

The Relationship between the Physico-Mechanical Properties and the Filler Concentration in the HD Polyethylene-Dispersed Filler System

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SYNOPSIS

The relationship of 10 basic physico-mechanical properties and the concentration of the filler is investigated through narrow filling intervals of seven different composite series containing various types of HD polyethylene and different grades of kaolin. A variety of mixing techniques for the preparation of the composites is used, and testing is carried out by applying different techniques and conditions. The investigations show that, in all cases when an identical mixing technique is applied for a given series of composite formulations, the relationship linking the physico-mechanical and dynamic-mechanical G' , G'' , and $\tan \delta$ properties with the concentration of the filler is not a monotonous curve, and displays a multiextremal character. We propose as one possible explanation that a periodic change in the free volume and the content of crystal polyethylene phase exists, as a function of the filling. The nonmonotonous character of the changes of properties is related to the proposed mechanism for the change of the physical structure of composites, which are composed of filler particles coated with n monolayers of polyethylene crystallites, when, as filling continues, periodically new types of filler particles are formed. The nonmonotonous character of the relationship between the properties and the concentration of the filler should be taken into consideration when these relationships are approximated or expressed in a mathematical-analytical form, especially when high amounts of fillers (more than 20 vol %) are used.

INTRODUCTION

Regardless of the keen practical interest toward polymer composites with dispersed fillers, for the present, a consensus about the character of the change which affects the physico-mechanical properties on the degree of filling, as well as the mechanism of this change, based on their physical structure has not been reached. The problem is further complicated by the fact that composites' properties are considerably affected by the type of the materials and last but not least by the mixing conditions.^{1,2} Special attention has been paid to the determination of the relationships of the elasticity modulus and

the tensile strength of polymer composites as a function of filling. Numerous equations have been proposed, according to which these relationships have a monotonous character and in some cases the tensile strength passes through a maximum.¹⁻⁶

During the investigations of the shape of the curves showing the relationship between various properties of phenol-aniline-formaldehyde resol resin and the amount of the filler (kaolin), a multiextremal, nonmonotonous relationship and a periodical change of the magnitude of the properties has been established with the addition of fillers.⁷⁻¹⁰ A supermolecular mechanism has been proposed for this change, according to which, when the amount of filler is increased in the composite, particles of a new type of filler are formed, coated with a full number of monoglobular layers composed of the resin's globules.^{8,9} It has been suggested that a similar

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mechanism of periodical changes of the properties with the filling process may be observed also in the case of other polymers composed of supermolecular structures with a certain distribution of their size.⁹ Such a polymer with typically particulate nature, which is retained also in its composites, is poly(vinyl chloride) (PVC).^{11,12} In a similar way, a periodical change of the properties is observed in the system PVC—finely dispersed calcium carbonate filler.¹³ A periodical change of the mechanical and structure-sensitive dynamic-mechanical properties during filling can be found not only in the case of composites of polymers with a typically particulate structure but also in the case of crystallizing HD polyethylene.^{14,15} Along with the characteristic changes of the dynamic-mechanical properties of polymers during temperature relaxation transitions at increasing temperature, in the case of HD polyethylene composites, identical “concentrational transitions” have been established by increasing the amount of dispersed filler.¹⁴

The present study is aimed at investigation of the relationship between the change of the physico-mechanical properties of HD polyethylene grades and kaolin, and various mixing and testing techniques. The results obtained lead to conclusions about the physical structure of the composites and the mechanism through which their properties change.

EXPERIMENTAL

The seven composite series studied were prepared using two different HD polyethylene grades: (1) HD polyethylene Stamylen 9309, a DSM (The Netherlands) product with a melt index 8 g/10 min, as determined by ISO 292 and (2) HD polyethylene Bulen, a product manufactured by the Chemical Works Neftochim (Bulgaria), stabilized and with a melt index 6 g/10 min.

Three grades of kaolin were used: (1) Icecap K, without surface treatment, (2) Burgess KE, surface-treated (both delivered by OMYA GmbH, Köln, FRG), and (3) “Enriched kaolin designed for the rubber and chemical industries” according to Bulgarian State Standard 3975-73, without surface treatment.

The composites of each series were prepared through narrow filling ranges of 2 vol % filler, up to the maximum possible filling at the given conditions. The composites of the S series (Bulen and Bulgarian kaolin), I series (Stamylen 9309 and Icecap K), and KE series (Stamylen 9309 and Burgess KE) were prepared by one and the same technique of hot roll

milling and homogenization. It was established that, using the same preparation technique of milling to a bright sheet for a homogenization time of 10–15 min, the values of the measured parameters change within the accuracy limits of the determination.

In order to avoid the human error factor during the preparation of the composites by roll milling, a standard technique was developed consisting of mixing the ingredients in a kneader type 50 of the Plastograph Brabender Model PL 3S to a constant torque, M_{end} , using two different temperatures of the mixer's walls: 463 K for the A series (Stamylen 9309 and Burgess KE) and C series (Bulen and Burgess KE), and 443 K for the B series (Stamylen 9309 and Burgess KE) and D series (Bulen and Burgess KE). Each separate composite was prepared three times, thus obtaining almost the same torque– and temperature–time diagrams.

