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MODIFICATION OF POLYETHYLENE WITH ACTIVATED NATURAL ZEOLITE

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ABSTRACT

In an attempt to improve its main physical and mechanical characteristics, the modification of high density polyethylene (HDPE) with activated (dehydrated) natural zeolite clinoptilolite, in an attempt to improve its main physical and mechanical characteristics is investigated. After dehydration at 350°C and cooling in an atmosphere of dry air, about 30% of the entire volume of the zeolite particle is freed. This free volume and the ensuing from the specific structure sorption processes-the possibility for sorption of the polymer chain on the surface channel of the zeolite particle-determine the active modification function of dehydrated clinoptilolite.

An experimental study has been carried out on some physical and mechanical properties of filled with activated zeolite polyethylene (HDPE) composites. The polyethylene composites containing 20 and 30% activated zeolite have optimal mechanical characteristics. Compared with the pure HDPE, these compositions show reduced density of the produced parts, compared with the theoretically established, an increase of the tensile strength, acceptable elasticity in impact strength, and the highest values of the modulus of elasticity, which means a better suitability for production of parts with construction application.

The addition of activated zeolite to HDPE affects the non-isothermal phase transitions. The compositions containing 20 wt% zeolite show an increased degree of crystallinity. The values for some morphological parameters during the process of non-isothermal melting, the energy of activation for transport through the phase boundary, the surface energy of the crystal, and the long period, are established for pure HDPE and for modified with 20 wt% activated zeolite HDPE-compositions.

INTRODUCTION

Modification of polyolefins has had a rapid development and increasing range of application in the past years. The preparation of polyolefin composites aims at improving the physical properties of plastic products and leads to production economies. The usage of different fillers as modificators of polyolefins is a logical and well-known idea. All traditional materials, applied as fillers for thermoplastic materials, are investigated as structure-modificators with the following main purpose-to change and improve some of their physical and mechanical properties, as well as to reduce the cost of the obtained polymer composites [1-8].

The interest in natural zeolite clinoptilolite as a modificator for polyolefins and especially for polyethylene is based on some specific qualities of this material which allow us to expect a new combined effect in the structure organization of the filled with activated zeolite polymer material. This paper reports on the investigation of the modification of HDPE with activated natural zeolite clinoptilolite, in an attempt to increase its utility properties and to improve its main characteristics while reducing its cost.

EXPERIMENTAL

Materials

The material used is HDPE "Bulen" with density 960 kg/m^3 and MFI 6.73 g/10min (463^{0}K/49.05 N). The modificator used is activated natural zeolite clinoptilolite $(K_2Na_2Ca)_3\ Al_6Si_{30}O_{72}\ .23H_2O$ with density 2200 kg/m^3 and particle size under 20.10$_{-6}$m, produced by Zeoproducts Ltd. Co., Bulgaria. The content of the modificator activated zeolite was varied in the range of 0 to 40 wt%.

Technological Equipment

The investigated compositions have been granulated at melt temperature in the range 150°C-180°C. Specimens with a size of the working sector 60 x 9.8 x 3.8 mm have been prepared by injection molding at melt temperature 180-220°C. The mechanical properties, tensile strength σ, elongation ε, modulus of elasticity E, of the investigated parts were determined by means of a dynamometer TIRATEST 2115.

The overall density of the investigated specimens was determined by the formula:

$$\rho = m/V, \tag{1}$$

where m is the mass of the specimen and V is its volume.

The calorimetric device (gas evolution apparatus), which measured the pressure of the gaseous products of the investigated compositions consisted of a decomposition tube, connected with a manometer (2.5 MPa). The decomposition tube was placed in a heating block with silicone oil. The heating rate of silicone oil was 2.5°C/min. The gas evolution kinetics of the investigated material was determined with this calorimetric device at 200°C.

The calculation of the gas yield of the investigated material was made using the equation of Gey Lusac for the state of ideal gases. The mole numbers, obtained by the thermodesorption of activated zeolite were calculated according to the following equation:

$$m = P.V/R.T \tag{2}$$

where P is the experimentally established pressure of gas evolution, V is the volume of the decomposition tube, T is the temperature of the conducted experiment, R is the universal gas constant.

