α$_c$ RELAXATION OF THE CONSTRAINED AMORPHOUS PHASE
Polyethylene-chalk composites

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The study presents properties of polyethylene commercial products with special attention to properties of a 'semi-ordered' amorphous phase. Although, one can hardly prove the existence of such an interphase, the results description based on the idea of coexistence of two amorphous fractions ('real' and 'semi-ordered') in one system gives a broader understanding of the relationship between product history and morphology of the resultant engineering products. Their supermolecular structures were explored using positron annihilation lifetime spectroscopy (PALS), calorimetry (DSC) and mechanical spectroscopy in a tensile and a torsion mode (DMTA). The stability of these structures is also discussed based on a simple statistical analysis of the thermodynamic and structural parameters. The study exhibited that chalk did not disturb too much the crystalline domains of PE-LD whereas it influenced the interphase. Mechanical study showed that such a product is not stable during long time storage. The comparison with previous results, obtained for PE-carbon black composites, revealed differences in the morphologies and the α$_c$ relaxations of PE chains, observed in the composites including various fillers.

Keywords: *amorphous phase, composites, PE-LD, thermal analysis*

Introduction

Polyethylene (PE) has been a subject of extensive investigation concerning its crystal structure, morphology and relaxation behaviour [1–8]. PE and other polyolefines are well known as high-performance engineering polymers. One can find in their final commercial products a wide variety of structural components. However, there is no doubt that an amorphous part of the structure plays an important role for their applications. It is commonly accepted that the glass transition temperature (T_g), which reflects the properties of amorphous phase, is one of the most important parameters characterising polymers. In some cases, two T_g values or T_g-distribution were observed in one polymeric system as a result of coexistence of two amorphous fractions ('real' and 'semi-ordered'). The main consequence of this coexistence is that some part of material is rubbery whereas the other part is glassy [9–16]. That might produce special, sometimes undesirable, properties of the commercial products. Owing to the fact that the second T_g is the consequence of the interphase existence, the properties of this interphase are only observed in the semicrystalline polymeric systems. In the case of polyolefines, the degree of crystallinity is rather high therefore the 'semi-ordered' fraction is a predominant amorphous structure. This fraction plays a role of a crystal-amorphous interphase. It was shown that temperature and time of annealing strongly determined the properties of the system with two T_gs, i.e. the system formed by two coexisted amorphous fractions [16–19].

As the crystal structure change requires rather strong stimulus, an amorphous phase is sensitive to weak external and/or internal disturbing factors. The final and finishing operations of some technology very often include heat treatment. A filler might be also such a disturbing factor. On one hand, the filler is introduced into the polymeric matrix in order to improve the properties, on the other hand, it reduces the cost of production. The mechanism of reinforcement of the composite structure by the filler was previously discussed [20, 21]. It was important from the technological and application points of view. However for macromolecular physics, the problems of structural rearrangement, relaxation and stability of a supermolecular structure of a polymeric matrix have attracted a greater interest.

The first studies of the internal friction of polyethylene of low density (PE-LD) were performed in 1953 [3]. The widely accepted description of the relaxation processes (α, β, γ) and the comparison of the results obtained by many authors have been collected in books [1, 2]. The activation enthalpies of the mentioned processes were found to be 105, 159 and 46 kJ mol^{-1}, for α, β and γ, respectively. The additional process, α', was observed in creep experiments but only for the samples

cast from solutions. According to the interpretations of some authors, the α relaxation is due to the motion of CH_2 units in the crystals [22–24] although the concept of constrained amorphous phase ('semi-ordered') has been applied by Struik *et al.* with success, too [9–12]. In our opinion, the requirements connected with the adequate free space and energy should restrict such a libration in the crystals. It is commonly accepted that a free volume of polymer, which may be estimated by dilatometric, X-ray or positron annihilation methods (PALS), strictly determines the relaxations found for polymeric systems.