After homogenization, the composites were pressed according to the ASTM D-1928-70 requirements at a temperature of 443 K and pressure of 15 MPa, then cooled at a rate of 40 K/min. The 1 mm thick pressed sheets were used for stamping test samples with two different shapes.

Ten different properties were studied for each composite.

TESTING METHODS

(a) The density of the pressed samples was determined by weighing in an immersion liquid—water/ethanol 1 : 1 at 20°C of 15–20 samples of each composite.

(b) The average density of the polymer share of the composites ρ_m was determined by applying the expression¹⁶

$$\rho_m = \frac{100\rho_k - \varphi_v\rho_f}{100 - \varphi_v} \text{ g/mL} \quad (1)$$

where ρ_m is the mean density of the polymer share in g/mL, φ_v is the volumetric concentration of the filler in vol %, ρ_k is the composite density in g/mL, and ρ_f is the filler density in g/mL.

(c) The stress to break, σ_B , was determined at different deformation rates by a dynamometer with a system of levers, Model ZMG (FRG), and dynamometers with tensiometric sensors using the Instron Co., Model 1115M¹⁵ and Zwick 1474.

(d) The work required for sample breaking, A , was determined by the area covered by the force–elongation diagram up to the break point. This work, when evaluated per unit volume of the working sec-

tion of the sample, gives the volumetric work (energy) required for breaking, A_v .

(e) The stress to break of the polymer phase, σ_{yp} , was determined by the expression given by Nicolais and Narkis.³

(f) The dynamic-mechanical tests for the determination of $\tan \delta$, G' , and G'' were carried out with a torsion pendulum at a frequency of 1 Hz, using 6–15 samples of each composite.

(g) The degree of crystallinity of the HD polyethylene in the composites W_c was determined by X-ray measurements as well as with DSC.

(h) The size of the HD polyethylene crystallites in the composites was checked by X-ray measurements, applying methods described in Ref. 17.

RESULTS AND DISCUSSION

When the composites within the set A, B, C, and D are prepared in the mixing chamber of the Brabender plastograph, nonmonotonous, multiextremal (with periodically repeated minima and maxima) relationships between the final torque, M_{end} , and the final temperature of the composite mass, T_{end} , are observed depending on the volumetric concentration of the filler, φ_v .

This fact suggests that the physical structure of the composites is formed during the mixing process. Depending on the volumetric concentration of the filler, composites are formed periodically with higher or lower friction, hence with a more or less elevated temperature of the composite mass, T_{end} . The relationship between the composite density ρ_k and the volumetric concentration of the filler, φ_v , determined by the least square method for the different series of composites is a linear function with a high coefficient of linear correlation, the respective 95% confidence intervals of the determined density being, however, periodically located above and below the evaluated linear relationship. This effect was studied in more detail by determining the relationship between the average density of the polymer share ρ_m and the volumetric concentration of the filler φ_v , using expression (1).

According to Rafikov et al., since the density of the polymer near the surface of the filler is lower, the mean density of the polymer share decreases monotonously with the rise of the amount of the filler and, at a definite concentration of the latter, the entire polymer share would undergo a transition into the state of adsorbed layer.¹⁶

However, as seen in Figure 1, periodic multiextremal relationships are obtained and a decrease of

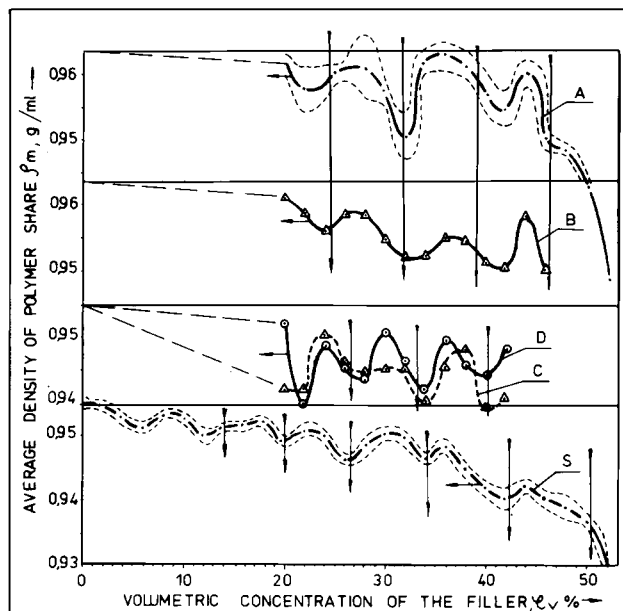


Figure 1 Average density of the polymer share ρ_m vs. volumetric concentration of the filler φ_v of the A, B, C, D, and S series; (---) 95% confidence interval.

the average density of the polymer share, ρ_m , is observed. This fact suggests the existence of a periodical alteration of the free volume in composites which may be related to the periodical change of the physical structure occurring as filling proceeds.