Taking into account the Avogadro law, according to which 1 mole of gas takes up a volume of 22.4 l, we determined the gas yield of the investigated material.

The morphological parameters of HDPE and modified with zeolite HDPE composites were defined on the basis of DSC-graphics, obtained with a differential scanning calorimeter Perkin-Elmer DSC-7 at a heating rate of 10°C/min.

The degree of crystallinity α was calculated by the formula:

$$\alpha = \frac{1}{\Delta H_m^0} \int_{T_1}^{T_2} \left(\frac{dH}{dT} \right)_{T_n} dT \tag{3}$$

where T_1 and T_2 are the initial and final temperatures of phase transition, T is the absolute temperature, H is the enthalpy, ΔH_m^0 is the melting enthalpy of the ideal PE crystal (4110 J/mol) and the $\left(\frac{dH}{dT}\right)_{T_n}$ values were taken from DSC-graphics.

The activation energy for transport through a phase boundary crystal melt, the surface energy of the crystal and the long period were calculated by the computer programs using the formulas of the non-isothermal melting kinetics theory [10-12]. According to this theory, the rate of a non-isothermal process G is proportional to the quantity of molten substance at a certain temperature, the rate of heating or cooling V_0 and a function describing the continuous depletion of the available polymer:

$$G = \frac{V_0\left(\frac{dH}{dT}\right)\Delta H}{\Delta H_m^0 \int_T^{T_2}\left(\frac{dH}{dT}\right)dT}, \tag{4}$$

where ΔH is the enthalpy of the phase transition.

Applying the method for the rate of isothermal melting G_m, described in [9], Nedkov *et al.* presented the non-isothermal melting as a sum of isothermal processes, performed at temperatures To ...Tn, then at every temperature the momentous melting rate can be determined by the DSC-graphics. Using the values obtained for G_m, the long period, the energy of activation for transport through phase boundary and the surface energy of the crystal were calculated by the following formulas: [10-12]

$$L = \frac{3a^2 M_c \Delta H_m^0}{(2.3tg\alpha_m)^2 M_0 T_m^0 A N_a k} \tag{5}$$

$$E_d = \left(\log G_m^0 - \log G_m\right)2.3kT \tag{6}$$

$$\sigma = \frac{L \Delta H_m^0 \Delta T}{2T_m^0} \tag{7}$$

where G_m^0 is a constant ($1\text{x}10^{13}$ s^{-1}), E_d is the activation energy for transport through phase boundary, a is the average intermolecular distance within the crystal ($6\text{x}10^{-10}$ m), M_c is the average molecular weight of the crystallite, L is the

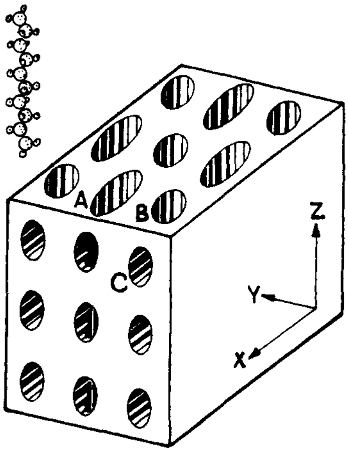

Figure 1. Scheme of the channels on the surface of a clinoptilolite particle. Left in the corner a polyethylene chain at the same scale is shown.

long period, L is accepted as equal to the thickness of the lamella, A is the length of a statistic segment ($2x10^{-9}$ m), M_0 is the molecular weight in monomeric units, T_m^0 is the equilibrium temperature of melting (414 K), $\Delta T = T_m^0 - T$, N_α is the Avogadro constant, k is the Boltzman constant.

RESULTS AND DISCUSSION

The interaction between the natural zeolite (clinoptilolite) and the polymers has been investigated and, basically, the modification effect of natural zeolite on HDPE has been examined. The structural preconditions for the interaction between clinoptilolite and polymers are based on the special character of the surface of zeolite particles. Clinoptilolite $(K_2,Na_2,Ca)\,Al_6Si_{30}O_{72}$. 23 H_2O is a natural alumosilicate with a specific structure, characterized with three systems of channels in the particle volume. The dimensions of the polymer chain are commensurable with the dimensions of these channels in the zeolite particles, which allow the process of adsorption of the polymer chain on the zeolite surface channels and determine the arising of strong connection and good adhesion between polymers and zeolite particles (Figure 1).

