Ultrahigh Molecular-Weight Polyethylene–Chalk Composites Resulting from In Situ Polymerization

V. M. GORELIK, *Institute of Petrochemical Synthesis, USSR Academy of Sciences, Moscow, USSR,* E. A. FUSHMAN, V. A. TOPOLKARAEV, and F. S. DYACHKOVSKY, *Institute of Chemical Physics, USSR Academy of Sciences, Moscow, USSR,* and L. A. SHESTENINA, L. F. BORISOVA, and V. I. SERGEEV, *Research Institute of Polymeric Materials, Moscow, USSR*

Synopsis

Ethylene polymerization on chalk surface under the action of $TiCl_4$–organoaluminium compound systems yields filled composites possessing high stress–strain properties and preserving their ductility up to the chalk content of 60–70 wt %. The kinetics of the process and the properties of the composites have been investigated, as well as the interrelation between catalyst fixation technique, polymerization rate, and the ductile properties of composites containing 50 wt % of chalk. The conditions leading to the formation of "homogeneous" composites with a high ductility are examined. The possible causes of the formation of composites with a low value of elongation at break are analyzed. The principal regularities of the mechanical behavior of composites are considered for the case when the process is taking place on the filler surface and leads to "homogeneous" composites.

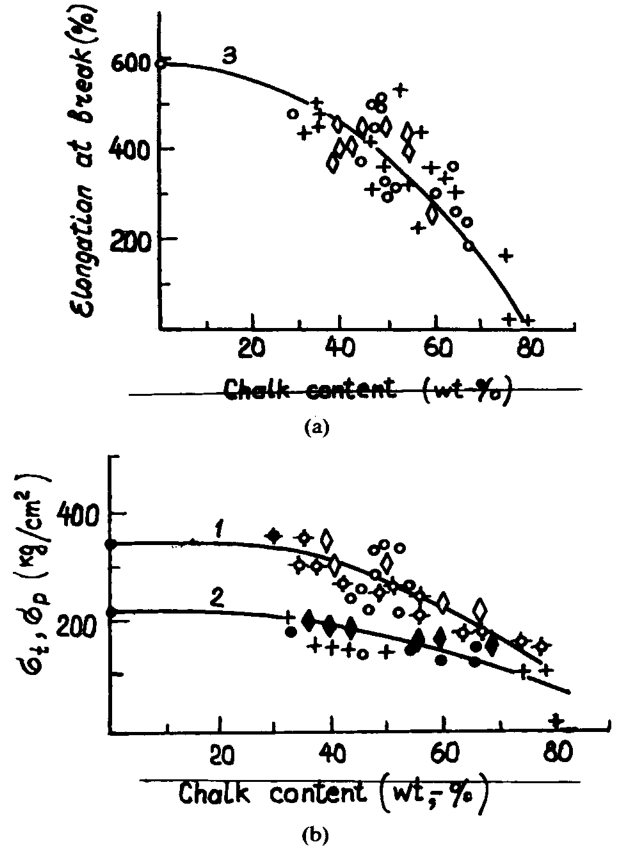
INTRODUCTION

Ethylene polymerization in the presence of mineral fillers under the action of organometallic catalysts yields ultrahigh molecular-weight polyethylene (UHMWPE)–chalk composites, combining a high ductility with sufficient stiffness.[1-3] In Ref. 2 it has been shown that, in order to obtain composites with high values of elongation at break (ϵ) at high filling levels (φ), the polymerization process must be localized on the filler surface. This can be accomplished, e.g., by using kaolin-fixed one-component catalysts that are active exclusively on the alumina–silica surface.

One-component organometallic catalysts are inactive in the presence of chalk,[2,4] whereas two-component $TiCl_4$-based systems allow obtaining highly ductile PE–chalk composites.[5,6] Moreover, as we have established,[6] the stress–strain properties of the best specimens of such composites are not inferior to those of the "homogenous" composites described in Ref. 2. The ϵ of the former is preserved at a level of 350–450% up to φ = 60–70 wt %, and their ultimate tensile σ_t and yield strength σ_p are sufficiently high (Fig. 1).

Presented in this paper are the results of studying the interaction of $TiCl_4$ and organoaluminium compounds ($AlEt_2Cl$, $AlEt_3$, $Al i\text{-}Bu_3$) with the chalk surface, as well as the effect of the way the catalyst has been fixed on the chalk surface upon the kinetics of ethylene polymerization. The interrelation

Journal of Applied Polymer Science, Vol. 40, 1095–1114 (1990)
CCC 0021-8995/90/07-81095-20$04.00



(a)

(b)

Fig. 1. Ultimate strength σ_t (1), yield strength σ_p (2), and elongation at rupture (3) vs. the filling level. Chalk/$TiCl_4$ 80°/Al system: (○, ●) $AlEt_2Cl$; (+, -◊-) $AlEt_3$; (◊, ♦) $AliBu_3$.

between the kinetics and the plastic properties of "polymerizationally filled" composites containing 50 wt % of chalk has also been investigated.

EXPERIMENTAL

Chalk, natural ground calcium carbonate with $S_{sp} = 4$ m^2/g, was used as the filler. Its size fraction composition* was as follows:

D (µm)	140–52	52–31	31–20	20–14	14–10	10–78
wt %	1.1	0.5	2.9	3.5	2.6	5.2
D (µm)	7.8–5	5–3.4	3.4–2.3	2.3–1.6	1.6–1.2	1.2
wt %	11.3	18.3	15	12.3	11.2	19.3

The chalk powder was heated for 4–5 h (250°C) under reduced pressure (2×10^{-2} mm Hg). According to titration by Fisher technique and the ethane

---

*The authors wish to thank I. L. Dubnikova for the measurements of the chalk size fraction composition on a Fritsche laser particle analyzer.

yield after treatment with $AlEt_3$,[7] the prepared filler samples contained $5–8 \times 10^{-6}$ mol/g of surface moisture $[H_2O]_F$.

Heptane of "reference grade" was purified by conventional techniques and stored over Na wire. Ethylene of "polymerization purity," after additional purification from oxygen and water in columns with pyrolusite and molecular sieves, contained no more than 20 ppm of H_2O and 10 ppm of O_2.

$TiCl_4$ of "special purity" grade was refluxed over copper chips with subsequent distillation. Organoaluminium compounds were used without any additional purification after analyzing for the Al, R groups, and chloride content. The interaction of $TiCl_4$ with organoaluminium compounds was studied in heptane. After the specified reaction time the filler was separated from the solution and dried *in vacuo* at 60°C.

The Ti and Al content in solution and on the filler surface was determined colorimetrically after extraction with $4N$ H_2SO_4, and the chloride content, by means of the Folgard technique. All operations with the catalyst components were carried out under dry, oxygen-free nitrogen.

Polymerization was conducted in heptane (0.12 L, chalk concentration 80 g/L) at 80°C under 3–5 atm in a thermostatic autoclave equipped with a stirrer and an inlet device for the catalyst components. Ethylene pressure was maintained constant. On completion of the experiment, the powder was separated from the solvent and dried *in vacuo* at 60°C. The φ value was controlled by the weight loss on combustion of the sample in a muffle furnace at 500°C.