The changes of the stress to break of four different composite series, as dependent on the volumetric concentration of the filler, are shown in Figure 2. The existence of extreme values of the curves is proved by the method of the representative average curve (RAC).¹⁵ As seen in Figure 2, in the cases of the S and I series the extreme points are connected by two smooth lines and the representative curves are traced in-between. The deviations of the minimal and maximal values from the RAC are considerable and surpass the 95% confidence intervals. The most clearcut multiextremal changes of the stress to break are obtained at higher volumetric concentrations of the filler—above 20 vol % (Fig. 2). The A and KE series have the same composition; they are prepared by different methods and display substantially different curves with retained multiextremal character.

In the case of the S series (Fig. 2) the stress to break, σ_B , of the composites decreases continuously with the rise of the filler concentration while the stress to break of the polymer share, σ_{yp} , increases continuously, the curve preserving its multiextremal character (Fig. 2, curve σ_{yp} -S).

Experimental data provide evidence that the curves of the relative strain at break, ϵ_B %, and the

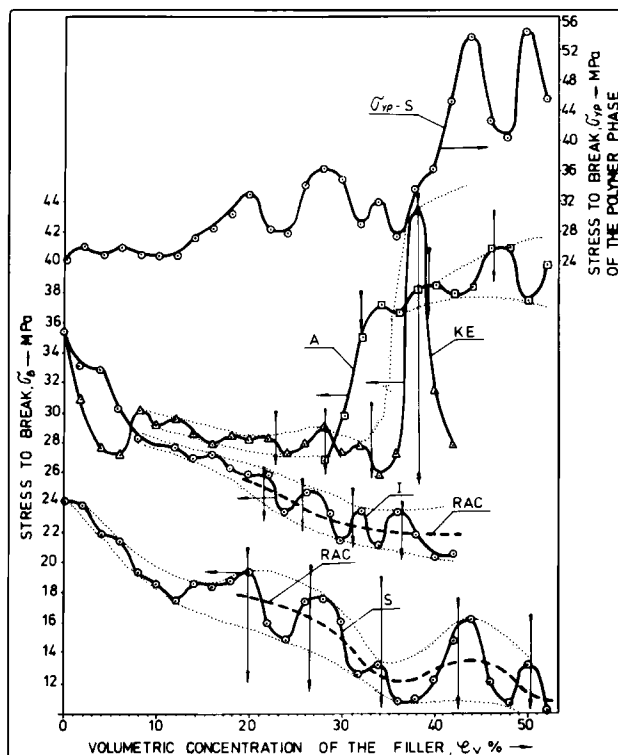


Figure 2 Stress to break of the composites, σ_B , and the polymer phase, σ_{yp} , vs. volumetric concentration of the filler φ_v in the S, I, KE, and A series: (S, I, KE, A) stress to break of the composites; (σ_{yp} -S) stress to break of the polymer phase³ in the S series; (RAC curves) representative average stress to break curves of the S and I series.

logarithm of the volumetric work for sample breaking $\log A_v$ as dependent on the volumetric concentration of the filler φ_v also have a multiextremal character. For a given composite series these curves show minima and maxima (extrema) at the same filler concentrations.

Nonbrittle (viscous) materials require a greater amount of energy to achieve destruction as compared with fragile ones.⁶ Consequently, the changes in $\log A_v$ and ϵ_B suggest that a periodic transition, through compositions with higher or lower brittleness and variable ductility, is observed with the rise of the filler concentration in polyethylene composites. An explanation for this phenomenon can be sought in the periodic change of the degree of crystallinity of these composites as the extent of filling increases, corresponding to periodic alteration in the content of amorphous and crystal structure of the dispersion medium—HD polyethylene (Fig. 3). As could be expected, the curves in Figure 3 show the same extrema as those of the average density of

the polymer share in Figure 12 (a series in Figs. 1 and 3).

The dynamic-mechanical properties, and above all the mechanical losses $\tan \delta$, are very sensitive with regard to the temperature relaxation transitions, structural inhomogeneities, and especially the morphological structure of the filled polymer composites.⁵ The changes of all these important characteristics as well as the change of the stress to break with the rise of the volumetric concentration of the filler, φ_v , in the composite series studied, show characteristic multiextremal dependences shown in Figure 4 (for the KE series).

The dashed line in this figure marks the regions of concentration transitions¹⁴ when the maxima of $\tan \delta$ and G'' coincide with the minima of G' . Within these regions the maxima of the stress to break are also obtained. As seen in Figure 4, the stress to break—volumetric concentration of the filler relationship displays a multiextremal character, which is retained when the determinations are carried out with different dynamometers at various deformation speeds,¹⁵ using separate forms of test samples. These transitions, at given concentrations of the filler, can be related to the relative minima of the density of the polymer share, ρ_m , which show maxima for the

