International Journal on
"Technical and Physical Problems of Engineering"
(IJTPE)
Published by International Organization of IOTPE

ISSN 2077-3528
IJTPE Journal
www.iotpe.com
ijtpe@iotpe.com

December 2021 Issue 49 Volume 13 Number 4 Pages 40-44

CHANGES OCCURRING IN STRUCTURE OF POLYETHYLENE + NANOCLAY NANOCOMPOSITES AFTER INFLUENCE OF AN ELECTRIC FIELD

M.A. Guliyev [1] **A.R. Sadigova** [2] **A.A. Hadiyeva** [2] **P.B. Asilbeyli** [2] **N.C. Mamedov** [3] **E.S. Safiev** [1]

1. Azerbaijan State Oil and Industry University, Baku, Azerbaijan, mehemmedquliyevsabah@gmail.com
2. Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan, arzu-sadigova@mail.ru
3. Azerbaijan State Agricultural University, Genja, Azerbaijan

Abstract- Structural changes under the influence of an electric field in polyethylene (PE) and nanocomposite have been measured by infrared spectroscopy, viscometry, and differential thermal analysis. Destruction of macromolecules occurs under the influence 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, Molecular Weight, Optical Density.

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 the variety of intramolecular and intermolecular interactions. Anisotropy is usually caused by mechanical loading in a large number of local centers and the effect of an electric field on the area, which is many times higher than the average value of the mechanical load and the electric field applied to the sample as a whole. The study of the 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 the studies [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 influence of external factors showed that decomposition of polymers and nanocomposites begins with the breaking of chemical bonds. The results of direct measurement methods can be used to study the rupture of a chemical bond.

In this study, we will study the role of NC in the destruction process after aging by studying the physical properties of nanocomposites based on polyethylene with the addition of NC after exposure to an electric field. Given this, changes in the structure that can occur after exposure to an electric field in nanocomposites will be investigated by infrared (IR) spectroscopy, viscometry and differential thermal analysis (DTA).

2. EXPERIMENTAL

After NC in the form of a powder in different percentages (1.0, 2.0, 3.0, 4.0, 6.0, 8.0, 10.0%) is mechanically mixed with polyethylene, by hot pressing (418 K, 15 MPa, 10 min), thin samples (50–70 μm) were obtained. Since both components are in powder form and have approximately the same density, a homogeneous mixture is obtained. The additive used as NC is montmorillonite layered silicate and the dimensions of these layers are approximate: 200 nm in length and 1nm in width [6]. In the center of the lattice structure of the MM crystal, there are Al, Mg and Fe atoms surrounded by a SiO_2 layer. The disturbance of the electrostatic equilibrium within the clay with such a structure increases, and an increase in the number of negatively charged particles outside the layer is expected. Negatively charged particles are neutralized by absorption of Na^+, Ca^+. The MM particles are in the shape of a plane; they, lying in an orderly manner, form a layered structure on their surfaces together with the polymer matrix.

According to experiments conducted by Giannelis [7], the production of nanocomposites involves three stages (Figure 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, an incorrect arrangement of the layers (disorientation) begins, the layers are completely separated. The uniform distribution of NC in the polymer indicates the ideal structure of the nanocomposite.

Aging of the nanocomposite based on PE and NC in an electric field was carried out in a test cell, schematically shown in Figure 2.

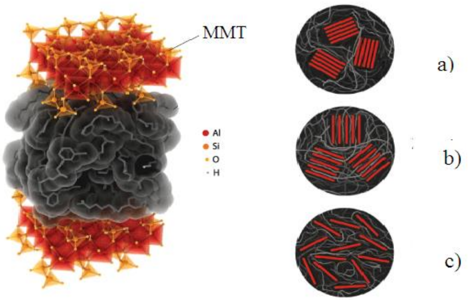

Figure 1. Three types of "polymer-layered silicate" composites

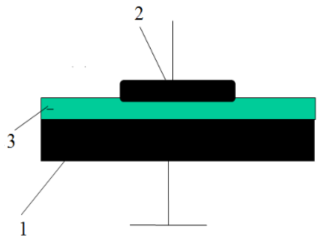

Figure 2. Test cell: 1- grounding electrode; 2- high voltage electrode; 3- studied sample

The samples were aged at room temperature for t =5; 10; 20; 40; 60 hours at an electric field intensity of 2.5×10^7 V/m. The IR spectroscopy method, which allows to obtain the oscillation spectrum of molecules of aged samples, is based on the interaction of matter with the field of electromagnetic radiation in the infrared region with a wavelength of λ=2.5-25 μm (4000-400 cm^{-1}). Molecular weight (MW) of the studied samples was measured by viscometrical method and thermodestructive properties by OD-102 MOM derivatograph.