Two glass transitions were previously found for PE-LD, $T_g(1)$ and $T_g(2)$ [16, 18, 25]. The transitions exhibited the features typical for the 'real' and the 'semi-ordered' amorphous structures, respectively. Thermomechanical spectra of PE-LD exhibited two structural relaxations, α_g and α_c. These relaxations should be treated as a long-scale motion of macromolecule segments, which are located in the 'semi-ordered' amorphous regions, α_c, or in the 'real' amorphous regions, α_g. The magnitudes of the loss peaks were quite sensitive to the free volume, which increased by drawing and decreased by irradiation [16, 18]. Also, the loss peaks were sensitive to the filler content. By adding a filler, a new phase (the interphase) is introduced whose structure depends on the filler and on the polymer matrix. The structure of this new phase depends on the interfacial tension (wetting), interaction forces between polymer/filler, degree of dispersion, structure of the filler, the polymer itself, and last but not least processing and degree of dispersion. However, the problems, mentioned above, were presented and discussed previously in details [16, 25–27]. The morphology description was done base on scanning electron microscope (SEM). The chalk agglomeration was estimated by dynamic light scattering (DLS) and the specific surface areas of the chalk were determined by nitrogen adsorption (the BET method). In this paper, we study the relationship between the filler agent and structural relaxation with special attention to 'semi-ordered' amorphous phase.

It must be emphasised, that the α_g and α_c relaxations in our papers are the relaxations labelled by some authors as γ and α, respectively [1, 2]. Experimental evidences supporting the new labelling of the relaxations were presented in our previous papers and the origins of both relaxations were explained [16–18, 25].

Experimental

Sample preparation

The composites were produced with commercial available PE-LD, type DO72 (Chem. Works 'Blachownia' Kędzierzyn Koźle), and the filler was chalk, originated from the Sobków deposit. Chemical composition of the chalk was: $CaCO_3$ (96.8%), Fe (0.033%), Mn (0.020%), H_2O (0.15%), Cu (traces) and insoluble residue (0.70%). The mixtures containing 10, 20 and 40 mass% of chalk were obtained by introducing appropriately weighed portions of chalk into molten polymer. After addition of each portion the mixtures were stirred for 20 min and were co-extruded using Barbander extruder. The temperature at the initial zone was 433, 438 K at the mixing zone, and 448 K at the pipe. The extruded composite was shaped to a strip and a part of as-produced material was taken for our study, it was the first group of samples. The detailed descriptions of the polyethylene composite preparation and the chalk modification process one can find in previous papers [25–27].

Three groups of the composite samples were studied: as-produced; annealed; stored. The first group was a set of samples cut directly from the produced composite materials (results are presented in 'Effect of concentration and chemical modification of chalk'). The set included the composites with the filler amount of 10, 20, 40 mass% (PE_{10}, PE_{20}, PE_{40}). Also, the composites with the amounts of 10 or 20 mass% ($PE(m)_{10}$, $PE(m)_{20}$) of the modified chalk were investigated. Granulated PE (PE_g), which was used for the composite production, was studied. One part of the produced polymeric composites was stored at room temperature (samples with subscript 's', e.g. PE_s, results in 'Storage at ambient temperature'). It was much above the first T_g value of pure PE-LD. The other part was annealed at 373 K over one hour (samples with subscript 'a', e.g. PE_a, results in 'Annealing above $T_g(2)$ but below T_m').

Methods

Dynamic mechanical thermal analysis was carried out in a tensile and a torsion mode with a PL DMTA Mk III system and a Rheometric Scientific ARES system, respectively. E'', E', G'' and G' curves were recorded within a frequency range of 0.01–300 Hz (15 Hz – ARES or 300 Hz – Mk III) and within a temperature range from 130 to 375 K after temperature stabilisation. The samples were cut down from the polymeric strips as bars of nearly the same sizes.

Calorimetric measurements were performed using a Perkin Elmer DSC7 type and the first heating run (20 K min^{-1}) was recorded. A small piece of 5 mg was used. The glass transition temperature (T_g) was determined from the inflection point of the change in a heat flow *vs.* temperature curve. It is commonly accepted that T_g is defined at the midpoint in the C_p *vs.* temperature curve. For several years, we have

proposed an inflection point as a proper, from the thermodynamic point of view, definition of the glass transition temperature [28, 29]. Also, the first derivative of the DSC trace was analysed when the glass transition was very broad in a temperature scale. The melting temperature (T_m) was found as the minimum of the melting endotherm.

A conventional slow-fast coincidence spectrometer with plastic scintillators (two cylindrical Pilot U scintillators, their dimensions are: ϕ=1.5" and h=1.0") were used. The time resolution of the spectrometer was determined by analysing the positron lifetimes in Kapton foils. Positron lifetime spectra were accumulated to approximately $0.5 \cdot 10^6$ counts. A positron source (^{22}Na, about 0.2 MBq) was sealed between two Kapton foils. The source correction was taken into account during numerical evaluations. All of the measurements were performed at room temperature. One spectrum, so as to reach the proper statistics, was acquired about 24 h. The shortest component, τ_1, is related to the annihilation of parapositronium (p-Ps), τ_2 is attributed to the annihilation of the free positrons and τ_3 describes the annihilation of orthopositronium (o-Ps) in crystallites. The component with longest lifetime, τ_4, is attributed to the pick-off annihilation of o-Ps. The relative intensities of each components are named I_1, I_2, I_3 and I_4, respectively. Detailed description of the method, one can find in our previous papers [16, 18, 30, 31].