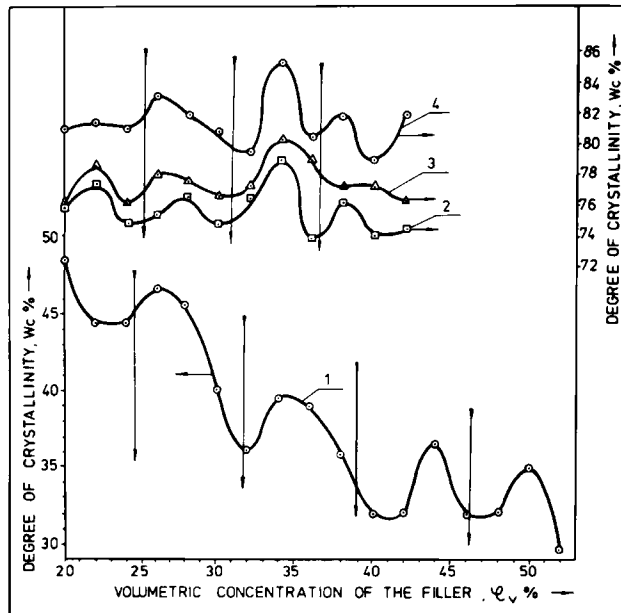


Figure 3 Relationship between the degree of crystallinity W_c and the volumetric concentration of the filler φ_v : (1) for the A series, determined by X-ray techniques; (2, 3, and 4) for the I series, determined by DSC; (3) first heating at a rate of $10^\circ\text{C}/\text{min}$; (2) second heating at a rate of $10^\circ\text{C}/\text{min}$; (4) first heating at a rate of $40^\circ\text{C}/\text{min}$.

free volumes, and with the relative maxima of the amorphous phase content in the polymer share (Figs. 1 and 3). The maxima of the free volumes and the amorphous phase content suggest an increase of the mobility of molecules and are displayed as minima of the modulus G' and maxima of $\tan \delta$ and the modulus G'' . The A and B series, as well as C and D with identical composition but processed at different temperatures of the kneader's walls (443 and 463 K), do not change the positions of their characteristic concentrations.

The changes in the Young's modulus of elasticity of the composites, as dependent on the volumetric concentration of the filler, are presented in Figure 5 for the A, C, and D series.

Obviously in this case the curves display a periodic nonmonotonous character, and hence cannot be approximated as monotonous curves according to the equations proposed in Refs. 1, 5, and 6 etc. The curves in Figure 5 show the same maxima and

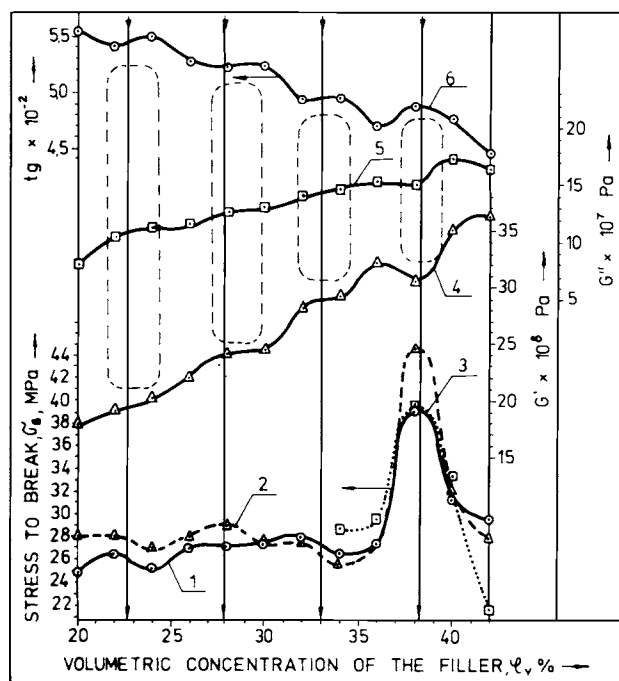


Figure 4 Stress to break σ_B (curves 1, 2, and 3) and dynamic-mechanical properties (curves 4, 5, and 6) vs. volumetric concentration of the filler ϕ_v for the composite of the KE series: (1) stress to break with a shovel 1 and deformation rate of 50 mm/min on a ZMG dynamometer; (2) stress to break after thermal treatment for 1 h at 100°C with test shovel 1 at a deformation rate of 50 mm/min on a ZMG dynamometer; (3) stress to break at a deformation rate of 10 mm/min, test carried out in RWTH Aachen (shovel 2); (4) G' ; (5) G'' ; (6) $\tan \delta$.

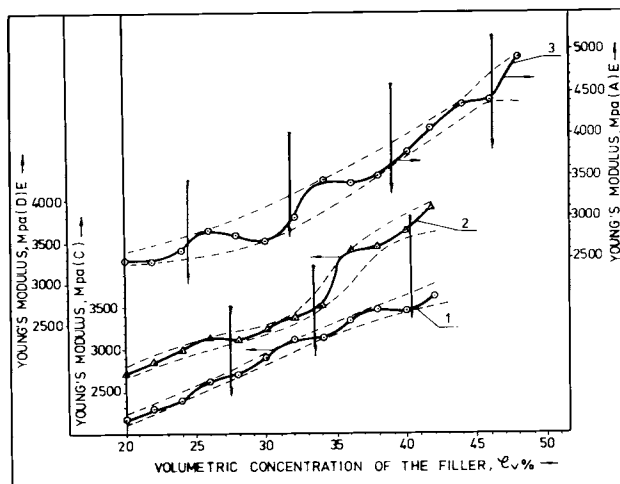


Figure 5 Relationship between Young's modulus E and the volumetric concentration of the filler ϕ_v : (1) composites of the C series; (2) composites of the D series; (3) composites of the A series.

minima as those of the degree of crystallinity and density of the polymer share. This is in agreement with existing data, showing that the elasticity modulus of polyethylene is related to its degree of crystallinity¹⁸ and relative volume.¹⁹ The increase of the elasticity modulus together with the augmentation of the degree of crystallinity is explained by the effect exerted by the crystallites, which act as if they are particles of a solid filler. Thus Nielsen⁵ considers the crystalline polymers as polymers filled with crystallites.