3. RESULTS AND DISCUSSION

The effect of NC on the mechanical and electrical strength of PE 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. We can give an idea of the mechanism of decomposition by studying the changes that can occur in the structure after the PE and NC nanocomposites are stored in an electric field at different times. With the device be less than the puncture shown in Figure 2, the samples were subjected to aging in an electric field (E_{aging} = 2.5×10^7 V/m) at different times. This value of E_{aging} is taken to area (E_{punc} = 5.5×10^7 V/m). Figure 3 shows the IR absorption spectra of the PE and PE+3.0% NC nanocomposite after 20 hours of exposure to electric field.

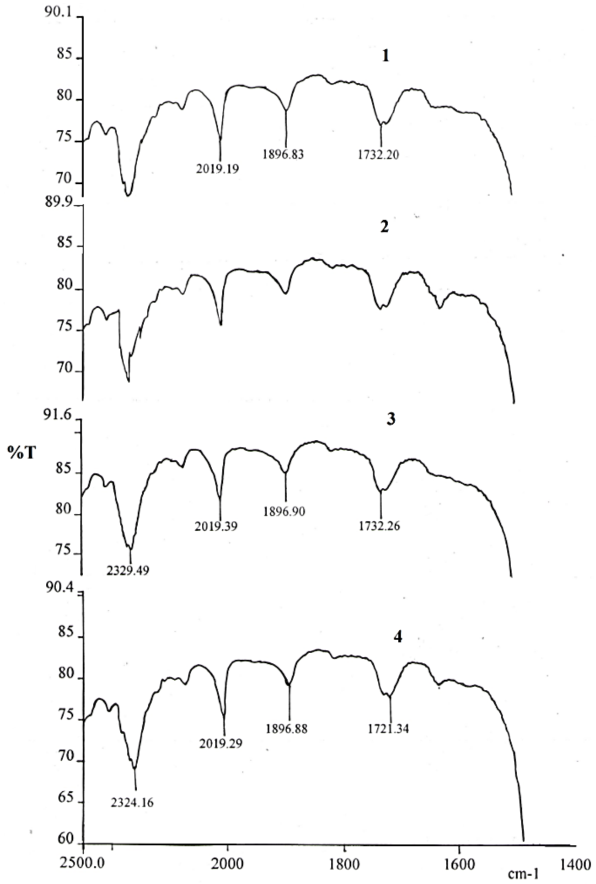

Figure 3. IR spectra of PE and PE+3,0% NC nanocomposite: 1,2 ~ pure PE; 3,4 ~ PE+3.0% NC; 1,3 ~ E=0 (t=0); 2,4 ~ $E=2.5\times10^7$ V/m (t=20 hours)

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

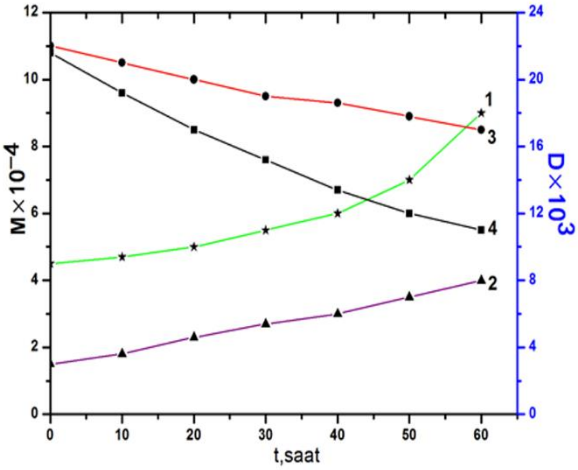

Figure 4. Dependence of optical density (D) and molecular weight (M) on the exposure time to an electric field 1,2 ~D; 3,4 ~M; 1,4~pure PE; 2,3~PE+3.0% NC

The optical density of the C=C group increases depending on the aging time. Ruptures occur in chemical bonds between atoms that form macromolecules due to the destructive effect of the field.

As *t* increases *D* of the PE increases faster than that of the nanocomposite. C=C double (pair) bond is the result of the rupture of macromolecules after the action of an electric field [2]. C=C group formation upon rupture of macromolecules should lead to a decrease in molecular weight (MW). Figure 4 shows the dependence of MW on *t*. The MW of both PE and nanocomposite decreases with *t*, while the decrease in PE occurs more rapidly. The change in MW and D depending on *t* is inversely proportional.