All instrument calibrations were performed according to the well-known standard procedures, describes in handbooks or manuals.

Results and discussion

Owing to the fact that the crystal-amorphous interphase plays a predominant role in a semi-crystalline polymeric system the processes describing the properties of the interphase region, i.e. α_c relaxation and the second glass transition, are the main subject of this paper. The experimental methods, i.e. differential scanning calorimetry (DSC), dynamic mechanical thermal analysis (DMTA) and positron annihilation lifetime spectroscopy (PALS) were applied for further morphology description of polymeric composite materials and for study of the segmental mobility of the polymer chains located in the interphase region. The morphology of the PE composites was previously described and the SEM micrographs were presented [25]. The size distribution of the chalk agglomerates was estimated by a dynamic light scattering method and specific surface areas of the chalk powders were also determined [25]. It seems to be very important whether or not the supermolecular structure of polymer includes free spaces which seem to be necessary for the activation of long-range molecular mobility. The free spaces can be evaluated from PALS. It is assumed that the lifetime (τ) of the longest lived components estimates the average size of the cavities (R_f – radii of the cavity) distributed in the amorphous or crystalline regions of the investigated polymeric structure, i.e. $R_f(4)$ and $R_f(3)$, respectively. In order to find some correlation between chemical composition of the PE composites and the average radii of the cavities, the study of the chosen polymeric materials was performed and the results are collected in Table 1.

Effect of concentration and chemical modification of chalk

In previous studies [9–16], it was found that the polymeric semi-crystalline sample, in some cases, could form the supermolecular structure included two amorphous fractions: the 'real' and the 'semi-ordered' amorphous one. The amount and the properties of those fractions strongly depended on a sample

Table 1 Results obtained for the material, studied six months after production process. The melting endotherms (ΔH_m) for the samples, presented in the table, showed two (three for PE(m)) minima. The highest temperature minima were found as follows: PE – 408.2; PE$_{10}$ – 405.3; PE$_{20}$ – 403.5; PE$_{40}$ – 402.5; PE(m) – 401.9 (399.6); PE$_g$ – 409.2. The $R_f(4)$ (an average radius of the cave located in the amorphous part of the polymeric material) and I_4 (an intensity of the fourth component of the PALS signal) values were calculated with accuracy of 0.02 Å and 0.3%, respectively ($R_f(3)$ – the cave radius in the crystal part, I_3 – the third component of the signal; 0.15 Å and 0.5%, respectively). I_3^* and I_4^* were calculated per real mass of polymer

Sample	$T_g(2)$/ K	$\Delta C_p(T_g(2))$/ J mol^{-1} K^{-1}	T_m/ K	ΔH_m/ kJ mol^{-1}	$R_f(3)$/ Å	I_3/ %	I_3^*/ %	$R_f(4)$/ Å	I_4/ %	I_4^*/ %
PE$_g$	337.3	1.49	386.0	1.69	–	–	–	–	–	–
PE	323.1	10.1	387.7	2.90	1.89	8.7	8.7	3.27	22.9	22.9
PE$_{10}$	321.7	11.5	383.8	2.73	1.72	9.1	10.0	3.34	21.5	23.9
PE$_{20}$	322.5	12.3	384.7	2.71	1.69	8.7	10.4	3.30	20.5	25.6
PE$_{40}$	321.3	13.5	383.4	2.79	1.77	7.4	10.4	3.26	17.0	28.4
PE(m)$_{10}$	321.6	5.08	385.8	2.74	2.00	7.7	8.5	3.37	21.3	23.4
PE(m)$_{20}$	320.8	6.91	382.3	2.73	1.78	7.2	8.6	3.36	19.2	23.0
PE(c)	347.3	9.8	379.6	2.47	–	9.1	10.3	3.33	21.9	24.7