Recently it became possible to determine with adequate accuracy the size distribution of crystallites in crystalline polyolefins by applying X-ray diffraction pattern techniques to the crystalline substances.¹⁷ The size of polyethylene crystallites in the composites of the A series is determined in three samples with different filler concentration by X-ray diffraction studies, and analysis of the 110 and 200 reflections, using four different methods[†]:

- \bar{N} —from the number distribution;
- \bar{D} —from the diameter distribution;
- \bar{F} —direct method from the Fourier coefficients;
- \bar{I} —from the integral breadth.

It is established that the mean crystallite size is 23.3 nm, this size changing slightly with the volu-

[†] The authors express their gratitude to Professor Bodor from the Research Institute of the Plastics Industry, Budapest for his kindness in providing the experimental data.

metric concentration of the filler till the achievement of maximal possible filling of about 52 vol %.

DETERMINATION OF THE CHARACTERISTIC CONCENTRATIONS OF THE FILLER O_n IN THE COMPOSITES

The characteristic concentrations of the filler O_n in the composites are determined by the points equidistant between two inflection points of the respective minima or maxima ("orientation extrema" according to Ref. 8), of the property–volumetric filler concentration curves. On the basis of the curves expressing the multiextremal relationships between 10 basic properties of the composites and the volumetric concentration of the filler, two types of characteristic concentrations were determined, each having a specific disposition. The first type of characteristic concentrations (concentrational transitions) are determined at the points of the orientation extrema at which the stress to break, σ_B , the strain at break, ϵ_B , the volumetric work for breaking, A_v , of the sample, the loss modulus G'' , and the mechanical losses $\tan \delta$ display maxima, while the mean density of the polymer share, ρ_m , the degree of crystallinity W_c in %, and the real modulus G' show minima. The characteristic concentrations of the first type are marked in Figures 1–5 with a vertical arrow pointing down. The second type of characteristic concentrations are located in-between, and are determined by the points of the opposite orientation extrema of the above-mentioned parameters. The accuracy of the thus determined characteristic concentrations of both types, applying the mean arithmetic values of the respective extrema and based on the curves of the ten properties, reaches in our case ± 0.5 – 1.0 vol % of filler at a 95% confidence interval.

PHYSICAL STRUCTURE OF HD POLYETHYLENE COMPOSITES CONTAINING DISPERSED FILLER

According to E. W. Fischer, lamellae are the basic form of all crystallization phenomena in polyethylene from solution or melt onto different substrates. During the epitaxial growth of HD polyethylene onto NaCl substrates, regardless of its molecular weight and degree of branching, oriented lamellae are obtained, standing perpendicularly on the substrate, the crystalline substrate enhancing the formation of crystal nuclei.²⁰ On the basis of electron micro-

scopic investigations by Gähde et al.,²¹ it has been established that, at 2% filling with pure kaolin, HD polyethylene displays a block lamellar structure. At higher amounts of kaolin the lamellar boundaries are no longer discrete and, as a whole, the structural uniformity of the matrix increases. A perpendicular orientation of lamellae to the filler surface spread over a distance of 0.3–0.5 μm is observed around the filler particles.²¹ The electron microscopic studies of Chacko et al.²² show that filling of linear polyethylene with CaCO_3 leads to vanishing of the far order in the microstructure of the polymer, i.e., to the disappearance of the spherulites, regardless of the molecular weight and the nature of the polymer–filler boundary. The particles of the filler in these composites are surrounded by an interlayer or radially oriented polymer lamellae which are spread 300–400 nm beyond the particle.²² Also, on the basis of electron microscopic studies of kaolin-filled linear polyethylene, Dolakova and Hudeček²³ have established that the kaolin particles are linked by fibrils with diameters of the order of magnitude 10^2 – 10^3 Å. During deformation of polyethylene composites, the links can be stretched, being finally destroyed on the fracture surface.²³ According to Chacko et al.²⁴ electron microscopic investigations have established that, after deformation, filled polyethylene displays cracks perpendicular to the direction of the stress, and has void-fibril structures, where separate fibrils are seen in the direction of the stress.

According to Solomko,²⁵ filling of crystalline polymers can be accompanied by various alterations of their supermolecular structure and degree of ordering evaluated by X-ray methods. In this respect, Grigor'ev et al.²⁶ have established that, upon filling of HD polyethylene with aerosil (SiO_2) and titanium dioxide, both the degree of crystallinity of the polymer and the longitudinal dimensions of the crystallites are changed. The X-ray investigations carried out in the present study show that in HD polyethylene composites with kaolin (A series) the average size of the crystallites is 23.3 nm and it decreases slightly (by 5–10%) with the rise of the filler concentration from 20 to 52 vol %.

