 10^4$) with 30% graphite S-1: 1—mechanically filled composite; 2—synthetic composite.

TABLE II

Properties of composites based on dichlorodiane polyterephtalate and graphite S-1

Type of composite	Thermolysis, 10^3 mol/unit-mol		Specific impact strength, kJ/m²	Specific electroconductivity · 10^{13-1}, m^{-1}
	CO	CO_2		
Mechanical composite	9	63	45	1
Synthetic composite	1	2	118	500

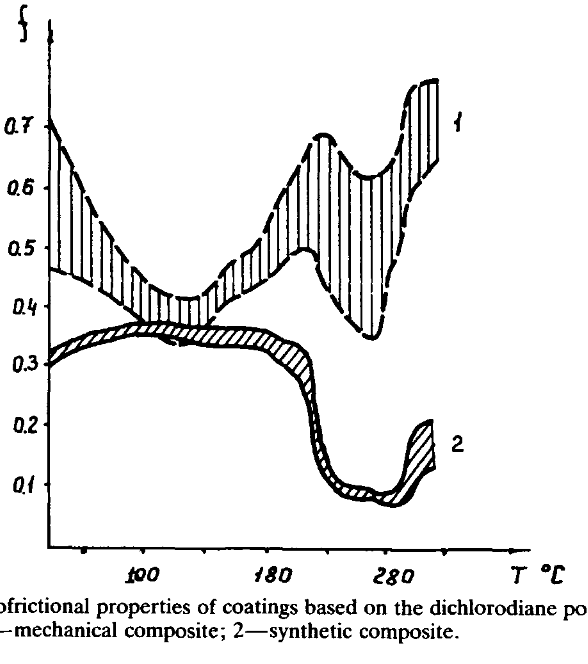

FIGURE 5 Thermofrictional properties of coatings based on the dichlorodiane polyterephtalate and 30% graphite S-1: 1—mechanical composite; 2—synthetic composite.

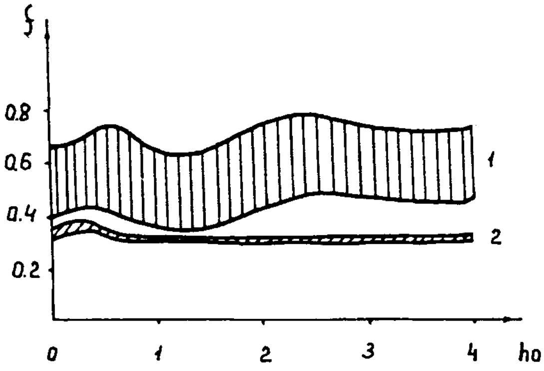

FIGURE 6 Frictional properties of coatings based on the dichlorodiane polyterephtalate and 30% graphite S-1: 1—mechanical composite; 2—synthetic composite.

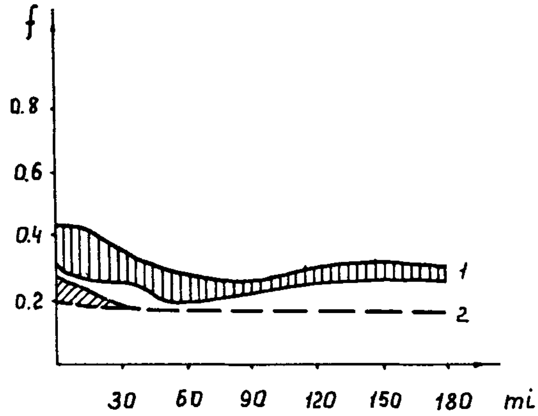

FIGURE 7 Frictional properties of the coatings based on the dichlorodiane polyterephtalate and 80% graphite S-1: 1—mechanical composition; 2—synthetic composite.

TABLE III

Dependence of free surface energy $\gamma_s = \gamma_h + \gamma_d$* on the duration of friction test of the coating based on dichlorodiane polyterephtalate and 30% graphite S-1

Duration of friction test, hour	Mechanical composite		Synthetic composite	
	$\gamma_h \cdot 10^3$, J/m^2	$\gamma_d \cdot 10^3$, J/m^2	$\gamma_h \cdot 10^3$, J/m^2	$\gamma_d \cdot 10^3$, J/m^2
Before friction	2.5	50.2	1.2	58.0
1	2.9	47.4	—	—
2	10.3	41.7	1.1	58.1
3	19.2	41.0	0.9	58.0

*γ_h and γ_d are the polar and dispersional parts of free energy γ_s.

synthetic composite. The softening temperature in the latter case is much higher than that of the mechanical composite (Figure 4).

The method of filling influences also the thermal stability of the composites. The thermal degradation of composites by destruction of the ester groups at 350° in vacuum appeared to be much higher in the case of the mechanically filled composite. According to the results of chromatography study of gaseous products of thermal destruction of the composites, the amount of carbon monoxide and dioxide evolved from the mechanically filled composite are 10 and 30 times higher, respectively, than those of the synthetic composite (Table II). This is also caused by a more intense interaction between polymer and filler in the synthetic composite.

The data presented in Table II reveal another advantage of synthetic filling. For instance, the value of specific impact strength of the synthetic composite is 2.5 times higher than that of the mechanical one. The electrical conductivity of the synthetic composite is 500 times higher.

The friction properties of the composites also demonstrate the advantage of synthetic filling. The data presented in Figures 5, 6 and 7 show a more stable character of friction of coating based on the synthetic composite. The friction coefficient of this coating is three times lower and it tends to decrease with an increase of the friction temperature (Figure 5) and test duration (Figure 6), than the friction coefficient of the coating based on the mechanical composite which increases with the increase of temperature and test duration. Even 80% of graphite in the composites does not change the unstable character of friction of the mechanical composite (Figure 7).

This can be caused by nonhomogeneous distribution of a filler in the mechanical composite. The electron microscopy data show that the surface of the coating based on the mechanical composite is more enriched with polymer. This fact leads to more intensive thermoxydation of the polymer on the frictional surface and, as a consequence, to an increase in the friction coefficient.

These results are confirmed by values of the free energy, γ_s, determined by standard techniques[5] (Table III).

The data presented in the Table III show that the polar part of free energy, γ_h, considerably increases during friction of the coating based on the mechanical composite while in the case of the synthetic composite it becomes constant. This indicates the higher thermoxydative resistance of the surface of synthetic composite. The greater value of dispersion part of free energy, γ_d, in the case of the synthetic composite can be caused by its more ordered structure as compared with that of mechanically filled composite.

In summary, we can conclude that the synthesis of polymers in the presence of heterogeneous and homogeneous matrices (fillers, polymers) provides the possibility to create multicomponent polymer systems with the properties which can be regulated by the content and nature of the matrices.

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