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Original Contributions

Non-isothermal crystallization of UHMWPE filled during polymerization with inorganic fillers

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Abstract: The non-isothermal crystallization of UHMWPE, filled with different inorganic fillers during the polymerization on the catalyst system $TiCl_4/(C_2H_5)_2AlCl/(C_6H_5)_2Mg$ has been studied by DSC and polarization microscopy. The melting conditions of UHMWPE have been established before the crystallization experiments. It is shown that the fillers act as nucleating agents only when the crystallization is carried out from a melt, obtained at temperature above the flow temperature of UHMWPE, and at slow cooling rate. It was established that the efficiency of nucleation passes through maximum at 50 wt.% of the filler. It is assumed that this is due to the reduction of the heterogeneous sites, because of the aggregation of the filler with high concentration. The non-isothermal crystallization kinetics is studied by Harnisch and Muschik method. The Avrami exponents do not change in the presence of a filler with concentration up to 90 wt.%.

Key words: Ultra-high molecular weight polyethylene, filled – non-isothermal crystallization kinetics

Introduction

The study of non-isothermal crystallization of polymers is of great technological significance, since most practical processing techniques proceed under non-isothermal conditions. Moreover, from a scientific point of view, non-isothermal experiments may mean a great deal in view of the understanding of the crystallization behavior of polymers, because the more used isothermal methods are often restricted to narrow temperature ranges.

Ultra-high molecular weight polyethylenes (UHMWPE) can have valuable physical and mechanical properties, such as high toughness, impact strength, abrasion and corrosion resistane and low friction coefficient. The melt index of UHMWPE approaches zero. So, it limits the possibility of the filling of the polymer by mixing the melt and the filler. The filling of UHMWPE is possible only during polymerization process. The method under consideration allows the obtaining of homogeneous, high-filled composite materials without using disperse agents. The composites of UHMWPE with $Al(OH)_3$ [1] or with siloxane [2] have incresed plasticity, strain capacity, tensile and impact strength.

The UHMWPE filled by inorganic fillers during polymerization on the catalyst system $TiCl_4$–$(C_2H_5)_2AlCl$–$(C_6H_5)_2Mg$ was studied in our previous papers [3, 4]. It was found that the filler particles are covered by a polymeric layer. It was established that the strength and the relative elongation values for filled UHMWPE up to filling degree about 20 wt.% are higher than those for unfilled one.

It is well known that the presence of the filler influences markedly the polymer crystallization behavior, which affects the physicomechanical properties. The investigations of filled polypropylenes and polyethylenes with isothermal methods show that the inorganic fillers ($CaCO_3$, glass fiber, carbon fiber) increase their crystallization rate [5–9]. The influence of inorganic fillers on the

Table 1. Characteristics of the fillers

Characteristics	Chalk	Marble powder	Bentonite	Dolomite	Perlite	Kaolin
Specific surface area (m^2/g)	3.1	4	70.1	2.5	0.9	22.3
Particle size (μm)						
		Different distribution (%)				
< 3	39	16.9	5.1	10.3	1.1	14.9
3–5	23.5	14	6.2	7.4	3.1	15.9
5–10	16	14.9	11.8	8.4	10.4	15.9
10–20	20.1	22	20.1	13.8	24.2	19.4
20–30	1.4	21	28.8	19.3	24.7	17.9
30–40	–	10.4	13	19.7	17.5	13
> 40	–	0.8	15	21.1	19	3

crystallization behavior of the UHMWPE have not been studied yet. This is probably due to the very high viscosity of its melt, which is why the establishment of the melting conditions before the crystallization experiments is difficult.

We consider it of interest to investigate the influence of different inorganic fillers with concentration up to 90 wt.% on the non-isothermal crystallization of filled UHMWPE, and to test the validity of the Harnisch equation for these systems, as well.

Experimental

Powder-like nascent samples of UHMWPE, filled by inorganic fillers during polymerization are investigated. The catalyst system $TiCl_4$–$(C_2H_5)AlCl$–$(C_6H_5)_2Mg$ is applied. The preparation of the filler-catalyst systems and the polymerization processes have been described [3, 4]. Chalk, marble powder, bentonite, perlite, dolomite, and kaolin are used as fillers (Table 1). Polyethylene samples with various degrees of filling are obtained: 12.2, 31.4 and 55 wt.% (marble powder); 11.4, 34, 45 and 90 wt.% (chalk); 7 wt.% (bentonite); 7.1 wt.% (dolomite); 20.2 wt.% (perlite); 32 wt.% (kaolin). The polyethylene obtained has molecular weight above 10^6, determined from the data of the characteristic viscosity.