On the basis of the above-stated data, it may be assumed that the composites we have studied are composed of kaolin particles (aggregates) with perpendicularly standing lamellae of HD polyethylene (several hundred nm long) fixed on their surface. The lamellae include fibrils with diameters of the order of 10 – 10^2 nm, composed of crystallites and an amorphous part. These lamellae, radially positioned toward the particles, form an absorption coating of crystallite layers. The crystallization of polyethylene

in its composites proceeds in the narrow gap between two opposite substrates. With the rise of the volumetric concentration of the dispersed filler, the mean size of the gap between the particles will continuously decrease and will be consecutively filled up by $n, \dots, 3, 2$ layers down to 1 layer of crystallites with definite dimensions. When the gap is filled up by an even number of crystallite layers, they will crystallize according to an oriented pattern upon the flat kaolin particles and new types of filler particles will be formed, coated by a whole number of crystallite layers. When the gaps are filled up by an odd number of crystallite layers, the oriented crystallization of the intermediate layer will be hindered and more amorphous phase and free volume will be created in the polymer share. In our opinion, these two basic structures determine the two types of characteristic filler concentrations, as well as the periodical changes in the physico-mechanical parameters with the rise of the filler content. This physical structure is similar to that proposed in the case of phenol-anilin formaldehyde resin composites.^{7,8}

According to data for the final torque M_{end} and the final temperature T_{end} of the composites in the Brabender plastograph as dependent on the filling, the polyethylene melt keeps a memory of the crystallites and the physical structure formed at the early stages of the mixing process at elevated temperatures.

QUANTITATIVE RATIOS FOR THE PHYSICAL STRUCTURE PROPOSED

According to the above proposed model, the composites comprise new types of particles consisting of kaolin particles (i.e., separate kaolin particles and/or aggregates of separate kaolin particles) coated with adsorbed layers of polyethylene crystallites. These new particles are packed in a solvation coating of the polymer in a pattern similar to the model proposed in Refs. 7 and 8. The average thickness of the adsorption layers, \bar{d}_{ad} , according to this model is expressed by the equation derived in Ref. 7:

$$\bar{d}_{\text{ad}} = \frac{100 - V_s - \varphi_v}{\varphi_v \rho_f F K_\varphi} \times 10^3 = 40.45 \frac{P_f - \varphi_v}{\varphi_v K_\varphi} \text{ nm} \quad (2)$$

where V_s is the concentration of the solvation coating in the composite expressed in vol %, $P_f = 100 - V_s$ is the packing fraction or the concentration of closely packed new types of particles in vol %, φ_v is the volumetric concentration of kaolin in the com-

posite in vol %, ρ_f is the kaolin density, 2.63 g/mL, F is the specific surface of the kaolin particles according to BET measurements, 9.4 m²/g for Burgess KE, and K_φ is a coefficient accounting for the degree of covering of the specific surface of kaolin particles by polyethylene crystallites at concentration φ of the filler, $K \leq 1$.

Expression (2) is most accurate for fillers with flat particles of the kaolin type and/or for fillers with particles or aggregates with other shapes but with a considerable ratio between their diameter and that of the crystallite—above 50, as in our case. Then the volume of each separate monocrystallite layer upon the filler particle will be the same and hence

$$V_s + nV_{\text{lad}} + \varphi_v = 100 \quad (3)$$

or

$$P_f = \varphi_v + nV_{\text{lad}} \quad (4)$$

where V_{lad} is the volume concentration of a monocrystallite polyethylene layer upon the kaolin particles in the composite and n is the number of adsorption monocrystallite layers of polyethylene upon the kaolin particles.

The characteristic concentrations $\varphi_v = O_n$ will appear through the adsorption monocrystallite layers which differ by 0.5n, i.e. at $n = 0.5, 1.0, 1.5, 2.0, \dots$

P_f is a constant value in expression (2) at different values of n since the shape of the new particles is retained, and only the scale factor is changed.^{7,8} This is especially valid for two adjacent characteristic concentrations with small difference between them. In this case the volume of one adsorption monocrystallite layer V_{lad} can be evaluated by the difference in the volumetric concentration of two adjacent characteristic concentrations:

$$V_{\text{lad}} = 2 [O_n - O_{(n+0.5)}] \quad (5)$$

thus offering a possibility to calculate also P_f by applying expression (4).

According to the model proposed, maximum filling will be achieved with one mean monocrystallite layer between the filler particles, i.e., at $n = 0.5$. At $n = 0$ the function will tend to the P_f values of the pure fillers given in Ref. 1. The characteristic concentrations by the concentration transitions are at $n + 0.5$ adsorption monocrystallite layers and the opposite ones are at a whole number— n layers. Thus the basic function $O_n = f(n)$ can be determined experimentally for each separate composite series.

