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Molecular processes occuring in high density polyethylene+nanoclay nanocomposites under the influence of an electric field

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Structural changes under the action of an electric field in high density polyethylene (PE) and a nanocomposite have been measured by infrared spectroscopy, viscometry, and differential thermal analysis. Destruction of macromolecules occurs under the action of an electric field. As a result, with the formation of C=C groups, the molecular weight decreases. After exposure to an electric field, the depolymerization temperature of the nanocomposite changes less than that of pure polyethylene.

Keywords: nanoclay, nanocomposite, electric field, C=C group.

Молекулярні процеси, які відбуваються у нанокомпозитах поліетилен високої густини + наноглiна під впливом електричного поля. *А.Р.Садигова, А.А.Хадiева, П.Б.Асiлбейлi, Х.О.Садиг, І.І.Аббасов, В.А.Алекперов*

Зміни структури під впливом електричного поля в поліетилені (ПЕВП) і нанокомпозиті вимірювалися методами інфрачервоної спектроскопії, віскозиметрії і диференціального термічного аналізу. Під впливом поля відбувається руйнування макромолекул. В результаті з утворенням C=C груп зменшується молекулярна маса. Температура деполимеризации нанокомпозиту після впливу електричного поля змінюється значно менше, ніж у чистого поліетилену.

1. Introduction

One of the most important structural properties of polymers and polymer composites is their anisotropic properties with respect to the applied mechanical load and electric field due to a variety of intramolecular and intermolecular interactions. Anisotropy is usually caused by mechanical loading in a large number of local centers and the action of an electric field that is many times greater than the average value of the mechanical load and the electric field applied to the sample as a whole. The study of physical properties of polymer composite materials can help to select samples with optimal properties in terms of their production technology and application. It is known that the temperature-time dependence of crystallization, thermal and electrical processes, types and concentrations of additives introduced, direct and preliminary (aging) effects of external factors (radiation, electric discharge and electric field, mechanical load, temperature, etc.) change the physical, mechanical, and electrophysical properties of polymer composites. Information on the internal structure can also be obtained by studying the thermal properties of composites obtained with the addition of small molecules and nanoparticles in the low- and high-temperature ranges.

In [1–5], the role of nanoclay in the mechanical and electrical decomposition of nanocomposites based on polyoefins with the addition of NC is considered. Changes in physical properties under the action of external factors showed that decomposition of polymers and nanocomposites begins with the breaking of chemical bonds. Direct measurement methods can be used to study the breaking of chemical bonds.

According to the experiments of Giannelis [6], the production of nanocomposites involves three stages (Fig. 1). In the first stage (a) the tactoid is formed: polymer chains cover the clay agglomerates from the outside. In the second stage (b), the chain segments enter the gaps between the clay layers, causing the layers to separate by 2–3 nm; in the third stage (c), the clay layers begin to diverge relative to each other, the arrangement of the layers (disorientation) becomes irregular and the layers are completely separated. The uniform distribution of NC in the polymer indicates the ideal structure of the nanocomposite.

In this work, we will study the role of NC in the destruction process after aging; the physical properties of nanocomposites based on polyethylene with the addition of NC will be studied after exposure to an electric field.

2. Experimental

NC in different weight percentages (1,0; 2,0; 3,0; 4,0; 6,0; 8,0; 10,0 wt.%) was mechanically mixed with 20806-024 type HDPE (average molecular weight M-96000, melting point $T_m = 1300$°C, density $d = 0.958$ g/cm^3, degree of crystallinity $k = 52$ %) and then the mixture was pressed in an open steel mold at a temperature of 425 K and a pressure of 15 MPa for 10 min followed by immersing in ice-water mixture for fast cooling. The samples with thickness 50–70 μm were obtained. Since both components are in a powder form, a homogeneous mixture is obtained. NC additive used was montmorillonite (MM) layered silicates of Dk 1 type with bulk density $d = 0.5$ g/cm^3. The dimensions of these layers are about 200 nm in length and 1 nm in width [7]. Al, Mg, and Fe atoms surrounded by a SiO_2 layer are located in the center of the MM crystal lattice. The electrostatic imbalance inside the clay with this structure increases, and an increase in the number of negatively charged particles outside the layer is expected. The negatively charged particles are neutralized by absorption of Na^+, Ca^+. Planar MM particles, lying in an orderly manner, together with the polymer matrix form a layered structure. Aging of the nanocomposite based on HDPE and NC in an electric field was carried out in a test cell, schematically shown in Fig. 2.