The non-isothermal crystallization of the samples is studied by polarizing optical microscopy and differential scanning calorimetry. The optical microscope observations are performed with a Reichert-Zetopan polarization microscope with a hot stage. The H_v-diffraction patterns of low-angle light scattering are obtained by applying the Bertran lens. The microscope is calibrated with a diffraction lattice with definite distance between the lines.

The DSC studies are carried out with a Perkin-Elmer DSC-7 apparatus in argon. DSC-apparatus is calibrated with indium and tin standards at various scanning rates. According to [10, 11], temperature calibration as function of cooling rate is required for the investigation of the non-isothermal crystallization kinetics. The value of 293.1 J/g is used for enthalpy of crystallization of 100% crystalline polyethylene [12].

Results and discussion

Study of the melting conditions

It has been shown by us [13] and by other authors [14] that UHMWPE exhibit high concentration of tie molecules. When the aggregates of the nascent UHMWPE are heated to 190 °C the polymer retains its appearance. The points of entanglement of the long molecules are preserved even after melting [15, 16]. The flow of UHMWPE occurs above temperature of 210 °C.

Thus, it could be assumed that the preexisting crystalline entities in UHMWPE cannot be completely destroyed by the melting process and therefore they can constitute nuclei of heterogeneous crystallization during cooling. Two parameters have to be considered for determining the melting conditions before studying the non-isothermal crystallization kinetics: The temperature of thermal treatment above the melting point (T_a)

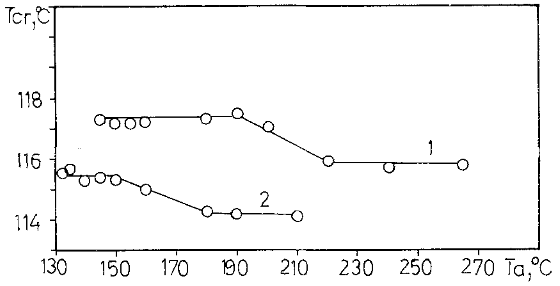

Fig. 1. Dependence of the temperature of crystallization (T_{cr}) of UHMWPE (curve 1) and of NMWPE (curve 2) on the temperature of the thermal treatment (T_a)

and the time at the temperature T_a. We fix the time parameter at 5 min. and vary the temperature T_a above the melting and the flow temperatures of UHMWPE. DSC was used to record the temperature of the crystallization of UHMWPE, thermally pretreated for 5 min at temperature T_a. Constant cooling rate (10 °C/min) was used. The same experiments were done with high density polyethylene with normal molecular weight (NMWPE) for comparison. It flows above the melting point owing to its low concentration of tie molecules [17].

The dependencies of T_{cr} of UHMWPE and NMWPE on the T_a are presented in Fig. 1. There is a temperature interval for UHMWPE (145–190 °C), where T_{cr} are almost constant while T_a increase. The same interval is observed for NMWPE at lower temperatures (132–150 °C). In the second temperature interval (190–220 °C for UHMWPE and 150–180°C for NMWPE) T_{cr} decrease while T_a increase. This result is due to the progressive destruction of all crystalline entities initially present in the polymers. The second temperature interval of UHMWPE coincides with its temperature interval of flowing. T_{cr} do not change with the increase of T_a in the last temperature interval ($T_a > 220$ °C for UHMWPE and $T_a > 180$ °C for NMWPE). In these intervals the thermal history of the polymers has been erased. Thus, it can be considered that at temperature 227 °C the pre-existing crystalline nuclei in UHMWPE have been destroyed. During the non-isothermal crystallization experiments, carried out on the microscope and on the DSC-apparatus, the UHMWPE melt was always obtained at temperature of 227 °C for 5 min. In these conditions the thermal history is destroyed and the degradation, which can occur at higher temperature, is avoided.