thermal history [18]. It is worth noticing that in the case of PE-LD two glass transitions were found [16, 22]. The glass transition temperatures of the 'semi-ordered' amorphous fraction ($T_g(2)$) for the studied composite materials are presented in the second column of Table 1. The third column shows the results of the changes of the specific heat, evaluated at $T_g(2)$. The temperature of the first glass transition for PE-LD is much below room temperature, i.e. ca. 180 K. Some correlation between the thermodynamic and the structural parameters, presented in Table 1, and the chalk concentration in the composites could be seen. The values for PE-LD filled with carbon black, PE(c) [16], are presented for comparison. Higher $T_g(2)$ and lower T_m among all values, presented in Table 1, were found for those composites. However, the radii of the free volume, $R_f(4)$, found for the both kinds of composites, i.e. PE(c) and PE$_{10}$, are the same. The concentration of carbon black was ca. 11 mass% therefore the values, estimated for PE(c), should be compared with the values obtained for the composites including 10 mass% of chalk, PE$_{10}$. The highest $R_f(4)$ values were found for the composites obtained with modified chalk (PE(m)$_{10}$, PE(m)$_{20}$). Moreover, the $R_f(4)$ parameter seems to be independent on the amount of the modified chalk in the composite.

The results for the composites with carbon black or chalk, presented in this paper, showed distinct differences for the melting process. Most likely, PE lamellae were grown in such a way that the grains of carbon black were built in the lamellae, hence, the crystalline phase was modulated and it included many defects. This phase situation was revealed in the low ΔH_m values. On the contrary to PE(c), chalk grains moved out of the PE lamellae, forming separate aggregates (see SEM micrographs in [25]). Only a small difference of the ΔH_m values for pure PE and the composites (PE$_{10}$, PE$_{20}$, PE$_{40}$, PE(m)$_{10}$, PE(m)$_{20}$) was found. It is worth noticing that the enthalpies of melting for all the composites gave an average value of 2.74±0.03 kJ mol^{-1}. (The given error is a standard deviation, SD, whereas the measurement error, resulted from the reproducibility of the calculated value, was 0.10 kJ mol^{-1}. It must be emphasised that the measurement error is a question of a baseline choice in the temperature range of the melting process and its subtraction from the DSC signal. In order to find the temperature range of the process, it is more convenient to use a first derivative of the signal. Then, it is much easier to point out the characteristic temperature points from the derivative than from the original signal. Owing to the fact that this choice is highly arbitrary, the enthalpy calculations should be repeated several times for the same curve. Hence, the

average value can be calculated with some standard deviation. This deviation is defined in this paper as a measurement error. None subtraction for empty pans and smoothing of the signal are not necessary.) The opportunity of the approximation of all melting enthalpies by one average value would confirm small perturbation of the crystalline phase with the increasing amount of the filler. The values of the parameters (Table 1) were calculated per real amount of polymer in the sample. Also, the radii of the free volume of the crystalline phase were almost the same giving an average value of 1.77±0.09 Å (the measurements error was 0.15 Å). The intensities of the third and the forth components (I_3, I_4) and the third and the fourth components calculated per mass of polymer (I_3^*, I_4^*) are presented in Table 1. The I_3 and I_4 values decrease with the increasing of the filler content due to decreasing of the total amount of the polymer. However, the increase of the I_4^* values shows that the calculation for the real amount of polymer in the composite sample is not proper in the PALS case. Most likely, some additional phenomenon occurs on the filler surface, that should be considered in the calculation. One can see in Table 1 that some parameters of the composites, produced with the modified chalk, are different as compared with the parameters for the composites with the same amount of unmodified chalk. However, the parameters describing the crystalline structure, ΔH_m and $R_f(3)$, are almost identical, hence, they were taken into account for the calculation of the average values mentioned above.