The characteristic peculiarity of zeolite, which determines its unique properties, is its ability to give off the hydrathwater without destroying the crystal

TABLE 1. Physical and Mechanical Properties of HDPE Compositions

Composition, (%)	Tensile strength, MPa	Elongation, %	Modulus of elasticity, MPa	Impact strength, kJ/mm^2	Heat resistance, ^0C	Density, g/cm^3	MFI, g/10min
PE 100 %	18,28	310,9	15215	do not break	120	0,96	6,73
PE 80%, Z 20%	20,22	24,62	19922	do not break	125	1,0897	4,48
PE 70%, Z 30%	21,77	11,64	38797	20,42	126	1,1295	3,5
PE 60%, Z 40%	18,95	2,36	36739	n. d.	n. d.	n. d.	n.d.

lattice. Exactly the process of dehydration is the process of zeolite filler activation. After dehydration at 350°C and cooling in an atmosphere of dry air, about 30% of the whole volume of the zeolite particle is freed. This free volume and the ensuing from the specific structure sorption processes - the possibility for sorption of the polymer chain on the surface channel of the zeolite particle - determine the active modification function of dehydrated clinoptilolite.

An experimental study has been carried out on some physical and mechanical properties of filled with activated zeolite polyethylene composites and the obtained results are shown in Table 1.

An increase of the tensile strength with the increase of the zeolite content is established and the PE composites containing 20 and 30% activated clinoptilolite possess optimal mechanical characteristics.

The increase of the modulus of elasticity by the addition of mineral fillers is a logical result, as well as the decrease of the impact strength. According to the obtained results, as optimal compositions are accepted the HDPE composites, containing 20% and 30% activated zeolite. Compared with the non-filled HDPE, these compositions show, respectively 10.7% and 19% increase of the tensile strength, acceptable elasticity in impact strength and the highest values of the modulus of elasticity, which means better suitability for production of parts with construction application.

It is of interest to note the density values of the examined HDPE composites, modified with natural activated zeolite. By the increase of the zeolite content, the studied PE composites show lower density than the theoretically predicted values. The explanation of this result should be searched again in the unique structure of dehydrated natural clinoptilolite. The dehydration of natural zeolite is the process of its activation. The dehydrated structure of zeolite has about 30% free volume. After dehydration at 350°C and cooling in atmosphere of dry air, an equilibrium saturation of the free volume with gases is achieved. The dehydrated zeolite sorps mainly nitrogen from the air. The desorption of nitrogen can be achieved by exchange of water steam or by heating. The total density decrease by the experiments carried out is about 10% for the HDPE specimens containing 20% activated zeolite, and about 16% for the HDPE parts with 30% activated filler, compared with the theoretically established composition density values. Consequently, the dehydrated zeolite is a low efficient physical blowing agent This conclusion is proved by the conducted gas release experiment. The results illustrated on Figure 2 show the kinetics of the gas release ability of the dehydrated zeolite at 200°C, and therefore, the activated zeolite can be considered as an a original low efficient physical blowing agent.

According to the conducted research, the activated zeolite liberates 8-8,5 ml/g gas, mainly nitrogen, during the heating process. More proof for this thermodesorption process is the microscope research, made with PE specimens, containing 20% activated clinoptilolite. Photographs of the structure of these specimens are shown on Figure 3. Small spherical bubbles with diameter reaching 0.1mm regularly distributed in the volume of the HDPE specimen, filled with 20% zeolite, are observed on the photograph (Figure 3).

Some morphological parameters of HDPE and modified with 20 wt% activated zeolite PE composites are determined according to formulas of the kinetics of non-isothermal melting. Figure 4 presents DSC-graphics obtained at a heating rate 10 deg/min. The dependencies ***dH/dT=f(T)*** refer to HDPE specimens and to filled with 20 wt% activated zeolite PE composites. The values of the activation energy for transport through the phase boundary, the surface energy of the crystal, the long period and the degree of crystallinity of the HDPE and of the modified with 20 wt% activated zeolite HDPE were determined by a corresponding treatment of the DSC-curves and the obtained results are presented on Table 2.