Morphology and spherulites' dimensions

When the unfilled and the filled UHMWPE crystallize from the melt, obtained at 227 °C for 5 min., spherulites are formed, as would be expected. At slow cooling rate (5 °C/min) the dimensions of the spherulites obtained in the filled UHMWPE are smaller than those of the spherulites in the pure UHMWPE (Fig. 2a, b). The average dimensions of the spherulites are

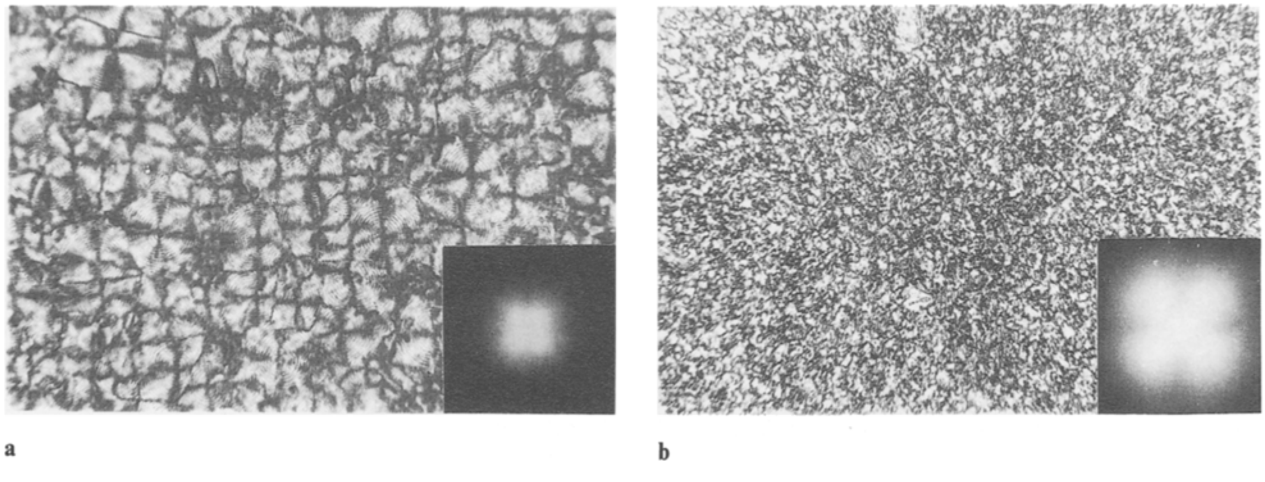

Fig. 2. Optical micrographs of spherulites of: a) pure UHMWPE, cooling rate 5 °C/min and corresponding H_v-pattern; b) UHMWPE with 12.1 wt.% marble powder; cooling rate 5 °C/min and corresponding H_v-pattern

determined from H_v diffraction patterns according to the equation [18]:

$$R_{sph} = c \cdot \lambda/(n \cdot \pi \cdot \sin\theta_m),$$

where R_{sph} is the spherulite radius, c is constant = 2.05 for spheres, λ is the wave length, n is refractive index of the medium, θ_m is the angle between incident and scattering beams corresponding to the maximum intensity of the pattern.

The size of the spherulites is determined as average value from 2–4 H_v patterns, obtained from one sample, when the crystallization has been completed. The average value of the spherulite radius R_{sph} decreases from 7 μm for the unfilled UHMWPE to 3–4 μm for the filled one when the concentration of the filler is up to 30 wt.%. It is difficult to obtain the H_v diffractograms from the filled UHMWPE with higher concentration of the filler (above 30 wt.%). This is due to the birefringence of the filler itself.

In the presence of the investigated fillers the polyethylene spherulites' size decreases, i.e., the nucleation density of UHMWPE increases [19]. When the filled UHMWPE crystallizes at high cooling rate (20 °C/min) the fillers do not play a nucleating role – the dimensions of the obtained spherulites do not decrease. The decrease of the nucleating role of the filler at higher cooling rate is also established for glass fiber filled polypropylene [7].

Non-isothermal crystallization kinetics

The crystallizations were performed at constant cooling rates 5°, 10°, and 20 °C/min, after the samples had been held in the molten state at 227 °C for 5 min. In Fig. 3 the dependencies of the crystallization temperatures of the samples (T_{cr}) at different cooling rates on the weight concentration of the filler are presented. T_{cr} of the peaks obtained at 5° and 10 °C/min cooling rates increases in the presence of all fillers (except in the presence of kaolin), i.e., the fillers act as nucleating agents for the UHMWPE non-isothermal crystallization. T_{cr} increases with the increasing of the filler concentration up to 40–50 wt.% and then decreases slowly. T_{cr} does not depend on the presence and on the concentration of the filler at high cooling rate (20 °C/min). The degree of crystallinity determined by the enthalpy of crystallization almost does not depend on the cooling rate (Fig. 4). The degree of crystallinity increases slowly with the increasing of the concentration of the filler up to 40–50 wt.% and then decreases (Fig. 4). UHMWPE filled with kaolin crystallizes at low temperatures with low degree of crystallinity at every cooling rate (Figs. 3, 4).

