

# MORFOLOGIA, PROPRIETĂȚILE MECANICE ȘI TERMICE ALE NANOCOMPOZITELOR PE BAZĂ DE POLIPROPILENĂ ISOTACTICĂ ȘI NANOPARTICULE DE DIOXID DE ZIRCONIU

## MORPHOLOGY, MECHANICAL AND THERMAL PROPERTIES OF NANOCOMPOSITES BASED ON ISOTACTIC POLYPROPYLENE AND ZIRCONIUM DIOXIDE NANOPARTICLES

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*In the present work, thermal and mechanical properties of nanocomposites PP+ZrO<sub>2</sub> are studied. The presence of zirconium dioxide in PP increases its thermal stability and mechanical properties of nanocomposites. The AFM studies show that a change in upper molecular structure of polypropylene as well as a chipping of structure elements of surface morphology occur with addition the nanosize powder to the polymeric matrix. The thermal stability and mechanical properties generally increases with increasing amount of zirconium dioxide. Improvement in thermal stability of PP occurs by the addition of 5% ZrO<sub>2</sub>. It was experimentally shown that increasing of volume content of ZrO<sub>2</sub> changes the mechanical durability of nanocomposite PP+ZrO<sub>2</sub> with extremum, i.e. the concentration of ZrO<sub>2</sub> up to 5% increase durability, and more than 5% decrease it. These results prove that ZrO<sub>2</sub> nanoparticles with concentration up to 5% are the centers of structure nucleation, and further increasing of nanoparticles concentration leads to destroying of physical structure of polypropylene.*

**Keywords:** Nanocomposites, mechanical properties, strength, mechanical testing, thermal analysis

### 1. Introduction

Polypropylene (PP) at the present time is one of the most prevalent synthetic polymer that is widely applied in many fields. Unfortunately, the relatively low fire resistance and thermal characteristics restrict the conditions and fields of its practical application. In the last time the new approaches for increasing of thermal durability and fire resistance of PP are based on usage of polymeric nanocomposites. Introduction of nanosized inorganic particles in polymer allow to design the structure of material by means of transfer of plain volume filled system to the system with given supramolecular architecture and spatial distribution of filler, that promotes the creation the polymer with new technological and operating properties. Despite there are some progress in this area the general regularity of polymer and nanosized filler interactions with properties of final composite material have not been found yet. The optimal nanoparticles concentration and their uniform distribution in polymer matrix are problems that have not been defined [1].

The most appropriate objects for targeting the structuring of nanomaterials are metal oxide nanoparticles with narrow size distribution, given morphology and content of nanoparticles. The ZrO<sub>2</sub> nanoparticles have high thermal and mechanical properties, optical transparency, chemical and corrosion durability, high coefficient of thermal expansion and low thermal conductivity [2]. The thermoplastic polymer such as polypropylene that fundamentally distinguishes by its structure and functional designation is a matter of interest in term of preparation on its basis of new nanocomposite polymer structures. The nanocomposite on the basis of above mentioned polymer and ZrO<sub>2</sub> nanoparticles have not been prepared yet, and it is a matter of indubitable interest for targeting the design of new nanocomposite materials. So, the study of the dependence of properties of nanocomposite from characteristics of its individual components can lead to the preparation of nanocomposite with set of practically important properties.

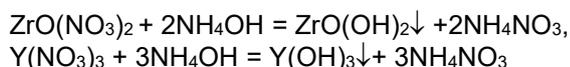
In the present work thermal and mechanical properties of nanocomposites PP+ZrO<sub>2</sub> are investigated.

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## 2. Experimental part.

### 2.1. Synthesis of polymer nanocomposites

An isotactic PP (04П000-X1, Russian) powder with particle size of 0.5–1.0 μm was used as the polymer matrix; zirconium dioxide (ZrO<sub>2</sub>) nanoparticles with average size of 21 nm stabilized with 3% yttrium oxide (Y<sub>2</sub>O<sub>3</sub>) were employed as the filler. Nitrate solutions corresponding to the stoichiometry of the final product were used to prepare the ZrO<sub>2</sub> nanoparticles. The precipitation was conducted in a Simax reactor in an aqueous solution of ammonia at room temperature for 1 h. The chemical reaction of the solutions leads to the formation of a precipitate composed of particles of zirconium and yttrium hydroxide:



After washing and filtration the powders were exposed to microwave heating, pulse magnetic field and ultrasound treatment. The calcination were carried out within the temperature range of 350-900°C [2-4].