The following linear equation was derived for the relationship between the volumetric characteristic concentrations O_n and the n values (up to $n = 4$) of the A and B series:

$$O_n = \int_{n=0}^{n=4} 57.012 - 7.20n \quad (6)$$

The relationships between O_n and n were presented graphically for seven composite series; then by applying an approximation based on the least square method to the initial linear part of the curves, the functions $O_n = f(n)$ were calculated. Up to $n = 3.5-4$, these functions are linear, suggesting that within this range P_f remains constant, while at higher n values they decrease slower. At $n = 0$, the calculated P_f value for a pure filler is within the limits 45–60% for the different composite series, i.e., the results are close to the data reported in Ref. 1 for P_f of kaolins.

By determining the P_f value according to expression (4) or eq. (6) at $n = 0$, one can evaluate the mean thickness of the adsorption layer \bar{d}_{ad} at each concentration of the filler, using eq. (2). Since there is no direct method for the determination of the coefficient of coverage K_φ , in practice one can calculate the value of

$$A_n = \bar{d}_{ad} \cdot K_n \text{ in nm, where } K_n \text{ is } K_\varphi \text{ for } O_n \quad (7)$$

The ratio between $A_{(n+0.5)}$ and A_n calculated for two adjacent characteristic concentrations (columns 5 and 6 in Table I) is equal to

$$\frac{A_{(n+0.5)}}{A_n} = \frac{n + 0.5}{n} \frac{K_{(n+0.5)}}{K_n} = \uparrow \frac{z}{n} \quad (8)$$

where $z = (n + 0.5)K_{(n+0.5)}/K_n$.

The mean thickness of the crystallite \bar{d}_k can be determined by the expression

$$\bar{d}_k = \frac{\bar{d}_{ad}}{n} = \frac{A_n}{n \cdot K_n} = \frac{B_n}{K_n} \quad (9)$$

where $B_n = A_n/n = \bar{d}_k K_n$ and K_n is the coefficient of coverage, K_φ , for a composite with filler concentration O_n , in vol %.

It follows that

$$K_n = B_n/\bar{d}_k \quad (10)$$

Since the aggregation of the kaolin particles decreases at lower volumetric concentrations of the filler while K_n increases and tends to its maximum value 1, B_n would also augment and tend to the mean thickness of the crystallite [eq. (9)]. Assuming that the experimentally determined mean thickness \bar{d}_k from all X-ray measurements is 23.3 nm, one can calculate also the real coefficients of coverage K_n for the different characteristic concentrations by means of expression (10).

QUANTITATIVE EVIDENCE FOR THE PROPOSED PHYSICAL STRUCTURE

Table I shows the experimental and calculated data for the linear relationship between O_n and n as well

Table I Evaluation of O_n , A_n , B_n , and K_n for the A and B Composite Series with the Characteristic Concentrations O_n

No. of O_n	Exptl-detd. O_n (vol %)	O_n Calcd by Eq. (6) (vol %)	$A_n = \bar{d}_{ad} \cdot K_n$ Calcd by Eqs. (2) and (7) (nm)	Ratio (8)		B_n Calcd Acc. to Eq. (9)	K_n Calcd Acc. to Eq. (10) at $\bar{d}_k = 23.3$ nm
				$A_{(n+0.5)}/A_n$ of Two Adjacent Charact. Concs $\downarrow \frac{z}{n}$			
1	2	3	4	5	6	7	8
$O_{0.0}$	—	57.01	—	—	—	—	—
$O_{0.5}$	—	53.41	—	—	—	—	—
$O_{1.0}$	49.70	49.81	5.85	1.0	—	5.85	0.25
$O_{1.5}$	46.32	46.21	9.46	$\downarrow 1.62$	1.50	6.30	0.27
$O_{2.0}$	42.80	42.61	13.67	2.00	$\downarrow 2.17$	6.84	0.29
$O_{2.5}$	39.25	39.00	18.68	$\downarrow 2.73$	2.50	7.47	0.32
$O_{3.0}$	35.52	35.40	24.69	3.00	$\downarrow 3.30$	8.23	0.35
$O_{3.5}$	32.04	31.80	32.07	$\downarrow 3.89$	3.50	9.16	0.39
$O_{4.0}$	28.10	28.10	40.14	—	$\downarrow 4.38$	10.04	0.43

as data for the calculated values of A_n , B_n , and K_n for the A and B composite series with identical characteristic concentrations O_n . The experimentally determined characteristic concentration $O_n = 46.32\%$ is identified as a concentration transition at $n = 1.5$. This concentration cannot be at $n = 2.5$ since then the maximum possible filling $O_{0.5}$ would be 60.6 vol % and P_f at $n = 0$ would be 64.21 vol %. It cannot be at $n = 0.5$ either since the maximum possible filling determined experimentally for the A series amounts to 52 vol %.

The coverage coefficient K_n increases as the volumetric concentration of the filler decreases, because the aggregation of the filler is less pronounced. Therefore the calculated ratios in columns 5 and 6 are almost similar to their respective numbers n but slightly higher in value [expression (8)]. This good agreement proves that composites at two adjacent characteristic concentrations differ by 0.5 adsorption monocrystallite layers, thus confirming the validity of the proposed model.