The interesting result is established that nucleation rates and crystallinity pass through maximum at 50 wt.% of the filler. In order to find some explanation for the decreasing efficiency of the nucleation at high filler concentration the overall non-isothermal crystallization kinetics of the samples have been studied by the Harnisch and Muschik method [20]. This method is based

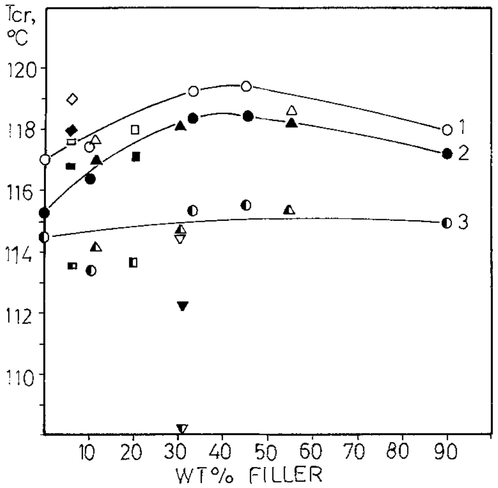

Fig. 3. Temperature of crystallization vs. concentration of the filler at cooling rate: 5 °C/min (curve 1, ○); 10 °C/min (curve 2, ●); 20 °C/min (curve 3, ◐). The fillers are: chalk (○), marble powder (△), bentonite (◇), dolomite (▭), perlite (▯), kaolin (▽)

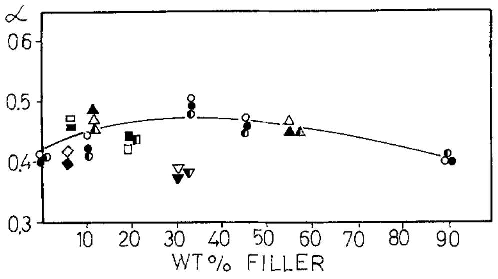

Fig. 4. Degree of crystallinity vs. concentration of the filler: chalk (○), marble powder (△), bentonite (◇), dolomite (▭), perlite (▯), kaolin (▽). Cooling rate: 5 °C/min (○), 10 °C/min (●), 20 °C/min (○)

on the well known Avrami theory for isothermal crystallization and gives the following equation for the determination of the Avrami exponent n:

$$n = 1 + (\ln \dot{x}_1/1 - x_1 - \ln \dot{x}_2/1 - x_2)/\ln \beta_2/\beta_1$$

at $T = T_c$, where $x_i(T)$ is the crystalline fraction calculated by integrating of the DSC exotherm; $\dot{x}_i(T)$ is the derivative of x, representing the dH/dT value of the exothermic curve; β_i is the cooling rate. The Avrami exponent n depends on the type of nucleation and on the crystal growth geometry. Each thermogram at certain cooling rate supplies a pair of values $x_i(T_c)$, $\dot{x}_i(T_c)$ for the chosen temperature T_c. The method requires the upper limit of the chosen T_c to be the $T_{\text{reaction maximum}}$, at which the fraction of the transformed material does not exceed 60%.

The Avrami exponents of the unfilled and the filled UHMWPE were determined by the plots of the values $\ln \dot{x}_i/1 - x_i$ vs. T for cooling rates 5 °C/min and 10 °C/min. The thermograms obtained at 20 °C/min cannot be used for determination of n of the filled UHMWPE. In Fig. 5 the DSC thermograms of the unfilled and some of the filled UHMWPE, and the corresponding Harnisch plots are shown. Three types of samples are presented in Fig. 5: an unfilled UHMWPE (a, a'); a filled UHMWPE with a filler, which increases its crystallization rate (b, b'); and a filled UHMWPE with a filler, at which a retardation of polyethylene crystallization is observed (c, c'). It is worth noting that the peaks of UHMWPE filled with a nucleating filler (b) are sharper than the peaks of the unfilled UHMWPE for both cooling rates (5 and 10 °C/min).