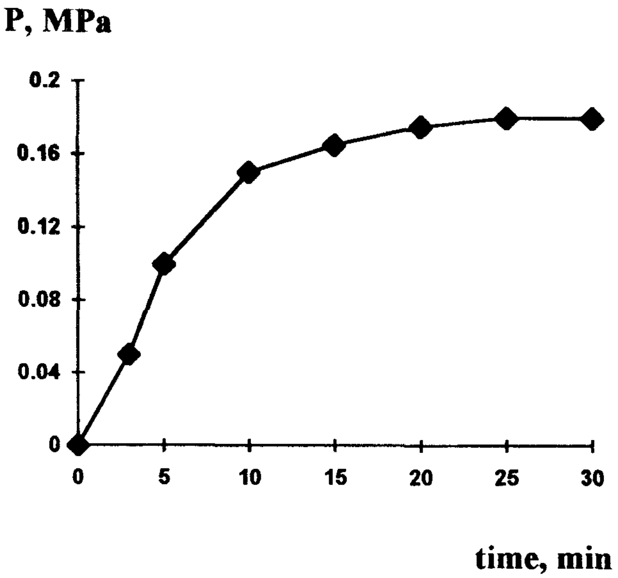

Figure 2. Pressure of the gas desorped from activated zeolite vs. heating time at 200°C.

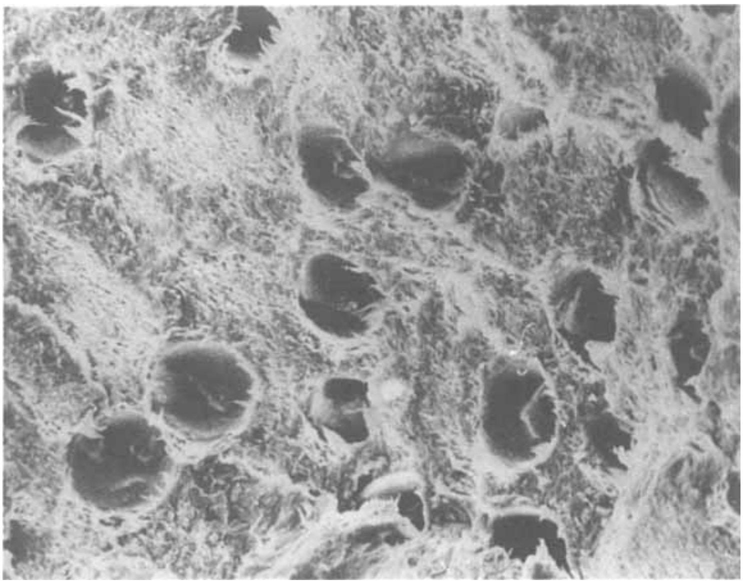

Figure 3. Structure of PE specimens, containing 20% activated clinoptilolite, x100.