The Ti–Mg catalyst (TMC), obtained as described in Ref. 8, had a $TiCl_4 \cdot MgCl_2 \cdot Mg(OEt)_2$ composition. Polymerization effected by this catalyst in combination with $Al\text{i-}Bu_3$ proceeded at a constant rate (25 kg/g Ti h atm) and gave PE with $\overline{MM}_\eta = 5 \times 10^6$.

Intrinsic viscosity $[\eta]$* of the polyethylene constituent was determined in decaline at 135°C after dissolution of the chalk in concentrated HCl. $\overline{MM}$ was calculated from the following formula:

$$[\eta] = 4.6 \times 10^{-4}\,\overline{MM}_\eta^{0.73}.$$

Homogeneity of the powders with respect to φ was estimated by fractionating them in i-PrOH–CCl_4 mixtures of differing density. For this purpose 3–5 g of the powder was suspended in CCl_4 and the flotated fraction was isolated from the "residue." The operation was repeated in mixtures of the above solvents with decreasing densities (0.1 g/mL step) until complete precipitation of every fraction. The isolated fractions were dried at 60°C *in vacuo*, followed by determining the filler content in them.

The homogeneity of composite films was determined by means of scanning electron microscopy (SEM) on a JSM-35C device. The sample preparation technique and filler distribution analysis have been described in Ref. 9. The σ_t, σ_p, and ϵ values were measured on an Instron 1185 instrument at a strain rate of 10 mm/min; the samples were cut from plates pressed at 190°C and 100 kg/cm².

---

*The authors wish to express gratitude to G. N. Kornienko for the measurements of MM of the samples.

RESULTS AND DISCUSSION

Adsorption of the Catalytic System Components on the Chalk Surface

We have established the interaction of $TiCl_4$ or $AlEt_2Cl(AlEt_3)$ with a chalk suspension in heptane, resulting in fixation of these compounds on the filler surface. The limiting quantity of Ti ion fixed on the surface (A_∞) depends on the reaction temperature (22 or 80°C) and amounts to $5\text{–}8 \times 10^{-6}$ and $15\text{–}25 \times 10^{-6}$ mol/g at 22 and 80°C, respectively (Fig. 2). At 80°C, as well as at 22°C, irrespective of the introduced amount of $TiCl_4$ (Ti_0), adsorption proceeds rapidly and terminates after a few minutes; prolonged exposure at $Ti_0 \gg A_\infty$ does not raise the observed sorption values. With $Ti_0 \leq A_\infty$ exhaustive adsorption of Ti ion takes place, i.e., no Ti ion is detected in solution (Ti_S). This finding, as well as the fact that adsorption values determined from the material balance ($\Delta Ti_S = Ti_0 - Ti_S$) and by direct analysis of the vacuumized filler after the interaction are similar, bears witness to the nonequilibrium nature of the process. This is obviously associated with the formation of sufficiently stable surface Ti compounds.

The compound formed at 80°C is particularly stable: In this case even addition of THF does not result in the appearance of Ti in solution. The difference in A_∞ at 80 and 22°C, which does not depend on the reaction time and Ti_0, allows one to assume that there exist at least two reactions of $TiCl_4$ with the chalk surface groups, taking place with different activation energies, and the reaction with a high activation energy is actualized only at elevated temperature.

According to rough estimates, $\sim 15 \times 10^{-6}$ mol $TiCl_4$ can be localized on the surface of 1 g of chalk used (containing $\sim 40 \times 10^{-6}$ CO_3^{2-} groups), i.e., A_∞ at 80°C corresponds to the monomolecular layer on the carbonate filler. On the other hand, coincidence of A_∞ (22°C) with $[H_2O]_F$ suggests that, in

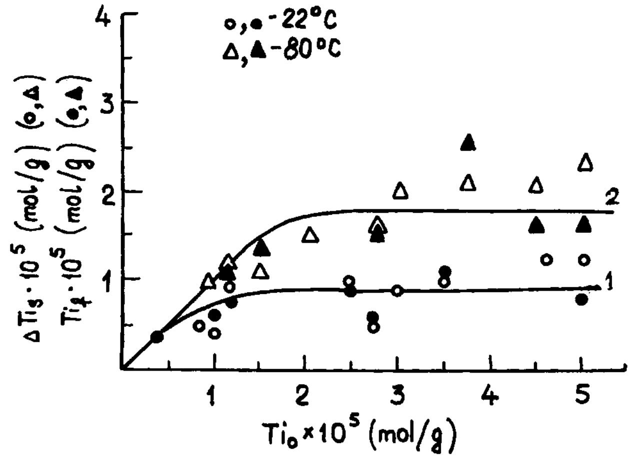


Fig. 2. Adsorption isotherm of $TiCl_4$ on the chalk surface: (1) 22°C; (2) 80°C.

this case, only the surface water molecules participate in $TiCl_4$ fixation. This assumption is supported by the fact that an increase in chalk humidity up to 20×10^{-6} mol/g, resulting from the introduction of additional H_2O, raises A_∞ (22°C) up to 20×10^{-6} mol/g of chalk.

The Cl/Ti ratio of the filler after the completion of the reaction is close to 4 irrespective of the reaction temperature. For organoaluminium compounds $A_\infty(80°C) = 20\text{–}30 \times 10^{-6}$ mol/g of chalk.

The Effect of Fixation Technique on the Filling Process

Prior to polymerization the filler was reacted (3–30 min) with Ti or Al components of the catalyst; their concentration ranges are given in Table I. In the chalk/Ti80°/Al system $Ti_0 \leq A_\infty$, while in the chalk/Al/Ti systems as a rule we have $Al_0 > A_\infty$. It is noteworthy that the systems obtained by chalk pretreatment with organoaluminium compounds in amounts close to A_∞ manifest a very slight activity and are activated upon the introduction of additional Al (chalk/Al/Ti/Al).

In all cases the polymerization reaction starts at the maximum rate; its value and intensity of decrease with time depend on the conditions of the catalytic system formation and the nature of the organoaluminium compound (typical kinetic curves of polymerization are shown in Fig. 3).

The kinetic curves are sufficiently well approximated by straight lines in the coordinates $1/W\text{–}\tau$ (Fig. 4). Such plots were used to estimate the initial specific activity $k_{o\,\mathrm{eff}}$ (Fig. 5) (by linear extrapolation to τ_0) and the deactivation rate constant k_d (by the slope of the curve).

In all the systems ultrahigh molecular weight PE can be obtained, and the limiting molecular mass of $1\text{–}2 \times 10^6$ is reached within a short time. The MM does not depend on Ti_0, and its dependence on Al_0 is determined by the way the catalyst has been formed (Fig. 6).

Depending on the conditions, the powders of the composites fractionated in the "gravity field" may contain: (1) one fraction (a "monodisperse" composite); (2) in addition to the main, monodisperse fraction, a small amount (1–9%) of heavy fraction enriched with the filler; (3) several fractions with a different filler content (Table II).