Two kinds of mechanical measurements were performed. Considering the mechanical properties in a torsion experiment, the G modulus was measured for each sample. When a tensile head was applied for measurement, the appropriate modulus was E (Young's modulus). The tendencies of G' and tgδ_G within a temperature range from 130 to 375 K are presented in Fig. 1. The torsion experiments revealed three relaxations, well known from [1, 2]. The origins of the relaxations were also discussed in our previous papers [16, 25]. Due to experimental restriction of the tensile method, applied in the case of our study, the real and imaginary parts of E were only measured within a temperature range of the α relaxation (in this paper labelled as α_c). The tgδ_E values are presented in Fig. 2. Although two different kinds of forces were applied, hence different mechanical properties were studied, both E' and G' increased with increasing filler content. It means that the material is more stiff when the larger amount of the filler is added. One could find that the structural relaxation for both applied forces was reduced for the samples with some amount of the filler. There was no drastic changes of tgδ_E and tgδ_G for
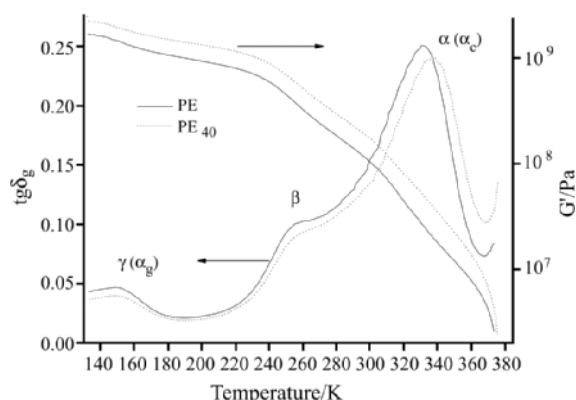
Fig. 1 Selected curves, obtained in the torsion mode, presenting three relaxation processes in the temperature scale: pure polymer (PE); the composite with 40 mass% amount of the chalk (PE$_{40}$)
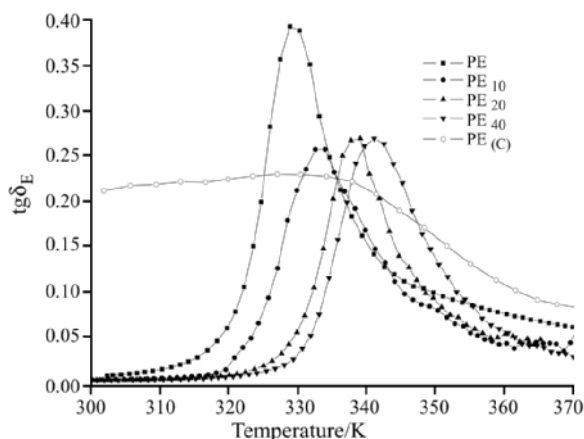

Fig. 2 The results of the measurements performed in a tension mode. The tgδ$_E$ curves are presented in the temperature range of the α$_c$ relaxation

the PE$_{10}$, PE$_{20}$ and PE$_{40}$ samples but a regular shift of both parameters maxima towards higher temperature with an increase of the filler amounts was recorded. The real and imaginary parts of G and E, evaluated at temperatures of the maxima of G'' and E'' curves (recorded at 1 Hz for the α$_c$ relaxation), respectively, are collected in Table 2. The activation enthalpies were calculated with the assumption that the process is the Arrhenius type [17, 32].

Annealing above T$_g$(2) but below T$_m$

It was shown in our previous papers concerning semi-crystalline polymers that temperature and time of annealing is very important for the possibility of supermolecular structure formation [28, 29]. When the polymeric system exhibits two amorphous fractions, hence two glass transition temperatures are observed, the annealing below or above $T_g(2)$ causes different rearrangement of chains [28]. If the annealing temperature is close to the melting temperature,

the changes can be also observed in the crystalline phase. In this paper, the annealing temperature was 373 K, that was much above $T_g(2)$ but within the temperature range of the melting process (the beginning of melting was assumed, from the first derivative of the DSC traces, to be 340 K for each calculation of the melting enthalpy). There was no sense to anneal the sample between $T_g(1)$ and $T_g(2)$ because the ambient temperature was in this temperature range. Therefore long time storage was only applied for one part of the samples (PE$_s$). The results are discussed in the separate section.

The thermodynamic and structural parameters are collected in Table 3. One can find that structural changes occurred in both the 'semi-ordered' amorphous fraction and the crystalline domains, as well. However, in contrary to the as-produced materials, it is impossible to find one average value of the melting enthalpies or one average T_g. The SD values calculated for the average values of ΔH_m and T_g exceeded the measurement errors significantly. The following values 2.48±0.16 kJ mol^{-1} (the measurement error was 0.11 kJ mol^{-1}) and 314.6±2.6 K (0.5 K) were calculated, respectively.

It is worth noticing that the radius of the free volume evaluated for the crystalline phase, $R_f(3)$, increased in the case of the annealed samples except PE(m)$_{10a}$. This is the same as for PE(m)$_{10}$ if one takes into account the measurement error (0.15 Å). The $R_f(4)$ radius also increased and the average value, 3.39±0.02 Å, was calculated for all annealed samples, except PE$_a$. Although, the $R_f(4)$ value for PE$_a$ deviated from the average value it might be supposed that the one-hour annealing was too short to cause the structural changes. For the longer period of annealing time, the average radius of the free cavities should be higher as for all other samples. Such behaviour was observed for other polyethylene

Table 2 Real and imaginary parts of G (and Young's) moduli measured at the temperature (T^*) of G'' (and E'') maximum. The results were obtained for the as-produced material. Measurement frequency was 1.6 and 1 Hz, respectively. The dimensions of the E'' and E' values, which are given in parenthesis, are 10^8 and 10^9 Pa, respectively