It is to be noted that, according to [8], such a radical is formed upon the loss of hydrogen of the methylene group forming the PE chain, mainly under the action of an electric field:

$$\sim CH_2 - \dot{C}H - CH_2 - - - CH_2 \sim$$

For the bond closest to the electron, which belongs to the radical (indicated by dotted lines), the activation energy of the rupture is 100 kJ/mol less than that of C-C ($E_{c\text{-}c}$ =335 kJ/mol). The reason for such a significant decrease in the bonds-rupture activation energy is the strong interaction of the unpaired electron in the radical with the valence electrons of the neighboring carbon atom. With a decrease in the C-C bond activation energy of in the macromolecule under the influence of external factors (electric field, mechanical load, etc.), thermal fluctuation create condition for the rupturing of the chemical bond, and the bond is ruptured:

$$\sim CH_2 - \dot{C}H - \dot{C}H_2 + \dot{C}H_2 \sim \rightarrow CH_2 - CH = CH_2 + \dot{C}H_2$$

As the effect of the electric field increases, the concentration of the C=C group will increase. For polymers with complex structures, various radicals are formed by rupturing the chain. In carbon-chain polymers $(\dot{C}R_1R_2-\dot{C}H_2-)_n$ R_1 and R_2 are different side groups (H, OH, CH3, COOH, COOOH3, etc.). As a result of the rupture of macromolecules, two types of radicals can form: $-CH_2-\dot{C}R_1R_2$ or $-\dot{C}R_1R_2- \dot{C}H_2$.

As can be seen from Figure 4, as the concentration of the C=C group formed by the radical in the macromolecule increases with aging time, the polymer chain length 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 depending on the aging time.

Studying the thermal properties of nanocomposites in the low-temperature and high-temperature ranges, it was considered how the properties of the additive change and the thermal destructive process after aging.

Figures 5 and 6 show the thermal spectra of the PE and PE+3.0% NC nanocomposite without the effect of an electric field and after exposure to an electric field.

Changes in thermal parameters in PE and nanocomposite are given in Table 1.

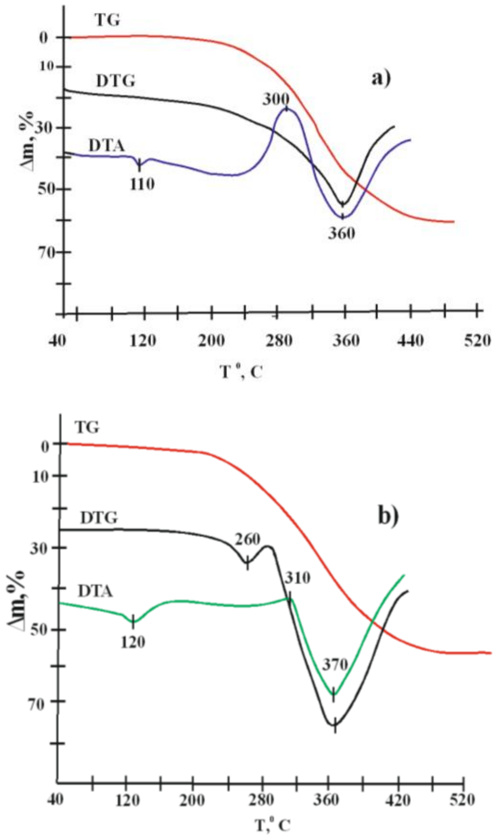

Figure 5. Thermal spectra without the effect of an electric field: a) pure PE; b) PE+3.0% NC

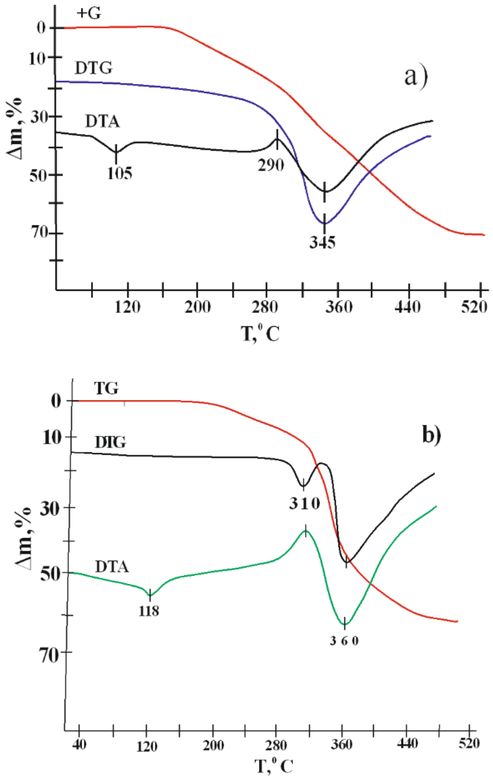

Figure 6. Thermal spectra after exposure to an electric field: a) pure PE; b) PE+3.0% NC E = 2.5×10^7V/m, t = 20 hours