A decrease in fixation time (τ_f) in the interval of 30–3 min increases significantly the amount of the fraction enriched with the filler (Table II), though the polymerization kinetics remains unchanged. Thus, the data on the fractionation of the composite powder refer to the case of $\tau_f \geq 15$ min, except for specially mentioned cases. All the methods of forming the catalytic system make it possible to obtain a 50% UHMWPE–chalk composite with $\epsilon = 350\text{–}450\%$ (Table II, Fig. 8).

Chalk/Al/Ti ($Al_0 > A_\infty$) (1a)

These systems with $AliBu_3$ and $AlEt_3$ are characterized by a continuous decrease in polymerization rate (Fig. 4). Within the period of time required to obtain a 50% composite (Table II), their activity decreases by a factor of 5–25, depending on Ti_0 and Al_0. In the case of $AlEt_2Cl$ the systems are much more stable.

TABLE I
Conditions of the Catalytic Systems Formation

System	Fixed compound	Fixation temp (°C)	Fixation time (min)	Concentration range		Notation
				$[Ti]_0 \times 10^6$ (mol/g of chalk)	$[Al] \times 10^6$ (mol/g of chalk)	
$TiCl_4 + AlEt_3$	$TiCl_4$	22	3 ÷ 30	4–16	80–150	Chalk/Ti22°/Al
$TiCl_4 + AlEt_2Cl$				4–10	80–150	
$TiCl_4 + AlEt_3$	$TiCl_4$	80	15 ÷ 30	4–20	80–500	Chalk/Ti80°/Al
$TiCl_4 + AliBu_3$				4–20	80–500	
$TiCl_4 + AlEt_2Cl$				4–20	80–500	
$TiCl_4 + AlEt_3$	Aluminium Compound ($Al_0 > A_\infty$)	80	30	3–20	150–350	Chalk/Al/Ti
$TiCl_4 + AliBu_3$				3–20	150–350	
$TiCl_4 + AlEt_2Cl$				10–20	150–350	
$TiCl_4 + AlEt_3$	Aluminium compound ($Al_{0I} \approx A_\infty$)	80	30	3	30/40	Chalk/Al/Ti/Al
$TiCl_4 + AliBu_3$				3	30/40	
$TiCl_4 + AlEt_2Cl$				20	40/100	

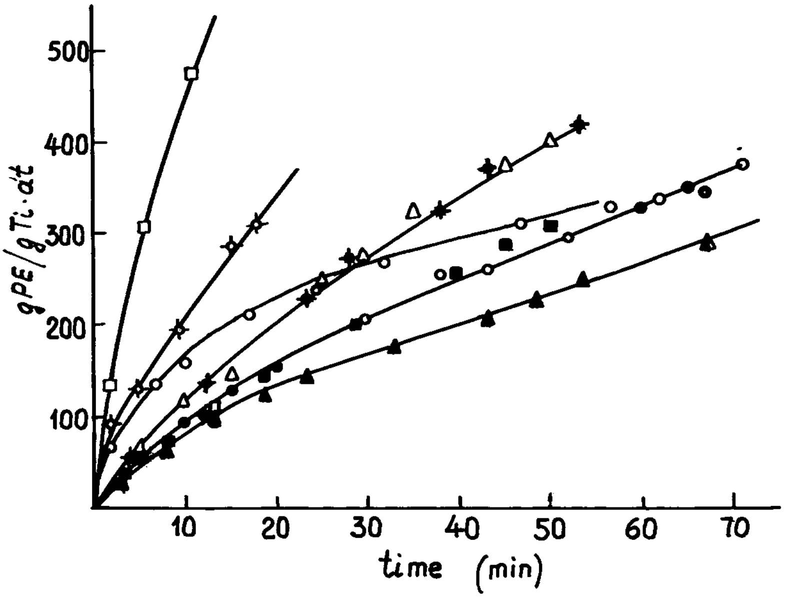


Fig. 3. Typical kinetic curves of ethylene polymerization. $Ti_0 = 10 \times 10^{-6}$ mol/g chalk, $Al_0 = 150 \times 10^{-6}$ mol/g chalk, 80°C, $P_{C_2H_4} = 5$ atm. $AliBu_3$: (□) chalk/Al/Ti; (■) chalk/Ti80°/Al; $AlEt_3$: (o) chalk/Al/Ti; (●) chalk/Ti80°/Al; (-ф-) chalk/Ti22°/Al; $AlEt_2Cl$: (△) chalk/Al/Ti; (▲) chalk, Ti80°/Al; (◆) chalk Ti22°/Al.

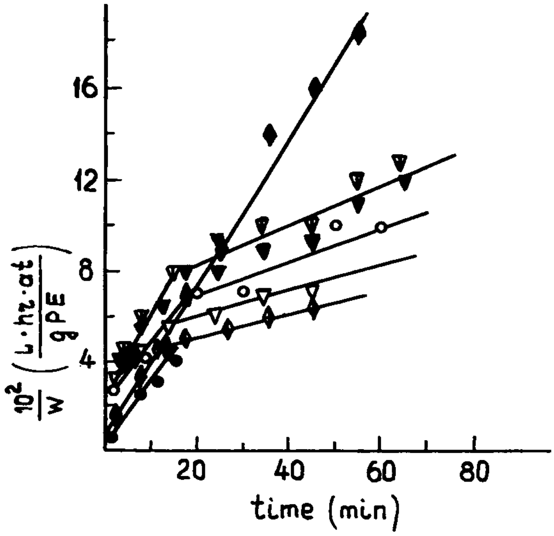


Fig. 4. Kinetic curves of Figure 3 in $1/w-\tau$ coordinates. $AliBu_3$: (⬘) chalk/Al/Ti; (△) chalk/Ti80°/Al; $AlEt_3$: (◆) chalk/Al/Ti; (▼) chalk/Ti80°/Al; (●) chalk/Ti22°/Al; $AlEt_2Cl$: (◈) chalk/Al/Ti; (▽) chalk/Ti80°/Al; (o) chalk/Ti22°/Al.

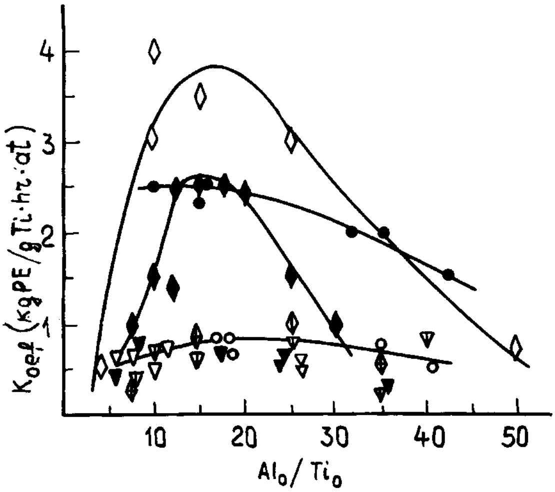


Fig. 5. Initial specific activity vs. the Al/Ti ratio (Ti_0 in mol/g of chalk × 10^6). $AliBu_3$: (◇) chalk/Al/Ti; (▽) chalk/Ti80°/Al; $AlEt_3$: (◆) chalk/Al/Ti; (▼) chalk/Ti80°/Al; (●) chalk/Ti22°/Al; $AlEt_2Cl$: (◈) chalk/Al/Ti; (▽) chalk/Ti80°/Al; (○) chalk/Ti22°/Al.

