

INFLUENCE OF ELECTRIC FIELD (AGING IN ELECTRIC FIELD) ON STRUCTURE AND PROPERTIES OF NANOCOMPOSITE POLYPROPYLENE-NANOCLAY

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In this paper, mechanical lifetime (τ_M), elongation at constant tensile of polypropylene (PP) and nanocomposites on the basis of PP with addition nanoclay (NC) were measured before and after influence of electric field and structure changes were investigated by Infrared spectroscopy (IR) method. Was found that changes in the structure connected with the breaking down of chemical bonds, and this is a reason for changes of mechanical and deformation properties.

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1. Introduction

Preparation of polymeric composite materials with new optimal properties is very interesting to researchers of various areas of science. Sometimes pure materials are destroyed depending on the situation in practice. The preparation of new polymeric composite materials is widely used in industry in order to increase mechanical lifetime and to prevent destruction of materials. Composite materials are materials made from two or more constituent materials with significantly different physical or chemical properties, that when combined, produce a material with characteristics that differ from properties of the individual components [1-3]. The sizes of homogenous composite materials change in interval from micrometers to few millimeters.

The composites on the basis of polymers are obtained in the 40s of the XX century. Elastomers and epoxies (fibreglasses) were the first polymers, which were used as matrixes. Thereafter to this purpose began to apply also thermoplastic polymers, including polyolefins. Now there are a big variety of additions for polymeric matrixes [4]. The substances used as additions, is possible divided into two main classes. First class additions (chalk, talc, aluminum hydroxide, soot, graphite and etc.) enter into polymers mainly for increase of rigidity, durability, stability and heat resistance, gas permeability of materials [1-3]. Second class additions apply to economy of organic raw materials and product depreciation.

In [5-9] studies, changing of the mechanical, electrical, deformation and optical durabilities of polymers with organic and inorganic additives were investigated and were given a little information about the mechanism of this changing.

In the early ninetieths researchers from Japan for the first time received a nanocomposite on the basis of layered silicate - montmorillonite and nylon-6 and studied its mechanical and heatphysical properties [10, 11]. It appeared that the module of elasticity of the received nanocomposite by 1.7 times, and mechanical durability by 1.4 times is exceeded than similar characteristics for pure nylon-6. Significant improvement of mechanical properties causes decrease of coefficient of thermal expansion by 1.5 times and increase of softening temperature from 65 to 152 °C at the maintenance of only 4.7%-mas. addition. Use of organoclays as a nanoaddition in

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polymers can change such properties, as destruction temperature, the glassing temperature, melting temperature, elasticity, tensile strength, gas and moisture permeability [12-14].

Both polymer composites and polymer nanocomposites distribution of additives are very important for change of physical properties of polymer matrix. It is practically and scientifically important to study the mechanical and deformation changes of the structure of nanocomposites on the basis of polymers with additive nanoclays after the influence of electric field (rapidly aging).

2. Preparation of samples

As polymer matrix we used isotactic polypropylene with addition of montmorillonite nanoclay. Polypropylene (PP), also known as polypropene, is a thermoplastic polymer used in a wide variety of applications including packaging and labeling, plastic parts and reusable containers of various types, laboratory equipment, loudspeakers, automotive components, and polymer banknotes. Nanoclays are nanoparticles of layered mineral silicates [15,16]. Plate-like montmorillonite is the most common nanoclay used in materials applications. Montmorillonite consists of ~ 1 nm thick aluminosilicate layers surface-substituted with metal cations and stacked in ~ 10 μm -sized multilayer stacks. Depending on surface modification of the clay layers, montmorillonite can be dispersed in a polymer matrix to form polymer-clay nanocomposite. Within the nanocomposite individual nm-thick clay layers become fully separated to form plate-like nanoparticles with very high ($\text{nm} \times \mu\text{m}$) aspect ratio (Figure 1). Al, Fe and Mg atoms are in the center and silicon oxide layers surround these atoms. Electrostatic imbalance increased inside the clay, resulting in an increase of the negative charge on the surface of which is compensated by adsorption of cations Na^+ , Ca^{++} and other alkali metals. Due to such "sheet" form of MMT particles it is possible to create the materials in which the MMT plates are arranged on each other forming highly textured layers in polymer matrix.