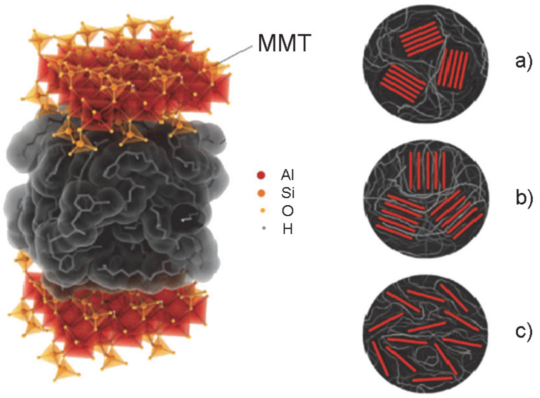

Fig. 1. Three types of "polymer-layered silicate" composites.

The samples were aged at room temperature for $t = 5$; 10; 20; 40; 60 hours at an electric field strength of $2.5 \cdot 10^7$ V/m. Molecular weight (MW) of the studied samples was measured by the viscometric method (decalin ($C_{10}H_8$) was used as a solvent, and for good dissolution of polyethylene, the system was heated to 70°C); thermal destructive properties were measured on a MOM OD-102 derivatograph, the spectrum of molecular vibrations was measured on an IR spectrometer (wave number 4000–200 cm^{-1} IR-SPECORD M-80).

3. Results and discussion

The effect of NC on the mechanical and electrical strength of HDPE was studied in our previous studies [4, 5]. It is shown that NC reduces the electrical strength, while the mechanical strength, depending on the amount of NC, first increases and then decreases. An idea of the decomposition mechanism can be given from the changes that can occur in the structure after keeping the HDPE and NC nanocomposites for different times in an electric field. In the test cell shown in Fig. 2, the samples were subjected to aging in an electric field ($E_{aging} = 2.5 \cdot 10^7$ V/m) for different times. The value of E_{aging} is taken to be less than the specific breakdown voltage ($E_b = 5.5 \cdot 10^7$ V/m).

Figure 3 shows the IR absorption spectra of HDPE and the HDPE + 3.0 % NC nanocomposite after 20 hours of exposure to electric field.

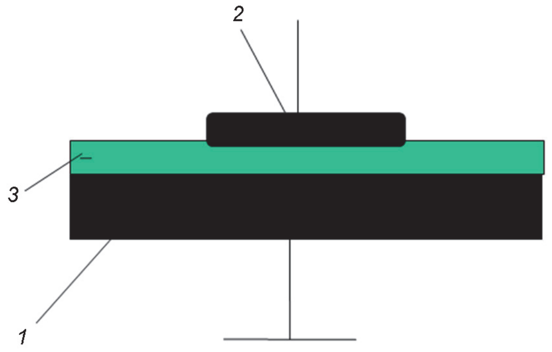

Fig. 2. Test cell: *1* — grounding electrode; *2* — high voltage electrode; 3 — studied sample.

The dependence of the optical density (*D*) of the C=C group on the time of exposure to an electric field at a wavelength of 1640 cm^{-1} is calculated from the spectra shown in Fig. 4.

The molecular weight (MW) of the studied samples was measured by the viscometric method. Decalin ($C_{10}H_8$) was used as a solvent, and for good dissolution of polyethylene, the system was heated to 70°C. Thermal destruction was measured by a MOM OD-102 derivatograph. The oscillation spectrum of the molecules was recorded using an IR spectrometer SPECORD M-80 with wavenumber 4000–200 cm^{-1}.

The optical density of the C=C group increases with the aging time. Breakings in chemical bonds occur between atoms that form macromolecules due to the destructive effect of the field. As *t* increases, optical density of PE increases faster than that of the nanocomposite. The C=C double (pair) bond is the result of the breaking of macromolecules after the action of an electric field [2]. The formation of the C=C group upon rupture of macromolecules should lead to a decrease in molecular weight (MW). Fig. 4 shows the dependence of MW on aging time. The MW of both HDPE and the nanocomposite decreases with *t*, while the MW decrease in PE occurs more rapidly. The change in MW and *D* depending on *t* is inversely proportional.

As can be seen from Fig. 4, since the concentration of the C=C group formed by the radical in the macromolecule increases with aging time, the length of the polymer chain is shortened and the molecular weight decreases. If a macromolecule is split into several parts due to the formation of double bonds (C=C), the number of ends of the skeletal chain increases and molecular mobility increases. This, in turn, leads to a decrease in mechanical strength with aging time.