A value of $n = 2.3$ was obtained for the unfilled polyethylene, which is characteristic for heterogeneous nucleation followed by spherulitic two-dimensional growth [19,21]. The change of n is not very significant in the presence of fillers with concentration up to 90 wt.%. The values of n of filled UHMWPE (except for the filler kaolin) are about 1.8–2. The very small decrease of n of filled UHMWPE is due to its higher crystallization rate [22]. For UHMWPE filled with kaolin $n = 2.3$.

The obtained results show that the decreasing of the nucleation efficiency of the fillers with high concentration is not due to a change in the crystallization mechanism (i.e., the type of nucleation and the geometry of the crystal growth). It could be assumed that when the filler is of high concentration (above 50 wt.%) an aggregation of the particles of the filler occurs. This probably leads to decrease of the nucleation ability of the filler, because the number of the heterogeneous nuclei decreases.

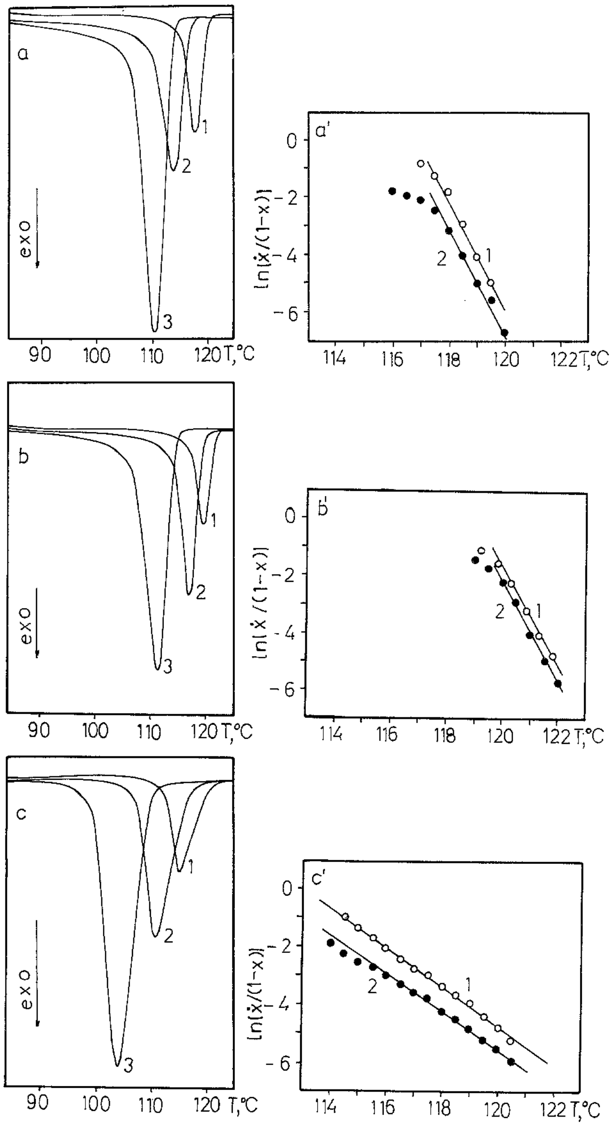

Fig. 5. DSC-thermograms (a, b, c) and corresponding $\ln[\dot{x}/(1 - x)]$ values vs. $T(a', b', c')$ of: UHMWPE (a, a'); UHMWPE with 34 wt.% chalk (b, b'); UHMWPE with 32 wt.% kaolin (c, c'). Cooling rate: 5 °C/min (curve 1), 10 °C/min (curve 2), 20 °C/min (curve 3)

Conclusion

The non-isothermal crystallization experiments of filled UHMWPE show that the fillers – chalk, marble powder, bentonite, dolomite and perlite – play a nucleation role for the UHMWPE crystallization only when: 1) the filled polyethylenes crystallize from melt, obtained at a temperature above the flow temperature of UHMWPE; 2) the crystallization is carried out at slow cooling rate. Decrease of the nucleation efficiency of the fillers is established at high filler concentration (above 50 wt.%). It is assumed that this is due to the aggregation of the filler particles, which probably reduces the number of the heterogeneous nuclei. It is shown that the Avrami exponent *n*, obtained by Harnisch and Muschik equation, almost does not change in the presence of a filler with concentration up to 90 wt.%.

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