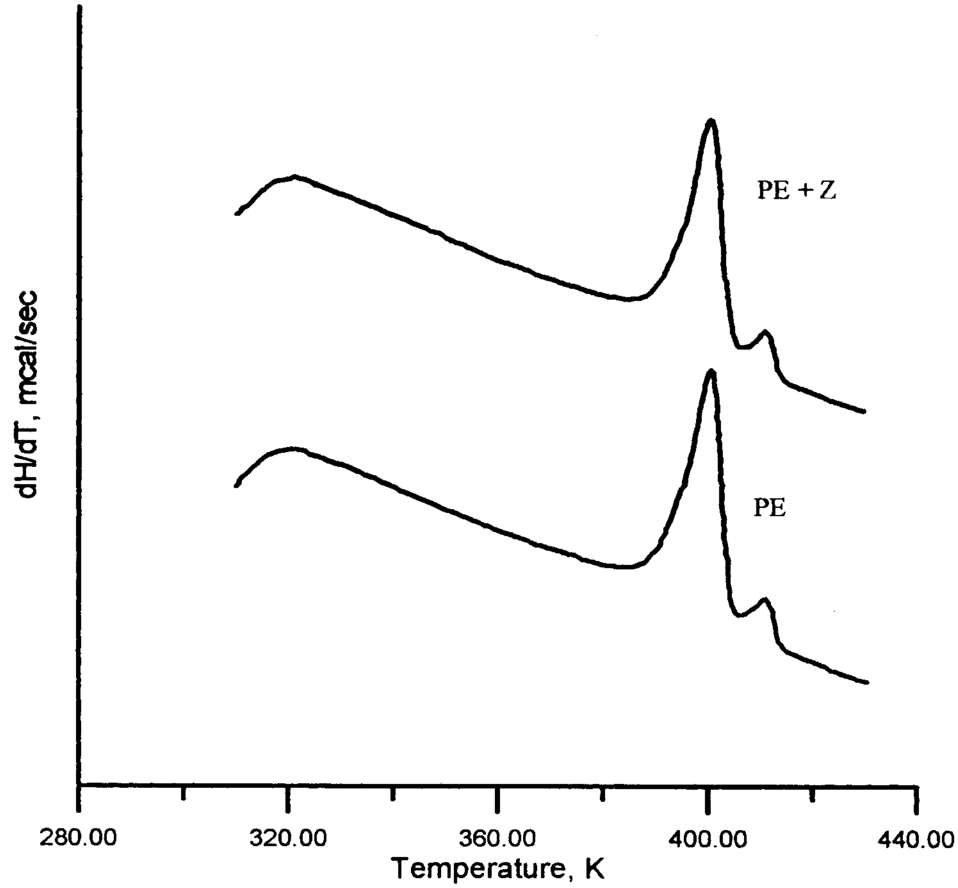

Figure 4. DSC curves of melting of E and PE with 20 wt% activated zeolite.

Degree Of Crystallinity α

The initial polyethylene has a linear molecular structure and the degree of crystallinity obtained for it is 43% in comparison with 48.3% for modified with zeolite composites, determined as a result of non-isothermal melting, respectively. The obtained α values confirm the expected fact that the degree of crystallinity increases with the increase of the zeolite content. Obviously, the presence of finely-ground zeolite particles, acting as nucleating agent, facilitates the crystallization process.

Activation Energy for Transport Through the Phase Boundary E_d

This is the energy of the phase transition. The data presented on Table 2 shows a decrease of the activation energy values with the addition of activated

TABLE 2. Non-isothermal Melting

	ΔH (cal/g)	α (%)	E_d (kJ/mol)	$\sigma \cdot 10^{-4}$ (J/m^2)	L (Å)
HDPE	29,4	43	79,5	2,5	712,4
HDPE with 20 wt.% zeolite	33,0	48,3	78,6	2,0	627

clinoptilolite to the initial HDPE. The decrease of the activation energy results from the presence of activated zeolite, which probably diminishes the barrier that has to be overcome during folding and unfolding of the molecules, and makes easier the process of passing from one phase into another.

Surface Energy of the Crystal σ

Surface energy of the crystal is the energy necessary to form a unit surface at the boundary between the two phases. As it is known, σ depends on the size of the forces on the boundary surface. The latter itself depends on many factors (temperature, presence of transitional chains, and ends of chains at the boundary between the two phases, defects, nucleating agents, etc.) that act in various directions. Therefore, it is completely acceptable that the value of the surface energy obtained by non-isothermal phase transition decreases with the addition of zeolite.

Long Period *L*

Long period is a measure for the thickness of the lamella. It is proportional to the surface energy and its dependence on the zeolite presence is similar to the one above.

The morphological parameters obtained as a result of the kinetics of non-isothermal melting are proved by the microscopic investigations of the structure of thin microtomed sections taken through the thickness of the studied specimens. When these sections are viewed between crossed polars on a transmission light microscope, spherulites are observed (Figures 5, 6). It was found, that in the