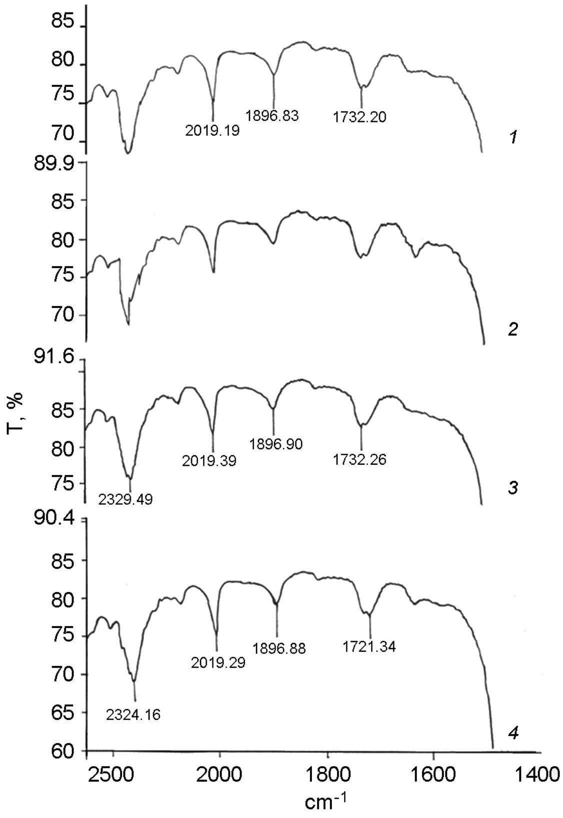

Fig. 3. IR spectra of HDPE and the HDPE + 3.0 % NC nanocomposite: *1*, *2* — pure PE; *3*, *4* — PE + 3.0 % NC; *1*, *3* — *E* = 0 (*t* = 0); *2*, *4* — *E* = 2.5·10^7 V/m (*t* = 20 hours).

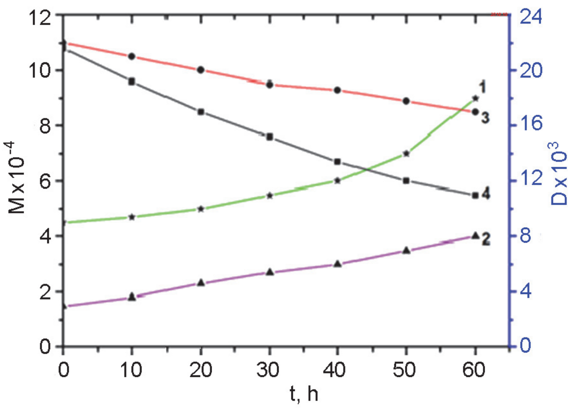

Fig. 4. Dependence of optical density (*D*) and molecular weight (*M*) on the exposure time to an electric field *1*, *2* — *D*; *3*, *4* — *M*; *1*, *4* — pure HDPE; *2*, *3* — HDPE + 3.0 % NC.

When studying the thermal properties of nanocomposites in the low-temperature and high-temperature ranges, the change in the properties of the additive and the thermod-

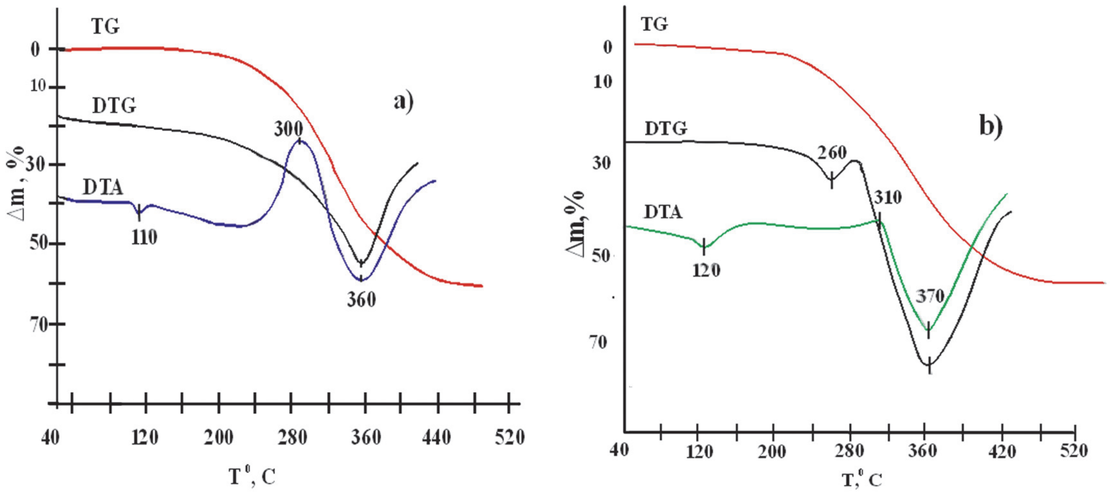

Fig. 5. Thermal spectra before exposure to an electric field: a) pure HDPE; b) HDPE + 3.0 % NC.

estructive process after aging was considered. Figures 5 and 6 show the thermal spectra of HDPE and the HDPE + 3.0 % NC nanocomposite before and after exposure to an electric field.

Changes in thermal parameters in HDPE and nanocomposite are given in the Table.