Sample	$T^*/$ K	$G''_{max}/$ 10^6 Pa	$G'(T^*)/$ 10^7 Pa	$\Delta H_\alpha/$ kJ mol^{-1}
PE	326.2 (325.6)	7.87 (7.26)	3.22 (1.91)	– (298±8)
PE$_{10}$	326.8 (327.4)	9.44 (4.89)	3.92 (2.36)	– (336±9)
PE$_{20}$	328.5 (330.1)	11.11 (4.53)	4.57 (2.25)	– (311±8)
PE$_{40}$	332.8 (333.2)	11.18 (4.86)	4.66 (2.07)	– (287±9)

Table 3 Samples annealed at 373 K over 1 h. The melting endotherms for the samples showed two (three for PE) minima. The lower temperature is given in the table whereas the higher temperature is as follows: PE – 412.5 (391.2); PE_{10} – 414.1; PE_{20} – 413.1; PE_{40} – 405.2; $PE(m)_{10}$ – 386.4; $PE(m)_{20}$ – 387.5

Sample	$T_g(2)/$ K	$\Delta C_p(T_g(2))/$ J mol^{-1} K^{-1}	$T_m/$ K	$\Delta H_m/$ kJ mol^{-1}	$R_f(3)/$ Å	$I_3/$ %	$I_3^*/$ %	$R_f(4)/$ Å	$I_4/$ %	$I_4^*/$ %
PE_a	316.6	3.95	382.7	2.50	2.01	8.6	8.6	3.36	20.7	20.7
PE_{10a}	316.8	3.61	382.5	2.31	2.18	7.3	8.0	3.39	21.7	23.9
PE_{20a}	312.8	4.75	383.1	2.39	2.28	6.3	8.1	3.40	19.7	23.6
PE_{40a}	315.1	5.01	383.1	2.35	2.19	5.5	7.6	3.39	15.9	22.3
$PE(m)_{10a}$	310.2	8.17	375.9	2.66	1.91	7.9	8.7	3.37	20.1	22.1
$PE(m)_{20a}$	315.9	7.79	377.5	2.67	2.11	7.3	8.8	3.39	17.6	21.1
$PE(c)_a$	314.3	5.68	385.8	1.93	1.76	8.3	9.4	3.38	21.6	24.4

systems previously [33]. Mechanical spectroscopy, applied for the studied PE composites, gave another one evidence. The curves, presented in Figs 3a and b, exhibit the same shape and vary a little one each other. It must be emphasised that one unexplainable behaviour of the *G'* curves was found. As the *G'* curve for the PE composite was shifted towards higher *G'* values in comparison with the curve for PE_{10}, the adequate *G'* curves for PE_a and PE_{10a} exhibited an inverse tendency, Fig. 3a. The *G'* values for PE_{10a} in the measured temperature range were lower than for PE_a. Precise data of the *G'* and *G"* moduli, at the temperature of *G"* maximum, for the annealed samples are given in Table 4 together with the activation enthalpies of the α_c relaxation. One can find that the enthalpies are almost the same, except PE_{10a}, that well correlates with the PALS results (correlation with $R_f(4)$) but does not correlate with DSC measurements (lack of correlation with T_g) at all. It might be another one evidence that α relaxation and glass transition are distinct physical phenomena.

Storage at ambient temperature

The polyethylene composite samples obtained just after technological process were not measured. First measurements were performed 6 months after their produc-

Table 4 Results obtained for the annealed samples. The temperature of annealing was 373 K, the time of annealing was 1 h. The *G* values are given at the T^* temperature, which was chosen at the same manner as for the results presented in Table 2

Sample	$T^*/$ K	$G_{max}^{''}/$ 10^6 Pa	$G'(T^*)/$ 10^7 Pa	$\Delta H_\alpha/$ kJ mol^{-1}
PE_a	333.4	6.28	2.66	133±3
PE_{10a}	333.0	5.87	2.38	137±2
PE_{20a}	333.2	7.53	3.08	128±5
PE_{40a}	333.9	9.10	3.89	128±5
$PE(m)_{10a}$	333.3	6.37	2.67	132±5
$PE(m)_{20a}$	333.2	8.01	3.25	132±5