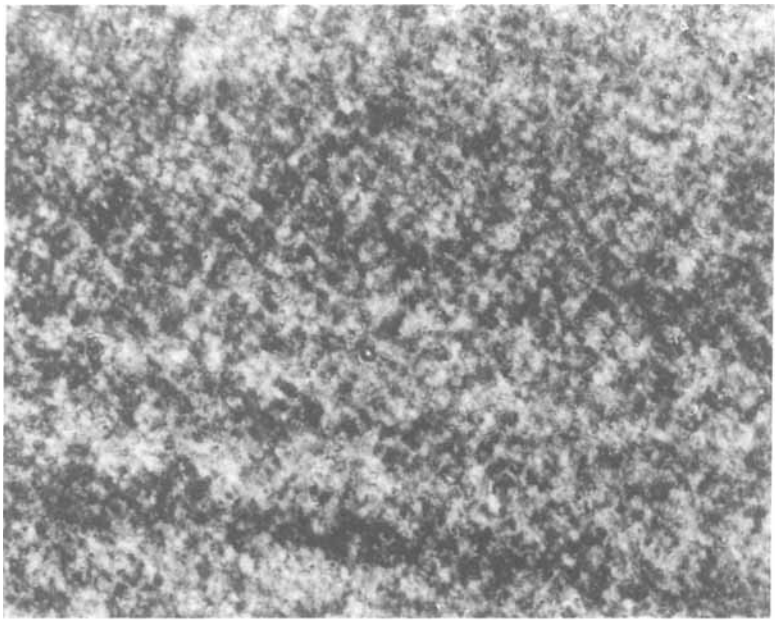

Figure 5. Polarized light micrograph of a thin microtomed section through HDPE specimen, x 1000.

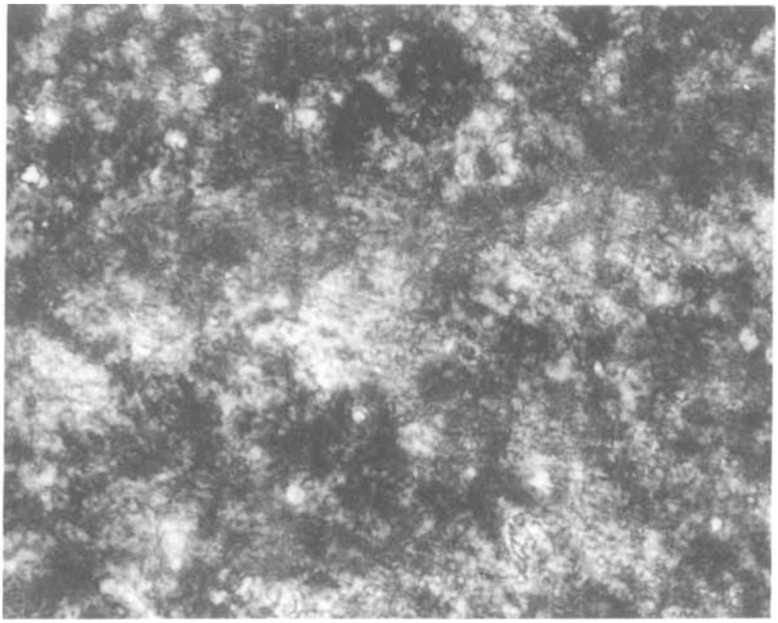

Figure 6. Polarized light micrograph of a thin microtomed section through HDPE specimen with 20 wt% activated zeolite, x 1000.

presence of activated zeolite the number of spherulites in the observed modified PE samples increase and they have greater dimensions. These results are in accordance with the values obtained for the morphological parameter degree of crystallinity α of the investigated compositions.

CONCLUSION

The possibility for applying dehydrated natural zeolite (clinoptilolite) as a filler-modificator of polyolefins is studied, and the obtained experimental results prove its positive effect on the physical and mechanical properties of HDPE. The HDPE composites containing 20 and 30% activated zeolite have optimal mechanical characteristics. These compositions show reduced density of the produced parts, compared with the theoretically established, which proves the action of activated zeolite as a specific physical blowing agent.

According to the obtained results the HDPE composites, containing 20% and 30% activated zeolite show an increase of the tensile strength. Compared with the non-filled HDPE these compositions show, respectively 10.7% and 19% increase of the tensile strength, acceptable elasticity in impact strength and the highest values of modulus of elasticity, which means better suitability for production of parts with construction application.

The addition of activated zeolite to HDPE affects the non-isothermal phase transitions. The compositions containing 20 wt% zeolite show an increased degree of crystallinity. The values for some morphological parameters during the process of non-isothermal melting, the energy of activation for transport through the phase boundary, the surface energy of the crystal, and the long period, are established for pure HDPE and for modified with 20 wt% activated zeolite HDPE-compositions.

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