As indicated in the Table and figures, in the case of $E = 0$, $t = 0$ in pure HDPE and HDPE + 3.0 % NC samples, the following changes have been observed:

1. The crystalline phase degradation temperature of pure HDPE is $T_{degr} = 110°C$ (endothermic effect); depolymerization temperature is $T_{depol} = 360°C$ (endothermic effect DTG); thermal oxidation temperature is $T_{ther\ oxid} = 300°C$ (exothermic effect); and residual mass is $\Delta m = 38\ \%$.

2. For the HDPE + 3.0 % NC sample, $T_{degr} = 120°C$; $T_{depol} = 370°C$; $T_{ther\ oxid} = 310°C$; $\Delta m = 45\ \%$.

As can be seen, after the addition of NC, the values of T_{degr}, $Tther\ oxid$, T_{depol} and residual mass increased. After exposure to an electric field, a decrease in the thermophysical properties of both samples is observed. In pure HDPE, the decrease is greater.

Thus, any change in the physical structure of PE+% NC nanocomposites (under the influence of additives or aging) that affects the mechanical properties can also change the thermophysical properties. The DTA method showed that during thermal degradation, the temperature corresponding to the initial endothermic peak and thermal depolymerization in the nanocomposite increases compared to pure PE. This means

Table. Values of thermal parameters in HDPE and the nanocomposite

Samples	DTA	DTG Endothermic effect, T°C	TG, Δm,,%	
			Endothermic effect, T°C	Exothermic effect, T°C
pure HDPE $E = 0$, $t = 0$	$T_{degr} = 110$ $T_{depol} = 360$	$T_{ther\ oxid} = 300$	360	38
HDPE + 3.0 % NC $E = 0$, $t = 0$	$T_{degr} = 120$ $T_{depol} = 370$	$T_{ther\ oxid} = 310$	370	45
Pure HDPE $E = 2.5{\cdot}10^7$ V/m $t = 20$ hours	$T_{degr} = 105$ $T_{depol} = 345$	$T_{ther\ oxid} = 290$	345	30
HDPE + 3.0 % NC $E{=}2.5{\cdot}10^7$ V/m $T = 20$ hours	$T_{degr} = 118$ $T_{depol} = 360$	$T_{ther\ oxid} = 310$	360	???

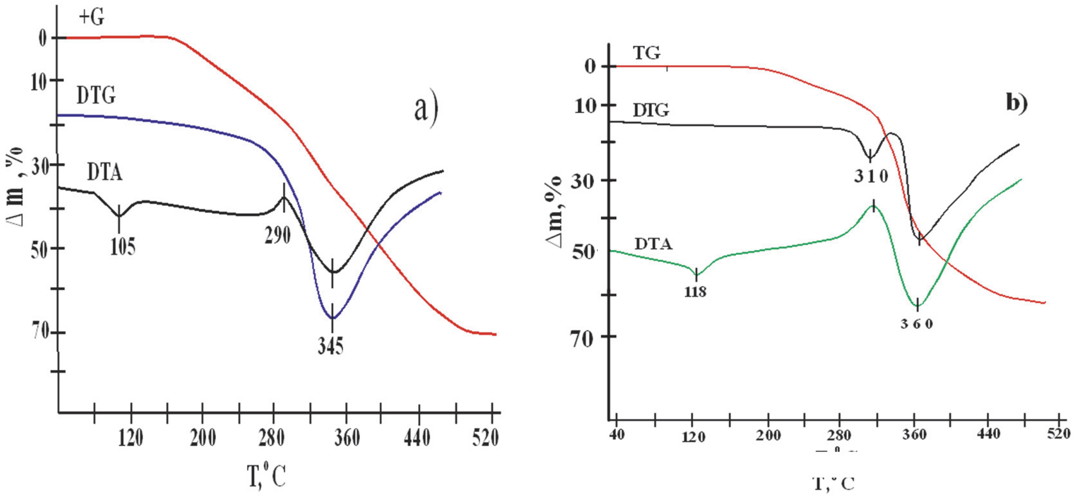

Fig.6. Thermal spectra after exposure to an electric field: a) pure HDPE; b) HDPE + 3.0 % NC.

that the nanocomposite is more resistant to oxidation.

4. Conclusions

1. Analysis of the spectra obtained by IR spectroscopy showed that the C=C groups are formed as a result of the breaking of chemical bonds in macromolecules under the action of an electric field. The optical density of these groups increases with the exposure time to the electric field.

2. After exposure to an electric field, a correlation between molecular weight and optical density of pure HDPE and the HDPE + 3.0 % NC nanocomposite was found; that is, a decrease in molecular weight with exposure time corresponds to an increase in optical density.

3. After exposure to an electric field, the depolymerization, degradation, thermal oxidation temperatures and residual mass of the nanocomposite change less than those of pure.

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