Irrespective of the absolute Al_0 and Ti_0, with an increase of their ratio $k_{0\,\mathrm{eff}}$ passes through a maximum (Fig. 5). This maximum is reached at Al/Ti = 15 (mol) and amounts to 3500, 2500, and 1000 g PE/(h atm g Ti) for AliBu, $AlEt_3$, and $AlEt_2Cl$, respectively.

k_d does not depend on Ti_0, and in the case of $AlEt_2Cl$ on its concentration (~ 0.6 atm L/g PE) either; for the systems with $AlEt_3$, k_d increases from 0.2 to 0.8 (atm L/g PE) as Al_0 increases from 150×10^{-6} to 350×10^{-6} mol/g of chalk. Within the same concentration range of $AlEt_3$, MM of PE drops from 1.6×10^6 to 0.4×10^6 (Fig. 6). It should be noted that, despite the fact that k_d does not depend on $AlEt_2Cl$ concentration, MM decreases significantly with increasing $AlEt_2Cl$ concentration (most likely because of the chain transfer onto $AlEt_2Cl$).

The chalk/Al/Ti systems are similar to colloidal-disperse catalysts.[10,11] Indicative of this are their activity values, the nature of activity dependence on the type of organoaluminium compounds ($AliBu_3$ > $AlEt_3$ > AlEtCl) and

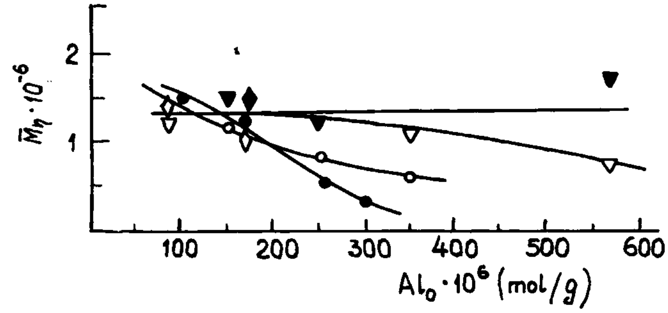


Fig. 6. $\overline{M}_\eta$ of PE vs. Al_0 concentration. $AlEt_3$: (●) chalk/Al/Ti; (▼) chalk/Ti80°/Al; (◆) chalk/Ti22°/Al; $AlEt_2Cl$: (○) chalk/Al/Ti; (▽) chalk/Ti80°/Al; (◇) chalk/Ti22°/Al. $Ti_0 = 10 \times 10^{-6}$ mol/g chalk.

TABLE II
Polymerization Time and Properties of the Composite (~ 50 wt % Chalk)

Catalytic system 1	Ti × 10^6 (mol/g) 2	Al$_0$ × 10^6 (mol/g) 3	Polymerization time (min) 4	$\overline{MM}_\eta \times 10^6$ 5	Character[c] of powder distribution 6	Content of the fractions with $\varphi \geqslant 50\%$ 7	ϵ (%) 8
Chalk/AlEt$_3$/Ti[a]	20	170	70	1.7	m	Traces	350
	10	200	240		b	3% (φ = 40%) 3% (φ = 56%) 1% (φ = 70%)	220
Chalk/AliBu$_3$/Ti[a,b]	10	80	25	1.0	b	40% (φ = 27%) 43% (φ = 33%) 16% (φ = 45%) Traces(φ ~ 60%)	380
	3	80	100	2.0	b	45%(φ = 48%) 7%(φ = 75%)	90
Chalk/AlEt$_2$Cl/Ti[a]	10	250	40	0.8	m	Absent	370
	10	350	70	0.6	b	45% (φ = 56%) 9% (φ = 77%)	150
Chalk/Ti80°/AlEt$_3$	10	170	70	1.5	m	Absent	330
	10	480	120	1.7	m	Absent	290
	5	170	500		m	Traces	300

(Continued from the previous page.)

Chalk/Ti80°/$AlEt_2Cl$	12	150	40		m	Absent	490
	12	560	607	0.8	m	Traces	220
	5	170	400	1.6	bim	7% (φ = 62%)	150
Chalk/Ti22°/$AlEt_3$	16	150	30		bim	2% (φ = 61%)	340
τ_f = 15 min	4	150	150		bim	2% (φ = 71%)	240
τ_f = 3 min	12	170	15		bim	2% (φ = 56%)	200 (considerable spread)
	5	170	150		bim	7% (φ = 70%)	30
Chalk/Ti22°/$AlEt_2Cl$							
τ_f = 15 min	10	170	100		bim	2% (φ = 70%)	400
	5	170	200	1.0		9% (φ = 70%)	50
						after separation of the "heavy" fraction	320
	5	80	250	1.3	m	Absent	420
τ_f = 3 min	12	170					230 (considerable spread)
Chalk/$AliBu_3$/Ti/$AliBu_3$	3	30/40	15				300
Chalk/$AlEt_2Cl$/Ti/$AliBu_3$	3	30/40					450

---

[a] The PE MM values in the isolated fraction are identical.

[b] φ = 35%.

[c] m = monodisperse, b = broad, bim = bimodal.

the character of their disactivation with time. This is associated with a large contribution of the polymerization process beyond the chalk surface, which leads to the formation of fractions with the filler content differing from the average one (Table II). Formation of a heterogeneous catalyst outside the chalk surface is especially facilitated if at the moment of $TiCl_4$ introduction there are organoaluminium compounds with a high reducing capacity ($AlEt_3$, $AliBu_3$) in solution.

Chalk/Al/Ti/Al (1b)

If an organoaluminium compound is introduced in two stages ($Al_{10} \approx A_{\infty}$, Table I), $k_{0\,\mathrm{eff}}$ is 600 and 1500 g PE/(h atm g Ti) for $AlEt_2Cl$ and $AlEt_3$, respectively; in this case, unlike the chalk/Al/Ti catalyst discussed above, the process is stabilized after a short initial period of activity decrease. Systems with a two-stage introduction of $AliBu_3$ are the most effective. Approximate $k_{0\,\mathrm{eff}}$ in this case is 5000–6000 g PE/(h atm g Ti).

Chalk/Ti80°/Al (2a)

With these systems, after a short period of time the process becomes practically stable (Fig. 3). The kinetic curves in the $1/w-\tau$ coordinates (Fig. 4) consist of two linear portions with $k_d = 0.2$ and 0.05 L atm/g PE, irrespective of the nature of the cocatalyst, Ti_0 and Al_0. These parameters affect the MM values (Fig. 6) only slightly. For the systems with $AliBu_3$, $AlEt_3$, and $AlEt_2Cl$ (Fig. 5), $k_{0\,\mathrm{eff}}$ reaches its maximum (600–700 g PE/(h atm g Ti) when $Al/Ti \approx 7$, and after that it depends very slightly on the Al/Ti ratio.