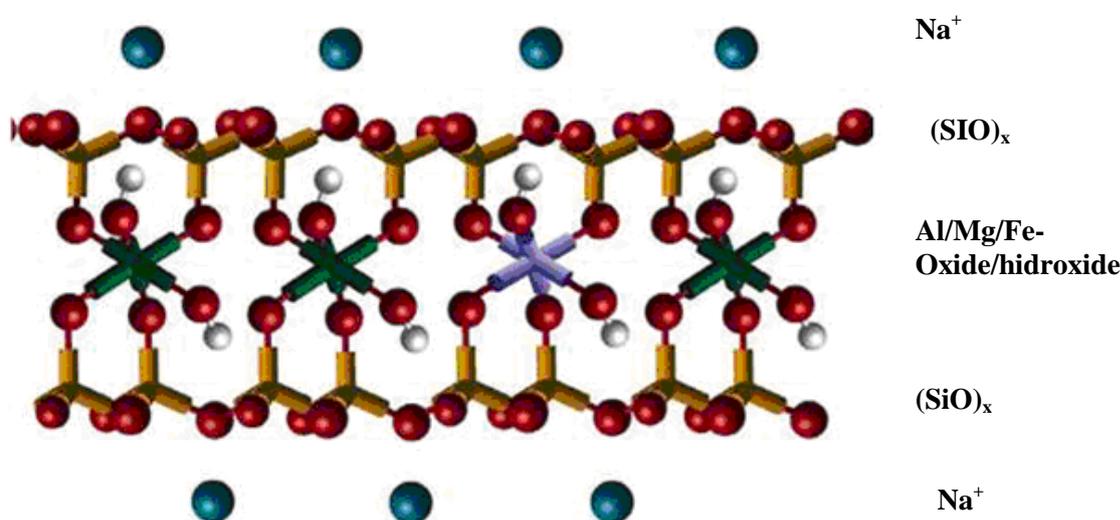


Fig 1. The structure of montmorillonite

Composites with different-nanoclay additive percentages (1,0: 2,0: 4,0: 6,0: 10,0) are used in the experiments. The PP powder is mixed with NC mechanically and samples with a thickness of 40-70 mm are prepared with the hot pressing method (15 MPa, 445 K, 10 min). Both components of composites were in powder form and its density is similar to each other, so homogeneous mixture is obtained.

First mechanical tension of nanocomposites with various percent content of NC is measured and the optimum sample is found [17]. To investigate the role of addition in changing of structure of nanocomposites, pure PP and PP+ 2,0 % NC nanocomposites samples were tested in order to find out aging dependence on time in electric field. A special cell consisting of two stainless steel electrodes is used for aging, during the experiment the samples have been compressing between a 30 mm diameter earthed electrode and another 10 mm-diameter electrode and was applied for alternating electric field $E=2 \cdot 10^7 \text{V/m}$ (less of breakdown tension). The IR spectroscopy was used to determine changing of nanocomposite's structure in 400-2500 frequency interval. The mechanical properties of composites were measured by breaking machine [18].

3. Experimental results

It is known that the mechanical destruction of the polymers begins with the breaking down of chemical bonds between the atoms of the macromolecules. Changes of structure of nanocomposites were observed after influence of external factors and proved by direct experimental methods. In order to study these changes infrared absorption spectrum of samples were analyzed in $400\text{-}2500 \text{ cm}^{-1}$ intervals before and after aging. In IR spectra of pure PP and nanocomposite PP+2,0 % NC after 10 hours exposure of electric field the size of the peak at 1640 cm^{-1} corresponding to C = C group increases. The results of electric field influences during $t=0$ and $t=60$ hours is shown in Fig. 2.