The polymer+ZrO<sub>2</sub>nanocomposites were prepared as follows: isotactic PP powders with particle size of 0.5–1.0 μm were dissolved in an organic solvent (toluene) at temperature of 120°C. Nanopowders composed of ZrO<sub>2</sub> and 3 mol % Y<sub>2</sub>O<sub>3</sub> with average particle size of 21 nm were added to the polymer solution kept at 120°C. To improve the sedimentation stability of the zirconia dispersion in the polymerization system, the nanopowders were initially wetted with a small amount of toluene and introduced into the polymer system. This procedure provided a uniform and stable distribution of the powdered filler in the initial polymer system and in the final material. Samples were transferred to a Petri dish and dried for one day. In order to remove the solvent samples were vacuum dried at a temperature below the melting point of polypropylene. Nanocomposite samples were prepared from these powders by hot pressing at the melting temperature of PP and a pressure of 10 MPa. Thus, nanocomposites containing 0.1, 0.5, 1, 2, 5, 7, and 10 wt % of the ZrO<sub>2</sub> filler were prepared. It was found that the limit of filling of the polymer with the filler is 10% ZrO<sub>2</sub>.

### 2.2. Nanopowders characterization

The zirconia nanopowders samples were characterized by X-ray powder diffraction and scanning electron microscope (SEM). X-ray diffraction (XRD) patterns of the nanopowders zirconia were recorded on a Rigaku Mini Flex 600s powder diffractometer. X-ray tube with copper anode (Cu-Kα radiation, 30 kV and mA) used for recording the diffraction patterns at room tempera-

ture. Diffraction patterns were taken at a range of angles 2θ = 10-100° in discrete increments mode Δ2θ = 0.05° and exposure time τ = 5 seconds.

Morphology and grain analysis of the zirconia nanopowders was studied by scanning electron microscopy (SEM, Jeol JSM-7600 F). Scanning was conducted in the SEI mode at an accelerating voltage of 5 kV and a working distance of 4.5 mm.

### 2.3. Characterization of polymer nanocomposites

The morphology of nanocomposite samples was studied by atomic force microscope Integra-Prima (NT-MDT, Zelenograd). For scanning was used special silicon cantilever, prepared by plasma chemical method of etching with radius of curvature of needle 20 nm and resonance frequency 1-5 Hz. The measurement was implemented at mode semi contact microscopy in air, where was fixed the vibration of cantilever needle, that determine the surface topography. The scanning rate and scanning lines number on the image are 1.969 Hz and 256 Hz correspondingly.

Thermogravimetric (TGA) analyses of samples were carried out on nanocomposites by using Perkin Elmer Pyris model Thermogravimetric Analyzer (TGA). Samples were heated from 25 °C to 550 °C at a heating rate of 20 °C/minute in nitrogen atmosphere with a purge rate of 20 mL/minute.

Differential scanning calorimetric analysis of nanocomposites was performed on nanocomposites by using Perkin Elmer Diamond model Differential Scanning Calorimeter (DSC). Samples were placed into aluminum sample pans and experiments were carried out under nitrogen atmosphere with a purge rate of 20 ml/min. Samples were heated from -50 °C to 250 °C then cooled to 25 °C, at second heating samples were heated from 25°C to 250 °C at a heating rate of 20°C/min.

Have been determined the mechanical durability of polymer nanocomposites on the base PP+ZrO<sub>2</sub>. To measure the mechanical durability necessary to satisfy two basic requirements: tensile stress and the temperature should not be changed during each test. As known, the test specimen during the test is extended, its cross-section decreases at a constant voltage and suspended loads increases. To maintain a constant voltage using a series of adaptations of the float or lever type, providing an automatic reduction in the load acting on the sample, as its extension. Was determined the time from the start of testing of mechanical strength until sample rupture at different mechanical stresses.

Technique to study the mechanical durability of the nanocomposites—based on PP+ZrO<sub>2</sub> was described in work [5 - 7].

### 3. Results and Discussion

X-ray diffraction patterns of nanopowders  $ZrO_2$  synthesized by zol-gel process are shown in Figure 1. The diffraction patterns show that the synthesized powder is a yttria stabilized zirconia nanoparticles corresponding to ICDD files 00-002-0536.