Thus, in the systems formed with a high-temperature $TiCl_4$ fixation, triethyl- and triisobutylaluminium cannot be considered as more active catalysts than $AlEt_2Cl$: Their $k_{0\,\mathrm{eff}}$ values are 3–5 times lower than in the chalk/Al/Ti systems, while, in the case of $AlEt_2Cl$, $k_{0\,\mathrm{eff}}$ decreases only by 30%. The constancy of catalytic activity with time, a weak influence of Al concentration on MM of PE, as well as the monodispersity of the composite powder (Table II) indicate that most of the active centers are localized on the surface.

The processes with the participation of surface water molecules (e.g., the hydrolysis of Ti compounds) are probably of minor importance for the formation of such active centers. This is supported by the proportional relationship between W_0 and Ti_0 (Fig. 7) up to the chalk concentration of 20×10^{-6} mol/g (much higher than $[H_2O]_F$) with the threshold value of $Ti_0 \sim 1 \times 10^{-6}$ mol/g of chalk, which is much lower than $[H_2O]_F$.

It is of interest to note that, for the catalysts obtained by $TiCl_4$ fixation at 80°C on the kaolin surface with much higher $[H_2O]_F$ values (30×10^{-6} mol/g), one also observes a proportional growth of W_0 in the same range of $TiCl_4$ concentrations with a similar threshold value of the latter (Fig. 7, curve 2). In the interval studied of $[H_2O]_F/Ti_0$ ratios, it can be assumed that no hydrolysis takes place under the given fixation conditions just as in the case when stoichiometric quantities of water interact with CH_3TiCl_3.[12]

A change in the usual order of cocatalyst activity seems to be caused by the modification of the active center owing to the formation of a sufficient bond

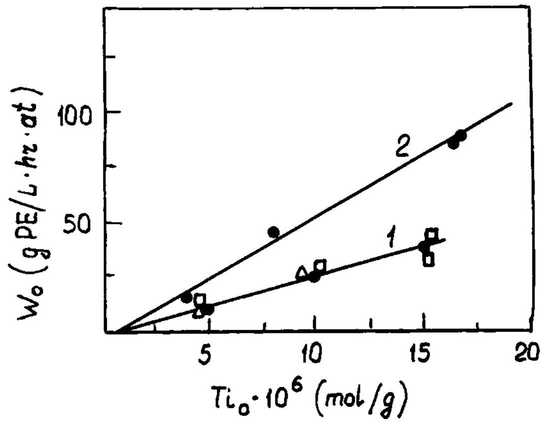
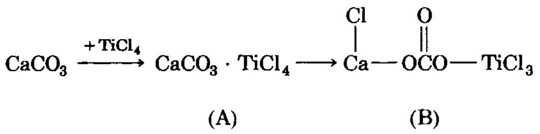


Fig. 7. Initial polymerization rate vs. Ti_0. 80°C, $P_{C_2H_4} = 5$ atm. (●, △, □) $AlEt_2Cl$, $AlEt_3$, $AliBu_3$. (1) chalk/Ti80°/Al, $Al_0 = 150 \times 10^{-6}$ mol/g chalk; (2) kaolin/Ti80°/Al, $Al_0 = 220 \times 10^{-6}$ mol/g chalk.

between the Ti compound and the carbonate groups, which is resistant to the cocatalyst action.

Since the complex with the carbonate anion (A) must be inactive because of the absence of the coordination site, the polymerization process can be associated with the surface compound Ti(B):

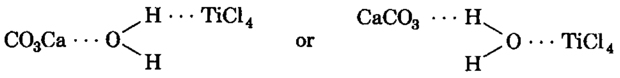


$$CaCO_3 \xrightarrow{+TiCl_4} \underset{(A)}{CaCO_3 \cdot TiCl_4} \longrightarrow \underset{(B)}{\overset{Cl}{\overset{|}{Ca}}-O\overset{O}{\overset{\|}{C}}O-TiCl_3}$$

Chalk/Ti22°/Al (2b)

The systems based on the products of $TiCl_4$ interaction with chalk at 22°C combine the features characteristic of systems **2a** and **1a**. On the one hand, at $Ti_0 \leq A_\infty$ their activity is also stabilized with time (Figs. 3 and 4). On the other hand, just as in the case of the chalk/Al/Ti systems, $k_{0\,\mathrm{eff}}$ depends significantly on the nature of aluminium compound (700–900 g PE/(h atm g Ti) for the catalysts with $AlEt_2Cl$ and 2000/2500 g PE/(h atm g Ti) for the systems with $AlEt_3$ (Fig. 5).

As already noted, adsorbed water molecules take part in $TiCl_4$ fixation at 22°C. It can be expected that their participation is reduced to the formation of aquacomplexes:



$$CO_3Ca \cdots O\begin{matrix}\diagup H \cdots TiCl_4 \\ \diagdown H\end{matrix} \quad \text{or} \quad \begin{matrix}CaCO_3 \cdots H\diagdown \\ H\diagup\end{matrix} O \cdots TiCl_4$$

In this case the $TiCl_4$ bond with the surface is weak and is disrupted in the course of interaction with organoaluminium compounds to form the $TiCl_3$ phase distributed over the chalk surface. As a result, for all the three cocatalysts the activity is close to that of the corresponding colloid-disperse systems.

As distinct from system 2a, the powder of the composite in all cases (with $Ti_0 \leq A_\infty$, as well as $Ti_0 > A_\infty$) contains a "heavy" fraction (Table II). As seen from the table, the formation of this fraction is facilitated by a decrease in Ti_0 and τ_f and the use of $AlEt_2Cl$. An enhanced yield of the "heavy" fraction in the case of polymerization with $AlEt_2Cl$ attests to the significant role of aluminium compound in displacing Ti compound into the solution. Reactions of this type are known to be promoted by the enhanced ability of Al to form complexes.[13]

Ductility of the Composites (φ = 50 wt %) and their Homogeneity

The σ_p of the composites with 50% of chalk depends only slightly on the method of catalyst preparation and on the concentrations of its components, amounting in all cases to 150–200 kg/cm^2. The ϵ of these composites depends substantially on the conditions of the catalytic system preparation and varies in the range of (450 ÷ 50)% (Fig. 8). As a rule, a decrease in ϵ is caused by an increase in the Al/Ti ratio, the intensity of such dependence being determined by the type of the catalytic system.

The weakest dependence of ϵ on the Al/Ti ratio is observed for systems **2a.** In this case a decrease in Ti_0 from A_∞ (20×10^{-6} mol/g of chalk) to 5×10^{-6} mol/g ($Al_0 = 150 \times 10^{-6}$ mol/g), or increase in Al_0 up to 500×10^{-6} mol/g ($Ti_0 = 10 \times 10^{-6}$ mol/g), does not practically change ϵ of the composites in the case of $AlEt_3$ or $AliBu_3$ and decreases it to ~ 200% in the case of $AlEt_2Cl$.

In the latter case a decrease in ϵ is not connected with the decrease MM of PE (Fig. 6). On the other hand, the powders of the composites obtained with the chalk/Ti80°/$AlEt_3$ $(AliBu)_3$ catalysts are monodisperse in the whole concentration range (Tables I and II), whereas in the case of $AlEt_2Cl$ a decrease in Ti_0 down to 5×10^{-6} mol/g results in the appearance of ~ 7 wt % of the "heavy" fraction (φ = 60 wt %), which is, evidently, responsible for the ϵ drop.