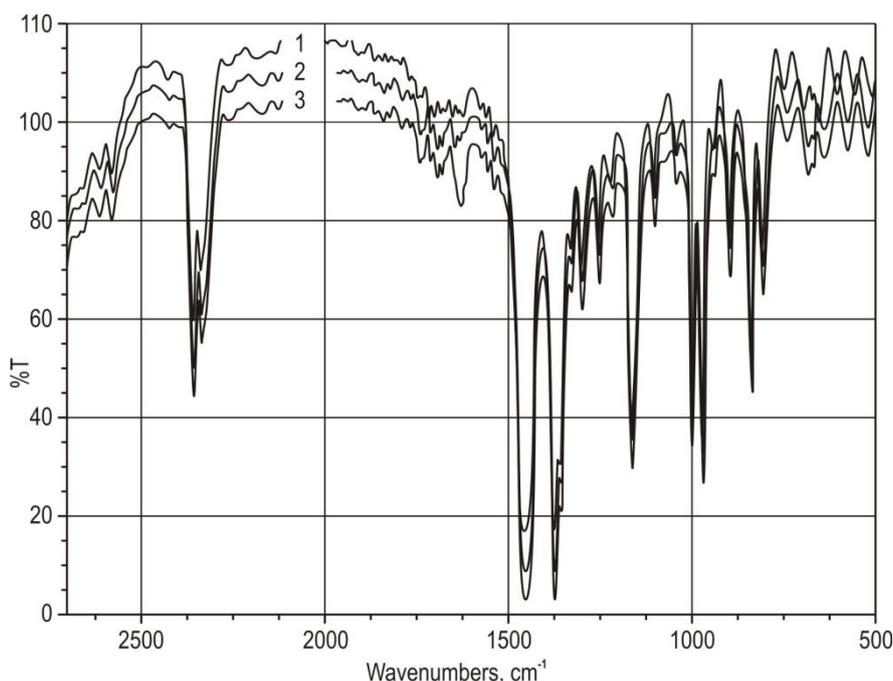


Fig. 2. FT-IR analysis of 1 ~ PP; 2 ~ PP+ 2,0% NC ($t=60$ hours);
3 ~ PP ($t=60$ hours)

Dependences of optical density (D) and molecular weight (M) of the pure PP and PP+ 2% NC nanocomposite on time of aging are shown in Fig.3. As it seen rate of increasing of optical density depending on time of pure PP's is comparably higher than in nanocomposite. Addition of NC prevents increasing of number of C=C double bonds.

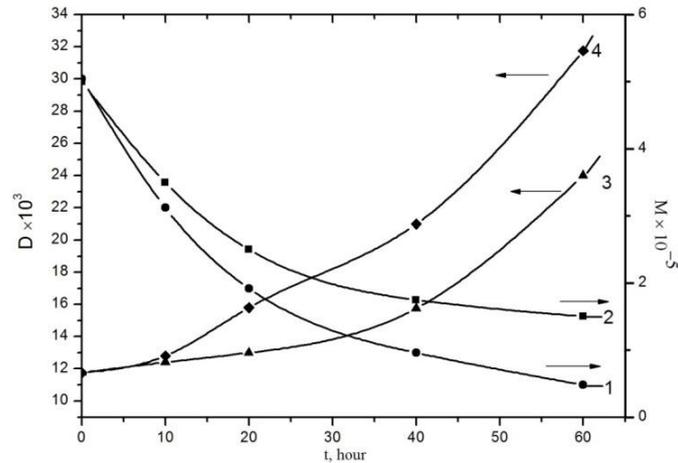


Fig. 3. Dependences of optical density (D) and molecular weight (M) on aging time:
 1,2 ~ M ; 3,4 ~ D ; 1,4 ~ PP; 2,3 ~ PP+2,0% NC

Lets consider how these changes of structure of pure PP and nanocomposite PP+2% NC influence on mechanical properties. Mechanical lifetime depending on mechanical tension σ is measured before and after aging of above mentioned samples. For PP+2% NC composites, the dependences of τ_M on σ at constant temperature are seen that the degradation of the composites agrees with thermofluctuation theory (Fig. 4). According to thermofluctuation theory, the fracture mechanism of polymers has a kinetic mechanism. Furthermore, the mechanical properties of pure PP and PP+2% NC nanocomposite before and after aging are listed in Table 1.