tion (Table 1). The next study was performed after next 18 months, that means 24 months from the production. The results concerning DSC, PALS measurements are presented in Table 5. Most of the parameters ($T_g(2)$, ΔH_m, $R_f(4)$) had one average value for the composites, independently on the chalk amount. It would suggest that due to some process, most likely structural relaxation of PE, the supermolecular structures formed after 24 months (most likely 6 months was not sufficient time) exhibit the same feature despite of various chemical composition of the composites. Hence, it means that the phase separation occurred and polymer arrangement is independent on the amount of the chalk, even for the
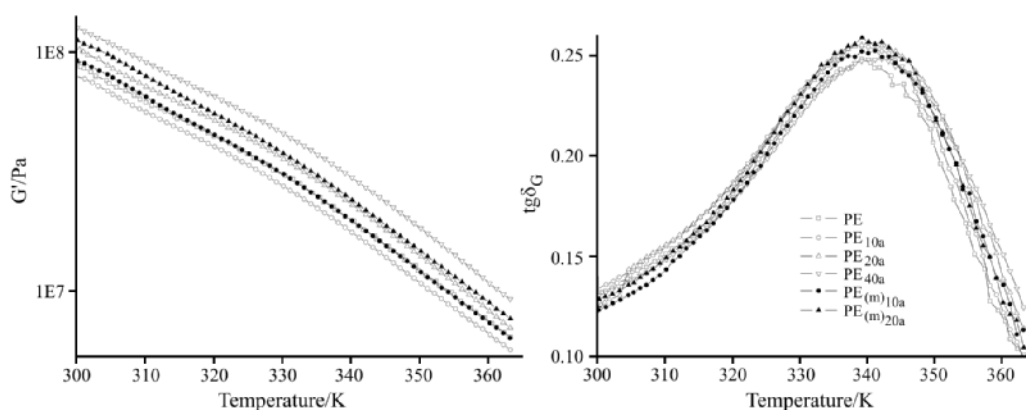

Fig. 3 a – Real part of the *G* modulus obtained for annealed samples; b – The tgδ$_G$ curves obtained for annealed samples

Table 5 Results obtained for the material, studied 24 months after production process. The same accuracies were achieved

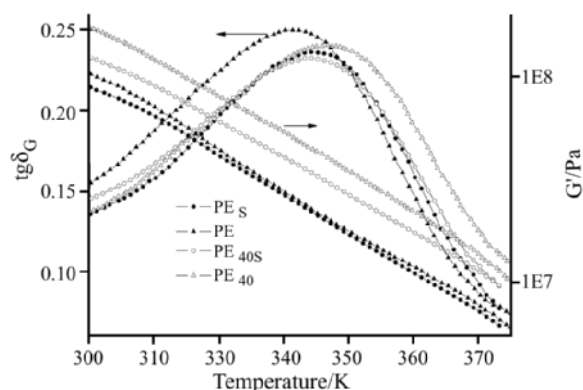| Sample	$T_g(2)/$ K	$\Delta C_p(T_g(2))/$ J mol^{-1} K^{-1}	$T_m/$ K	$\Delta H_m/$ kJ mol^{-1}	$R_f(3)/$ Å	$I_3/$ %	$I_3^*/$ %	$R_f(4)/$ Å	$I_4/$ %	$I_4^*/$ %
PE$_s$	320.2	7.73	388.7	3.11	–	11.0	11.0	3.29	22.5	22.5
PE$_{10s}$	320.4	8.49	385.3	2.96	–	7.4	8.1	3.29	23.3	25.6
PE$_{20s}$	320.1	8.74	384.9	3.03	1.83	5.5	6.7	3.33	21.2	25.5
PE$_{40s}$	321.0	7.16	385.2	2.86	1.67	3.1	4.3	3.28	17.6	24.7
PE(m)$_{10s}$	320.2	8.07	384.8	2.99	2.11	4.3	4.7	3.33	21.6	23.7
PE(m)$_{20s}$	321.3	6.11	385.1	3.05	–	9.0	10.8	3.28	21.0	25.2

Fig. 4 The tgδ_G and G' curves for the as-prepared and stored samples: PE – pure polyethylene; PE$_{40}$ – the composite including 40 mass% of chalk

Fig. 5 The representative DSC curves of the studied materials

modified chalk. Mechanical spectroscopy confirmed such a conclusion. The curves recorded for the composites, 6 and 24 months after the production, are presented in Fig. 4. One can easy find that there is no big difference in the tgδ_G values between the PE$_s$ and PE$_{40s}$ composites. Although the real and imaginary parts of the G moduli for both composites are different (that was a result of chalk contents evidently), the temperatures of the G'' maxima are the same, 320.5±0.5 K (0.5 K). The parameters are presented in Table 6. However, it must be emphasised that the increase of the G' and G'' parameters with the increasing amount of chalk in the composites is not so regular as we should have expected. Both G' and G'' for PE$_{40s}$ were lower than for PE$_{20s}$. The activation enthalpies are higher as compared with the adequate values for the annealed samples.