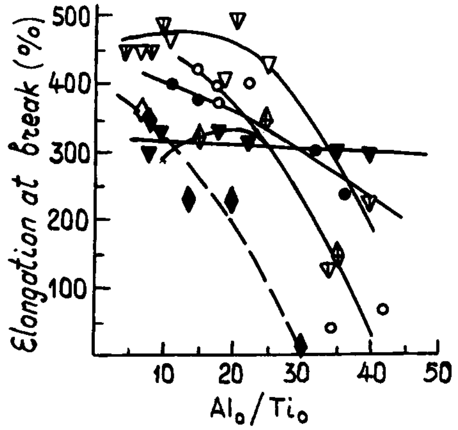


Fig. 8. ϵ values of the composites with 50 wt % of chalk vs. the Al/Ti ratio. $AliBu_3$: (◇) chalk/Al/Ti; (▽) chalk/Ti80°/Al; $AlEt_3$: (◆) chalk/Al/Ti; (▼) chalk/Ti80°/Al; (●) chalk/Ti22°/Al; $AlEt_2Cl$: (◈) chalk/Al/Ti; (▽) chalk/Ti80°/Al; (○) chalk/Ti22°/Al.

In systems **2b**, composites with $\epsilon = 350$–450% can be obtained in the range of $Ti_0 = 8$–16×10^{-6} mol/g at $Al_0 = 150 \times 10^{-6}$ mol/g. A decrease in Ti_0 to 4×10^{-6} mol/g leads either to a decrease in ϵ to 250% ($AlEt_3$) or to a complete loss of ductility ($AlEt_2Cl$). It should be noted that in the latter case the lowering of Al_0 to 80×10^{-6} mol/g results in the restoration of a high ϵ value (up to 400%). Thus, ϵ depends to a greater extent on the ratio of the components than on their absolute concentrations.

Since MM of PE does not decrease (Fig. 6), the drop of ϵ for $AlEt_2Cl$ can be attributed to the "heavy" fraction content rising from 1 to 9% (Table II), the more so that the removal of this fraction results in ϵ rising up to 300%.

It has already been noted that a decrease in τ_f from 15 to 3 min leads to an increase in the "heavy" fraction content. The influence of τ_f is especially strong at low Ti_0 (5×10^{-6} mol/g). In this case at $\tau_f = 3$ min the powder contains ~ 7% of the "heavy" fraction ($\varphi = 70$ wt %), with ϵ of the block material being ~ 30%.

The sharpest decrease in ϵ with increasing Al/Ti ratio occurs in the composites obtained after chalk pretreatment with an excess of $AlEt_3$ or $AliBu_3$ (from 350–380% at Al/Ti = 10 to 10% at Al/Ti = 30). A decrease in ϵ in these cases can be attributed not only to a certain deterioration of the composite homogeneity (Table II) but also to the MM decrease[14,15] (Fig. 6).

The above peculiarities of filler distribution in the powder obviously bring about, in a block material, characteristic dependences of the distribution of the distance between the particle surfaces on the method of composite preparation. It is also possible for the particles to adhere to one another with the polymerization simultaneously taking place on the chalk surface and beyond it, as well as for large particles present in the initial chalk powder to be destructed. According to Refs. 2 and 15, the average sizes of particles, as well as their size distribution and agglomeration, exert a significant influence on the composite deformation and fracture process.

SEM studies of composite films have shown the monodisperse powder obtained in the **2a** system, where the polymerization process occurs on the filler surface, to cause (in accordance with Ref. 2) the formation of a homogeneous texture (Fig. 9) in the block material. In the case of polymerization with the **1** system, where the contribution of the process outside the chalk surface is significant, even a monodisperse in the powder 50% composite, turns out to be markedly inhomogeneous.

To describe quantitatively the filler size distribution in the composites obtained with systems **2a** and **2b**, the size distribution of particles and agglomerates of contacting particles (f_d) in the material has been estimated. The distribution is characterized by the following mean values:

$$\overline{M}_n = \frac{\sum_{j=1}^{k} f_j d_j}{\sum_{j=1}^{k} f_j d_j^{n-1}}$$

where $n = 1, 2, 3$; f_j is the numerical fractions of particles and agglomerates of the d_j size, and k is the total number of particles and agglomerates

Fig. 9. Microphotograph of the composite-film low-temperature fracture surface, obtained with the chalk/Ti80°/Al catalytic system (50 wt % of chalk).

TABLE III
Structural Characteristics of the Composite Films (According to SEM)[a]

System	φ (wt %)	M_1 (μm)	M_2 (μm)	M_3 (μm)
1. Chalk/Ti80°/Al	50	2.9	4.1	5.6
2. Chalk/Ti80°/Al	70	3.4	4.4	5.5
3. Chalk/Ti22°/Al (after the separation of the "heavy" fraction)	50	3.0	4.0	5.2
4. "Heavy" fraction	70	6.3	9.1	12.5

[a] M_n = the corresponding moment of size distribution of contacting particles in the composite.[9]

analyzed. The mean M_1 and M_2 of the above function characterize the number-average and weight-average sizes of particles and agglomerates in the system; large particles and agglomerates, accounting for the right wing of the F_d function, make the main contribution into M_3. The structural characteristics obtained for the studied composites are given in Table III.

It is noteworthy that the composites obtained with system **2a** are characterized by similar size distribution of the particles and the agglomerates of contacting particles, irrespective of φ. The mean size of effective inclusion is approximately 3 μm*; the distributions dispersion differ insignificantly. The fraction of inclusions with sizes larger than 8 μm are not to exceed 2–3%.

---

*M_1 determination is estimated since it is difficult to determine quantitatively the fine fractions (≤ 1 μm) with the procedure used.

In the composites with "bimodal" distribution of the powder (system **2b**) the main fraction does not differ by the distribution characteristics from the above monodisperse composite. At the same time, the distribution function in the "heavy" fraction ($\varphi = 70$ wt %) is shifted towards larger sizes; the composite contains ~ 2% of particles > 20 μm in size, and the average size of the effective inclusion rises up to ~ 6 μm. Qualitative analysis of the fracture surfaces indicates that the filler particle dispersity in the composite (sample 4) is also lowered in comparison with samples 1 and 2 (Table III). The influence of this small amount of large agglomerates is so strong that if the sample contains 7% of the fraction incorporating them, it can cause complete embrittlement of the material.

Comparison of the effective particle size distribution in "homogeneous" composites containing 70% of chalk and in the "heavy" fraction with the data on particle distribution in the initial chalk makes it possible to assume that the "heavy" fraction is formed on the basis of large filler particles whose "internal surface" does not take part in polymerization. The filler fixation conditions determine the catalytic complex concentration on the surface of these particles and the intensity of their destruction in the course of polymerization and polymer layer formation.