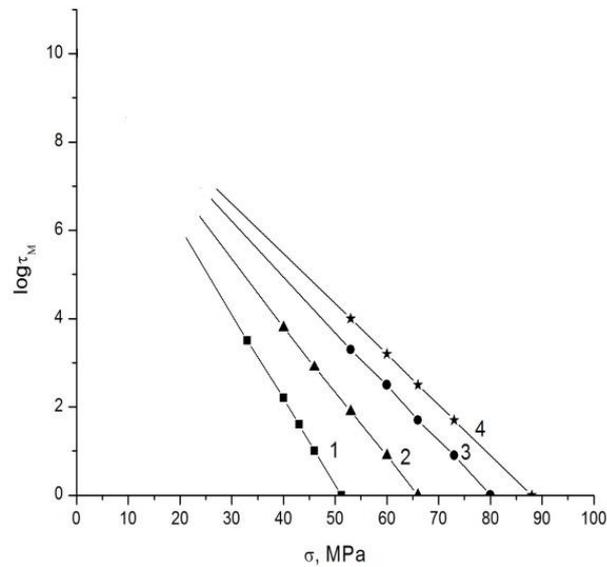


Fig. 4. Dependence of $\log \tau_M$ on σ : 1 ~ PP ($t=60$ hours); 2 ~ PP ($t=0$ hour); 3 ~ PP + 2,0 % NC ($t=60$ hours); 4 ~ PP + 2,0% NC: ($T=293K$)

Table.1 Variation of mechanical characteristics of PP and nanocomposite PP+ 2,0%NC

Samples	t=0 hour ; E=0					t=60hour; E=2·10 ⁷ V/m					$\tau_{0,S}$ (T=293K, $\sigma=45$ MPa	T=60s, E=2·10 ⁷ V/m
	σ , MPa	l_0 , mm	l , mm	Δl , mm	ε , %	σ , Mpa	l_0 , mm	l , mm	Δl , mm	ε , %		
Pure PP	65	10	13,2	3,2	32	52	10	16,1	6,1	61	220	3
PP+2% NC	88	10	11,3	1,3	13	80	10	12,1	2,1	21	41,3·10 ⁴	7,2·10 ³

As shown in Table 1, before aging (t=0) τ_M the σ of nanocomposite is much more higher than for pure PP (36%). The dependence of σ from the time of influence of electric field t is shown at Fig.5. It was found that increasing of t led to decreases σ for both samples. After aging, the rate of σ decrease of nanocomposite is less than for pure PP.

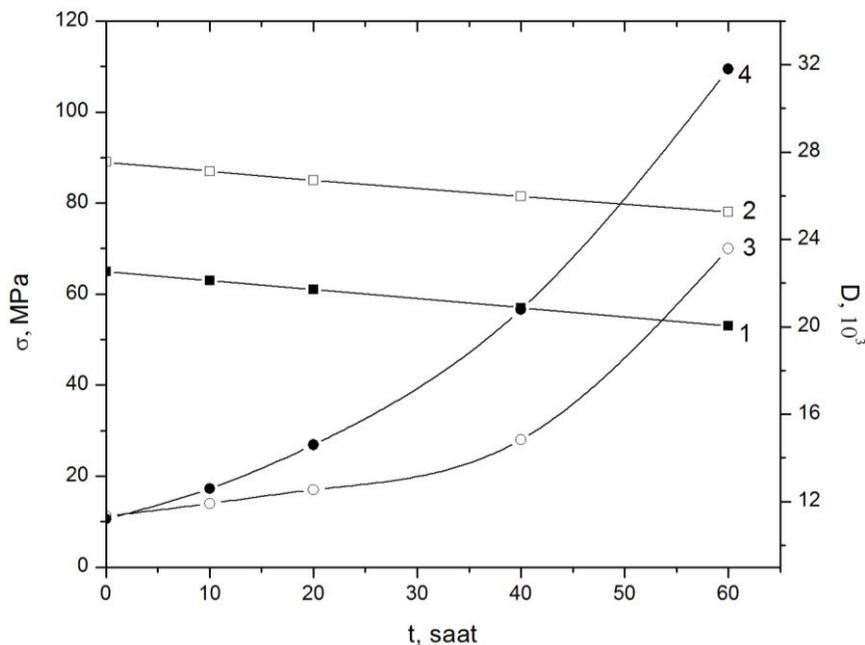


Fig. 5. Dependences of σ (1, 2) and D (3, 4) on aging time: 1,4 ~ PP; 2, 3~ PP+ 2,0% NC

After addition of NC and aging in an electric field the structure changes of nanocomposite occur as well as the change of mechanical tension. The value σ decreases according to the increase of optical density. At the same time addition of NC led to declining of rates of σ decrease and ε increase.