The B_n values are calculated for each O_n by means of expression (9) and are given in column 7, Table I. Since K_n increases and tends to 1 with decrease of the volumetric concentration of the filler, the value of B_n also increases and tends to the order of magnitude of polyethylene crystallites.

CALCULATION OF \bar{d}_{ad} AS A FUNCTION OF THE MEAN SIZE OF THE FILLER PARTICLES (AGGREGATES)

To carry out these calculations, we used the statistical mean size of the particles (aggregates) of the polydisperse pure filler (kaolin) in the composite, \bar{D}_f . The mean size of the new particles in the composite is equal to $\bar{D}_f + 2n\bar{d}_k$ since the adsorption coating is taken into account, the latter being composed of n crystallite layers of polyethylene with mean size \bar{d}_k . Assuming that P_f of the new particles, i.e., the volume they occupy in the overall bulk of the composite, is constant and equal to that of the pure filler, while only the scale factor is changing,⁷ in the case of round (or cubic) filler particles one obtains the following equation:

$$\varphi_v = P_f \frac{\bar{D}_f^3}{(\bar{D}_f + 2n\bar{d}_k \cdot 10^{-3})^3} \% \quad (11)$$

where φ_v is the volumetric concentration of the pure filler in the composite in vol %, P_f is the packing fraction of the new particles in % [in the case of kaolin $P_f = 45\text{--}60\%$ ¹ while according to eq. (6) this

value of the filler Burgess KE in the A series is 57.012%], \bar{D}_f is the statistical mean size of the particles (aggregates) of the pure filler in the composite in μm (according to data presented by OMYA GmbH, in the case of Burgess KE $\bar{D}_f = 0.81 \mu\text{m}$), \bar{d}_k is the mean size of polyethylene crystallites in the composite in nm, determined by X-ray methods ($\bar{d}_k = 23.3 \text{ nm}$ in the case of the A series), and n is the number of crystallite layers in the adsorption coating.

According to eq. (6) and data for A series in Table I, during the increase of the filler content from 28.1 vol % to the maximum filling of 53.4 vol %, the value of n changes between 4 and 0.5. Assuming that in both cases $\bar{D}_f = 0.81 \mu\text{m}$ (without aggregation), one obtains by means of eq. (11) $\varphi_v = 30.62 \text{ vol } \%$ (for $n = 4$) and $\varphi_v = 52.36 \text{ vol } \%$ (for $n = 0.5$), these results being quite close to the real values of the volumetric concentration of the filler. The precise values of φ_v , however, are obtained by the assumption that $\bar{D}_f = 1.1 \mu\text{m}$ at $n = 0.5$ and $\bar{D}_f = 0.7 \mu\text{m}$ at $n = 4$, i.e., the mean particle size (aggregates) in the composite filled up to the maximum is 1.6 times higher than that of the composite containing 28.1 vol % filler. The adjacent orientation extrema, calculated by the statistical mean size of Burgess KE kaolin particles using eq. (11), coincide with the experimentally determined values of O_n , and confirm the proposed supermolecular mechanism in that each subsequent orientation extrema differs from the preceding one by $0.5n$ in the adsorption coating.

According to the calculations carried out on the basis of the mean size of the filler particles using eq. (11) as well as based on the site of the orientation maxima O_n according to eq. (6) and Table I, and of the BET specific surface of the filler using eq. (1), it is shown that, within the filling range of the A series ($\varphi_v = 20\text{--}52 \text{ vol } \%$), the mean thickness of the adsorption coating on the filler particles is changed approximately 5–0.5 times the size of the polyethylene crystallites in the composites, determined by X-ray techniques. These quantitative data confirm, and characterize the physical structure assumed for the studied composites.

CONCLUSION

The investigation of the seven series of HD polyethylene and dispersed kaolin composites, each prepared by identical mixing techniques, shows that the changes of the physico-mechanical properties, as dependent on the filler concentration, are not represented by monotonous curves. They are in fact

nonmonotonous, periodic-multiextremal curves. This pattern of the curves is retained at different preparation conditions and testing techniques of the composites of each series. The periodic nonmonotonous change of properties with the filling is related to the periodic change of the free volumes and the content of crystalline phase of polyethylene in the composites as a function of the extent of filling. This in turn leads also to periodic changes of other properties of the composites.

According to the model proposed, the composites comprise filler particles coated with a number n of adsorbed crystallite polyethylene monolayers. As filling continues, new types of particles with different numbers of monolayers n are formed when certain characteristic concentrations of the filler are reached. Passages through the so-called concentrational transitions occur in a way similar to the temperature relaxation transitions of polymers. Characteristic concentrations relate with high accuracy to typical changes mainly of the dynamic-mechanical properties as well as mechanical strength and other properties of the composites. These concentrations, which are related to the consecutive number of n adsorbed layers upon the filler particles are quantitatively confirmed by calculations.

The nonmonotonous character of the relationships between the physico-mechanical properties of the composites and the volumetric concentration of the filler should be taken into consideration in their presentation as mathematical-analytical expressions.

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