The influence of the polymer layer thickness at a given filler concentration has been demonstrated in the synthesis of the composites consisting of the "concentrate" (10–20 wt % of UHMWPE) and "free" UHMWPE-"diluent". The concentrates were obtained by ethylene polymerization effected by the "optimum" system, chalk/Ti80°/$\mathrm{AliBu_3}$; the filler activation in this case ensures the "break-up" of large chalk aggregates (Fig. 9). It has been shown by the ESCA technique* that if the "concentrate" contains even 10 wt % of PE, the chalk surface is completely covered by the polymer.

Dilution of the "concentrate" by PE down to its concentration of 50–60 wt % was carried out by *in situ* polymerization with TMC. TMC polymerizes ethylene outside the chalk surface [in the 50% PE–chalk composites obtained with TMC the extent of surface coverage, according to ESCA, does not exceed 60% and $\varphi = 14\%$ (Table IV)]. In some experiments 50% chalk composites were obtained by simultaneous polymerization of PE on the filler activated with $\mathrm{TiCl_4}$ at 80°C and in the bulk, with TMC as a catalyst (similarly to Ref. 5).

According to the fractionation data, the dilution of the "concentrate" with PE results in a powder consisting of two fractions corresponding to the "concentrate" and pure PE; "synchronous" polymerization catalyzed by the chalk/$\mathrm{TiCl_4}$/TMC–$\mathrm{AliBu_3}$ system leads to a broad distribution of material with respect to φ. The ϵ of the composites proved to depend only on the PE content in the "concentrate." Similarly to homogeneous composites, the composites containing a "concentrate" with 15–20% of UHMWPE and "diluted" UHMWPE have $\epsilon = 350$–450%. A decrease in the PE content in the "concentrate" to 10 wt % results in ϵ dropping to 40% (Table III).

Thus, there is a limiting size of the polymer layer between the chalk particles which makes it possible to obtain 50% composites of UHMWPE with

---

*The authors wish to express gratitude to L. N. Grigorov for the ESCA analysis of composites.

TABLE IV

Stress–Strain Characteristics of the Composites Obtained in Polymerization Process with TMC ($[\text{AliBu}_3]_0 = 150 \times 10^{-6}$ mol/g; $[\text{TMC}]_0 = 0.8 \times 10^{-6}$ mol/g)

Preparation technique	$[\text{TiCl}_4] \times 10^6$ (mol/g)	PE content in the concentrate (%)	$\overline{\text{MM}}_\eta \times 10^{-6}$ of the concentrate	PE content of the composite (%)	Characteristics		
					σ_t (kg/cm^2)	σ_p (kg/cm^2)	ϵ (%)
Chalk–TMC/AliBu$_3$	—			62	160	—	14
Dilution of the "concentrate" by PE	5.8	10	1.3	62	180	180	40
	5.8	17	2.2	57	320	200	470
	3	22	2.7	63	210	180	215
	5.8	27	2.5	59	230	190	370
"Synchronous" process	12			54	180	160	320
	12			57	200	170	290
	5.8			63	210	190	400

a high ductility. It can be assumed that fluctuations of the density of the filler local distribution prove to be dangerous when polymer layers between the filler particles are incapable of withstanding the local stresses applied to the agglomerate, and their breakup results in the formation of large vacuoles. Otherwise, if the polymer interlayers are effective enough in load bearing, the existence of the aggregates of contacting particles not separated by the polymer layers becomes the determining factor.

It should be emphasized that the effect of a small number of large defects on the strength of plastic flow regions in the filled composites requires comprehensive studies. Such defects can decrease the effective cross section in the zone of the flow by initiating the formation of large pores, as well as increase the local stress and strain concentrations.

Stress–Strain Characteristics of "Homogeneous" Composites

Let us consider the main regularities in the mechanical behaviour of composites when the polymerization is actualized on the filler surface (chalk/Ti80°/Al) and results in the formation of "homogeneous" composites.

Concentration dependences of σ_t and σ_p are presented in Figure 10. They can be described by the following equation, which holds true for a large number of filled polymeric systems[15, 16]:

$$\sigma^c = \sigma^m(1 - \alpha\varphi^{2/3}) \qquad (1)$$

where σ^c is the strength or yield strength of the composite, σ^m is a similar characteristic for a matrix polymer, and α is the coefficient depending on the particle size, when the debonding of particles is incomplete, and on the level of adhesive interaction at the interface.[17]

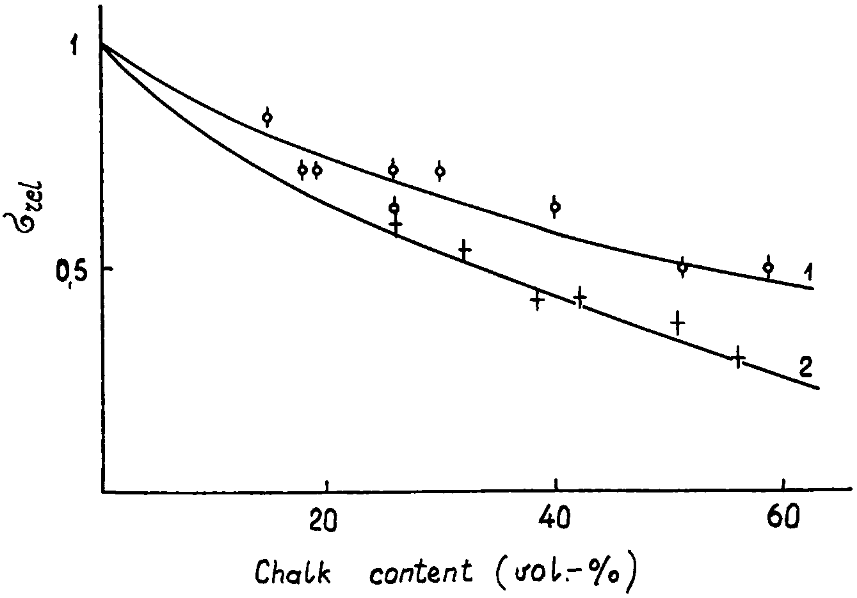


Fig. 10. Relative yield strength (1) and relative strength (2) vs. the filler volume content in the composites. The curves correspond to calculations according to the equation $\sigma_{rel} = 1 - \alpha\varphi^{2/3}$.

Equation (1) is substantiated by the effective cross section model, which assumes the debonding of matrix polymer from the filler, stress redistribution on polymer layers, and their subsequent uniaxial deformation. In the absence of adhesion and complete debonding of the filler from the polymer, $\alpha = 1 \div 1.21$. In the case in question $\alpha_p \sim 0.77$ and $\alpha_t \sim 1.05$, which indicates a partial debonding of the filler from the polymer, with the peeling process continuing after the yield strength has been reached and right up to destruction of the material.