Analysis of DSC curves

Representative DSC curves for the studied products are shown in Fig. 5. The curves are presented in a temperature range which only includes the melting process. It is seen that the shapes of the melting endotherms differ and depend on the thermal history of the composites. The curves for PE and PE$_s$ differ drastically. Whereas the PE$_s$ curve reflects only one melting process, the PE curve exhibits that the crystalline phase is not homogenous and two melting processes might occur. The parameters of all samples, cut out from the
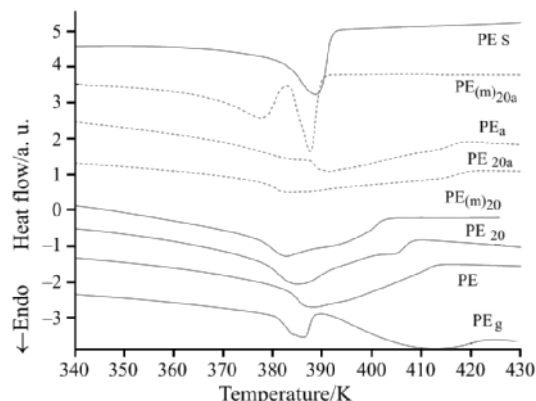
stored products, are presented in Table 5. The shape of the DSC curves are almost the same for all the stored materials. It means that the crystalline structure of the polyethylene in each product is the same. The endotherm being the overlapping of two melting peaks means that two crystalline structures have been formed during the production of the composites. The open question on the polycrystallinity should be solved by X-ray measurements. However, the DSC study exhibits distinctly that the room temperature is sufficient for changing the arrangement of chains in the crystalline phase of PE-LD. It is worth noticing that the annealing of the investigated composites at 373 K does not change the endotherm shape too much. However, the curves for the composites including the modified chalk exhibit two well separated peaks, that is similar to the curves found for the annealed composites including carbon black [16].

Table 6 Results obtained for the storage samples. The G values are given at the T^* temperature, which was chosen at the same manner as in Table 2

Sample	$T^*/$ K	$G''_{max}/$ 10^6 Pa	$G'(T^*)/$ 10^7 Pa	$\Delta H_\alpha/$ kJ mol^{-1}
PE$_s$	331.8	5.80	2.42	145±3
PE$_{10s}$	330.8	6.13	2.58	145±3
PE$_{20s}$	330.5	9.56	4.02	143±5
PE$_{40s}$	331.5	9.03	3.95	135±5
PE(m)$_{10s}$	330.4	6.61	2.77	140±2
PE(m)$_{20s}$	330.6	7.97	3.32	140±2

Conclusions

As the results of the performed measurements, we have found that small change of the amount of the crystalline phase is observed when 10, 20 and 40 mass% of the chalk is added. It would mean that there is not much nucleating power of the filler. The filler does not disturb too much the crystallisation process of PE-LD, occurring during the composites production. Most likely, only a small number of defects is created in the crystalline domains. However, the crystal-amorphous interphase is disturbed by the presence of the filler. The low amount of the filler in the composites acts like a stretching agent of the chains located in the interphase. It results in the increase of the activation enthalpy of the α_c relaxation and the free volume. When a larger amount of the filler is introduced in the polymer matrix (the sample PE_{40}), the free volume and the molecule fluidity are the same like for the pure polymer. Hence, the filler forms separate aggregates, which do not disturb the polymer matrix and the polymer is only a binding material. The stiffness of the polymeric composites rises with the increasing amount of chalk.

Lack of regularity for G' and G'', observed for the stored and annealed samples might suggest that the chalk as the filler of PE-LD gives the products which properties are not stable in time and temperature. Moreover, a component separation in the composites after the annealing and storage exhibits that the chalk, used in our study, modifies the PE-LD supermolecular structure only during the production. It would mean that PE-LD is the strong component, which adopts its own supermolecular structure, removing outside the filler. In such a situation, the filler will form aggregates during the composite annealing or storage. This conclusion, drawn from DMTA (the α_c relaxation) and DSC (the glass transition), is the confirmation of the observation performed by SEM. Finally, one might conclude that the properties of the composites, i.e. the supermolecular structure of the PE-chalk system will drastically change in time.

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