In order to find the influence of electric field on the deformation properties of nanocomposites, the deformation curves under the constant tension and fixed time were written in breaking machine. Calculated results from these curves are shown in fig. 6 and in Table 1.

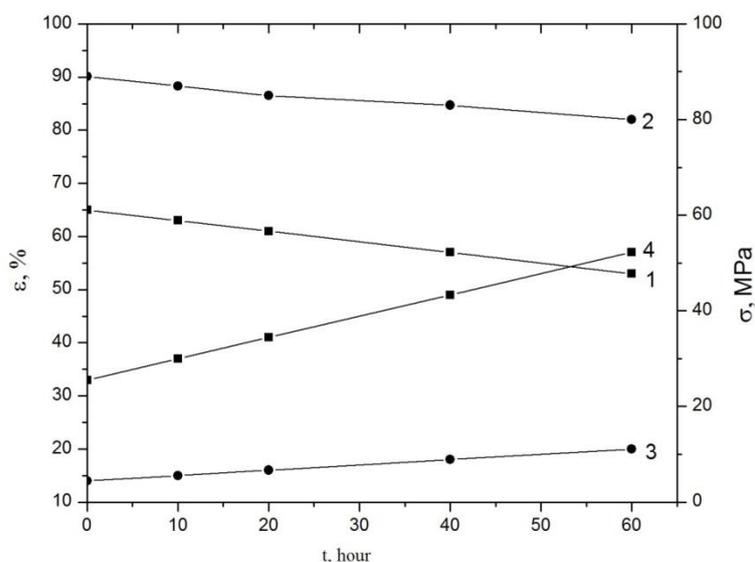


Fig. 6. Dependences of σ (1, 2) and ε (3, 4) on aging time: 1,4 ~ PP; 2, 3~ PP+ 2,0% NC

The elongation at break (ε) without influence of electric field is less for nanocomposite in comparison with pure PP. Addition of NC prevents elongation and at the same time decrease rate of ε depending on aging time is less than in pure PP. As seen from the Fig. 6 ε increases with the decrease of σ . Increasing of ε in nanocomposite is reduced depending on exposure time of electric field.

Occurance of changes in the structure of PP and PP+2% NC nanocomposite either related with NC as well as with influence of electric field in dependence on time showing itself in the change of mechanical properties. Increase of number of double C=C bonds as a result of breaking interatomic bonds in a polymer structure under stress is a reason for increase of D_{1640} . At the same time formation of double bonds is responsible for decrease of mechanical tension (σ) and increase of elongation (ε). As a result of breaking down of chemical bonds in macromolecules, interactions between molecules weaken and elongation increases. NC prevented for formation of double bonds with increasing interaction between molecules.

Samples pure PP and PP+2% NC was prepared by the hot pressing method, in which the samples kept for 10 min at 445 K and 15 MPa pressure and then cooled quickly. As a result, it simplify the partial transition of macromolecules to nanoclay layers. Homogeneous distribution of the nanoparticles increases and at 2% volume content of nanoclay interaction between nanoparticles and macromolecules increases, that leads to change of structure and physical properties of a nanocomposite.

4. Conclusion

In this paper, the mechanical and deformation properties of PP and PP+2% NC nanocomposites before and after aging were investigated experimentally. It was found that the addition of NC into PP and aging in a electric field had a significant effects on structure, mechanical and deformation properties of PP. Increase of optical density with breaking down of chemical bonds in macromolecules is a reason for decrease of mechanical lifetime and increase of deformation. Addition of NC into PP effects the rate of this changes.

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