According to the SEM fractography data, the debonding with subsequent viscous rupture of polymer interlayers results in the "facet" pattern characterized by destruction pits, whose geometry depends on the size and location of the debonded filler particles. It may be assumed that, the flow being of localized nature, the plastic deformation of the sample will be taking place until the maximum strength in the zone of the flow will be no less than the stresses required for the plastic flow to develop in the sample ($\sigma_t^c \geq \sigma_p^c$). Taking into account that, according to Figure 10, $\sigma_t^c = \sigma_t^m(1-1.05\,\varphi^{2/3})$ and $\sigma_p^c = \sigma_p^m(1-0.77\,\varphi^{2/3})$, one can estimate the critical concentration of the filler, resulting in the embrittlement of the material, i.e., in a loss of its ability to macroscopic plastic flow:

$$\varphi_{cr} = \left(\frac{\sigma_t^m/\sigma_p^m - 1}{\left(\sigma_t^m/\sigma_p^m\right)1.05-0.77}\right)^{3/2} = 56\%\ (\mathrm{vol})$$

where $\sigma_t^m/\sigma_p^m = 1.67$ for analyzed UHMWPE.

As follows from Figure 11, this estimation of φ_{cr} gives a quite reasonable prediction of the filling level at which the transition to macroscopic brittle failure of the material takes place. The extremely high φ_{cr} values result, on the

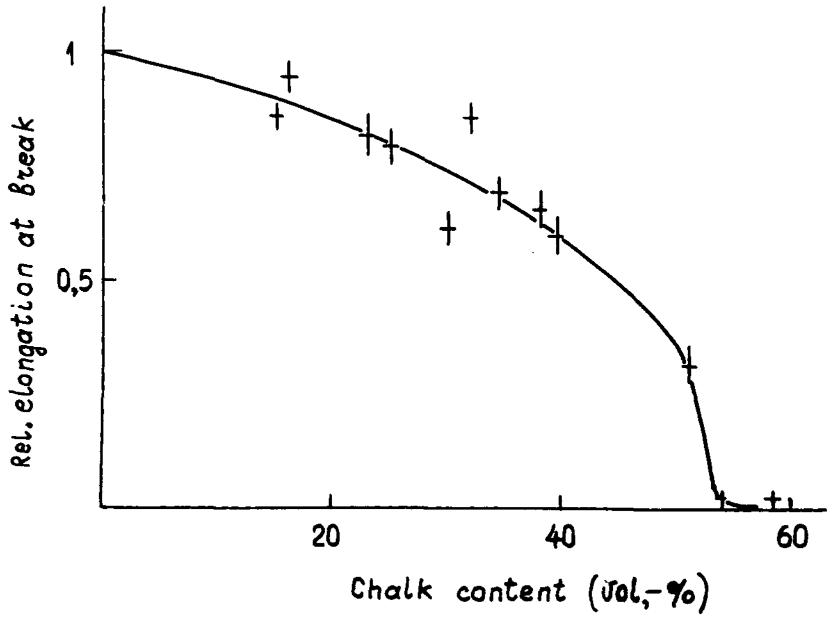


Fig. 11. Relative elongation at rupture vs. the filler content in the composites.

one hand, from the ultrahigh molecular mass of the studied polymer and its unique strain hardening characteristics[18, 19] and, on the other hand, from a high uniformity of filler distribution in the composite. The obtained φ_{cr} values prove to be not lower than those obtained in Ref. 15 when studying the deformation properties of the composites based on UHMWPE and narrow fractions of aluminium hydroxide.

A monotonic decrease in elongations with increase in filler content to 50 vol % (Fig. 11) may be due to the fact that nondeformable particles of the filler restrict the plastic deformation of polymer. This effect would be more pronounced the lower the fraction of debonding filler particles.[20]

References

1. L. A. Kostandov, N. S. Yenikolopov, F. S. Dyachkovsky, L. A. Novokshonova, O. I. Kudinova, Yu. A. Gavrilov, L. A. Akopyan, and Kh.-M. A. Brikenshtein, U.S. Pat. 4241112 (1980); Fr. Pat. 7828024 (1980).

2. E. G. Howard, R. D. Lipscomb, R. N. McDonald, B. L. Glazar, C. W. Tullock, and J. W. Collette. *Ind. Eng. Chem. Prod. Res. Dev.*, **20**, 421 (1981).

3. F. S. Dyachkovsky and L. A. Novokshonova. *Usp. Khim.*, **53**, 200 (1984).

4. N. V. Semikolenova, G. A. Nesterov, and V. A. Zakharov, *Visokomol. Soed.*, **A27**, 1988 (1985).

5. W. S. Schöpel and K.-H. Reichert, *Makromol. Chem. Rapid Commun.*, **3**, 483 (1982).

6. V. M. Gorelik, V. Sh. Berner, L. F. Borisova, L. A. Shesternina, N. M. Bichkov, R. N. Durnova, E. S. Skvortsova, G. N. Kornienko, V. I. Sergeev, and E. A. Fushman, in *Complex Organometallic Catalysts of Olefin Polymerization*, Institute of Chemical Physics, Akad. Nauk SSSR, Chernogolovka, 1986, vol. 10, p. 44.

7. V. M. Gorelik, L. A. Shesternina, A. D. Yemelyanova, L. F. Borisova, E. A. Fushman, V. Sh. Berner, and N. N. Korneev, *Zh. Obshch. Khim.*, **55**, 2506 (1985).

8. Ger. Pat. 1795197 (1968) (Hoechst A. G.); *Chem. Abstr.*, **73**, 778349 (1970).

9. Yu. M. Tovmasyan, V. A. Topolkaraev, M. N. Knunyants, V. G. Oshmyan, A. A. Berlin, E. F. Oleinik, and N. S. Yenikolopyan, *Dokl. Akad. Nauk SSSR*, **270** (3), 649 (1983).

10. I. N. Meshkova, S. M. Kumankova, V. I. Tsvetkova, and N. M. Chirkov, *Visokomol. Soed.*, **3**, 1817 (1961).

11. N. N. Severova, E. V. Veselkovskaya, A. D. Pechenkin, E. N. Nalivayko, B. I. Sazhin, *Plast. Massi*, **12**, 24 (1976).

12. O. M. Chukanova, N. E. Khrushch, F. S. Dyachkovsky, and N. S. Yenikolopyan, *Izv. Akad. Nauk SSSR, Ser. Khim.*, **12**, 2686 (1986).

13. O. H. Ellestad and U. Blindheim, *J. Mol. Catal.*, **33**, 289 (1985).

14. I. L. Dubnikova, I. N. Meshkova, V. G. Grinev, Yu. M. Tovmasyan, and F. S. Dyachkovsky, *Dokl. Akad. Nauk SSSR*, **281**, 629 (1985).

15. V. A. Topolkaraev, Yu. M. Tovmasyan, I. L. Dubnikova, I. N. Meshkova, Al. Al. Berlin, Yu. P. Gomza, and V. V. Shilov, *Mekh. Kompos. Mater.*, **4** 616 (1987).

16. E. Nielsen. *J. Appl. Polym. Sci.*, **10**, 97 (1966).

17. K. Mitsuishi, S. Kodawa, and H. Kawasaki, *Polym. Eng. Sci.*, **25**, 1069 (1985).

18. V. A. Marikhin and L. P. Myasnikova, *Supermolecular Structure of Polymers*, Leningrad, 1977, p. 237.

19. P. Chacko, R. J. Farris, and F. F. Karasz, *J. Appl. Polym. Sci.*, **28**, 2701 (1983).

20. V. G. Oshmyan, thesis, Chernogolovka, 1986.

Received April 20, 1989
Accepted July 13, 1989