Table 1. Changes in thermal parameters in PE and nanocomposite

Samples	DTA		DTG Endothermic effect, *T* °C	TG, Δm, %
	Endothermic effect, *T* °C	Exothermic effect, *T* °C		
Pure PE E=0, t=0	T_{degr}=110 T_{depol}=360	$T_{theroxid}$=300	360	38
PE+3.0% NC E=0, t=0	T_{degr} =120 T_{depol}=370	$T_{theroxid}$=310	370	45
Pure PE E=2.5×10^{7}V/m t=20 hours	T_{degr} =105 T_{depol}=345	$T_{theroxid}$=290	345	30
PE+3.0% NC E=2.5×10^7 V/m t=20 hours	T_{degr} =118 T_{depol}=360	$T_{theroxid}$=310	360	39

As can be seen from the table and figures, for the nanocomposite and pure PE, the melting point of the crystalline phase decreased with the amorphization of the crystalline phase of the matrix after exposure to an electric field. At E = 0, the depolymerization temperature of the PE+3.0% NC nanocomposite increased by 10 °C compared to pure PE. In our previous studies [5, 9, 10] we showed that the addition of NC increases the mechanical strength of polyolefins. That is, NC plays an important role in slowing down destructive processes. In the study of thermal properties, the depolymerization temperature of 3.0% NC-added nanocomposite increased by 15 °C compared to pure PE after exposure to an electric field. While the residual mass of PE was 30%, the residual mass of the PE+3.0% NC nanocomposite was 39%. If in pure PE after exposure to an electric field, weight loss began at 160 °C, then in PE+3.0% NC nanocomposite this temperature starts from 170 °C.

Thus, any change in the physical structure of PE+3.0% NC nanocomposites (under the influence of additives or aging) affecting the mechanical properties can also change the thermal and physical properties. Thermal destruction investigated by the DTA method showed that the temperature corresponding to the initial endothermic peak and thermal depolymerization in the nanocomposite increased in comparison with pure PE. This means that the nanocomposite is more resistant to oxidation.

4. CONCLUSION

1. Analysis of the spectra obtained by IR spectroscopy showed that the C=C groups are formed as a result of the rupture of chemical bonds in macromolecules under the action of an electric field. The optical density of these groups increases depending on the exposure time to the electric field.
2. After exposure to an electric field, a correlation is observed between *M* and *D* of pure PE and PE+3.0% NC nanocomposite, that is, a decrease in *M* depending on the exposure time corresponds to an increase in *D*.
3. After exposure to an electric field, the depolymerization temperature of the nanocomposite changes significantly less than that of pure PE. Before exposure to the electric field T_{depol}=370; 360 °C, and after exposure T_{depol}=360; 345 °C.

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BIOGRAPHIES

Mahammad A. Guliyev was born in Baku, Azerbaijan on September 7, 2001. He is studying final course at the University of Azerbaijan State Oil and Industry, Baku, Azerbaijan. His profession is Chemical Engineering. He was the III place winner in the Olympics of Young Chemical Engineers (2018). He has attended "Oil and Gas Engineering" Master Class (2021).

Arzu R. Sadigova was born in Baku, Azerbaijan on October 6, 1977. She received the B.Sc. and M.S.E. degrees from Baku State University, Baku, Azerbaijan in 1998 and 2007, respectively and was the Ph.D. student at Institute of Physics, Azerbaijan National Academy of Sciences, Baku, Azerbaijan in 2008-2011. Her research interests are nanostructure physics and technology.

Aynure A. Hadiyeva was born in Baku, Azerbaijan on December 26, 1982. She received the B.Sc. and M.S.E. degrees from Baku State University, Baku, Azerbaijan. She Scientific degree is Ph.D. Her topic of Ph.D. thesis is Influence structure of nanocomposites polypropylene + nanoclay of D_{k1} to their strength.

Parvana B. Asilbeyli was born in Baku, Azerbaijan on July 18, 1980. She received the B.Sc. and M.S.E. degrees from Baku State University, Baku, Azerbaijan. Her Scientific degree is Ph.D. Her research interests are nanostructure physics and technology.

Nizami C. Mamedov was born in Gedebey, Azerbaijan, 1947. Currently, he is an Associate Professor of Azerbaijan State Agricultural University, Baku, Azerbaijan. His research interests are semiconductors and polymers.

Elshad S. Safiyev was born in Azerbaijan, 1951. He is a Candidate of Technical Sciences, and an Associate Professor of Azerbaijan University of Oil and Industry, Baku, Azerbaijan. He is an author of over 70 scientific papers and textbooks. He has three inventions.