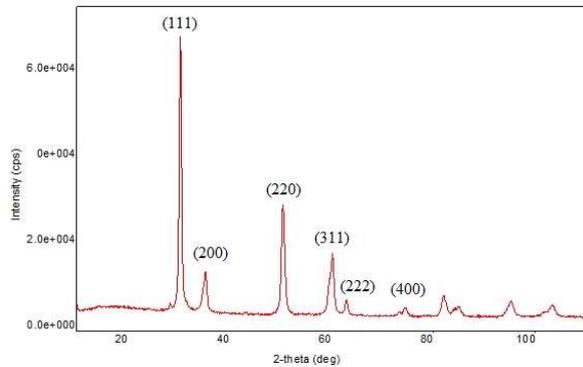


Fig. 1- XRD pattern of zirconia nanopowders.

Nanopowders of zirconia were studied by scanning electron microscopy. Scanning electron microscopic images reveal that zirconia nanoparticles have the spherical shape and average size of nanoparticles is 21 nm (Figure 2).

Figure 3 demonstrates the AFM images of PP+ $ZrO_2$  nanocomposite surfaces obtained by addition the  $ZrO_2$  nanoparticles at 1%, 5% volume content. As can be seen a change in upper molecular structure of polypropylene as well as a chipping of structure elements of surface morphology occur as a result of addition the nanosize powder to the polymeric matrix. The AFM studies show that roughness of surface decreases for 5% amount of nanoparticles  $ZrO_2$ .

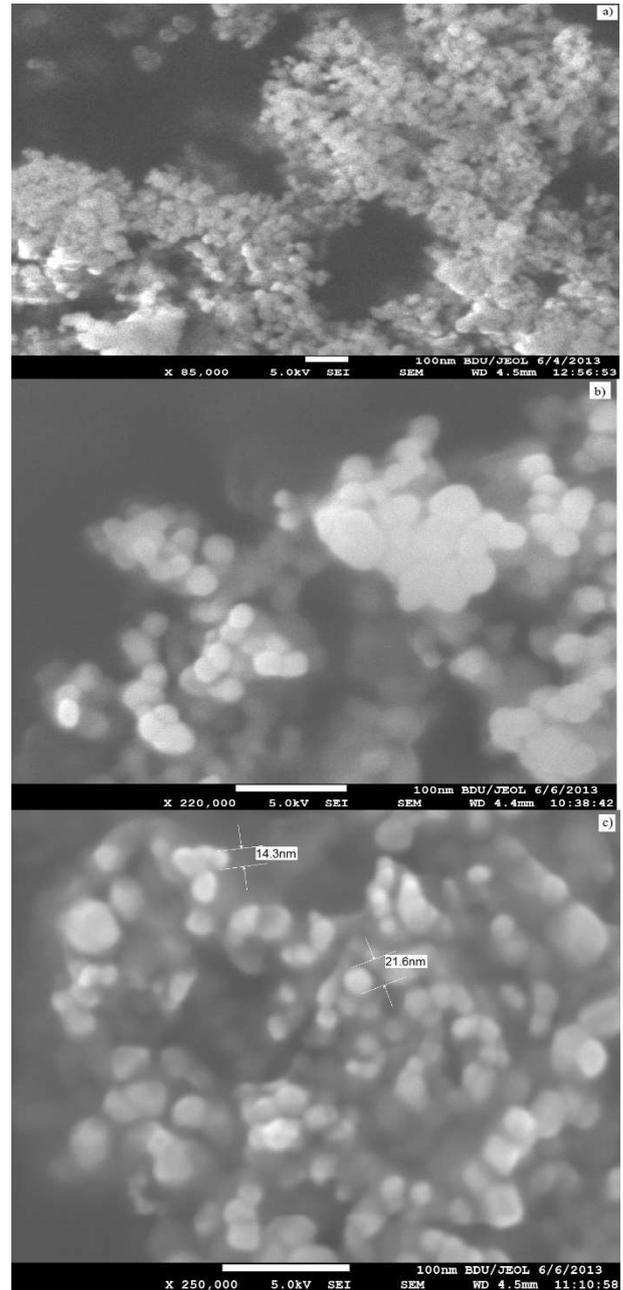


Fig.2 - SEM images of zirconia nanoparticles.

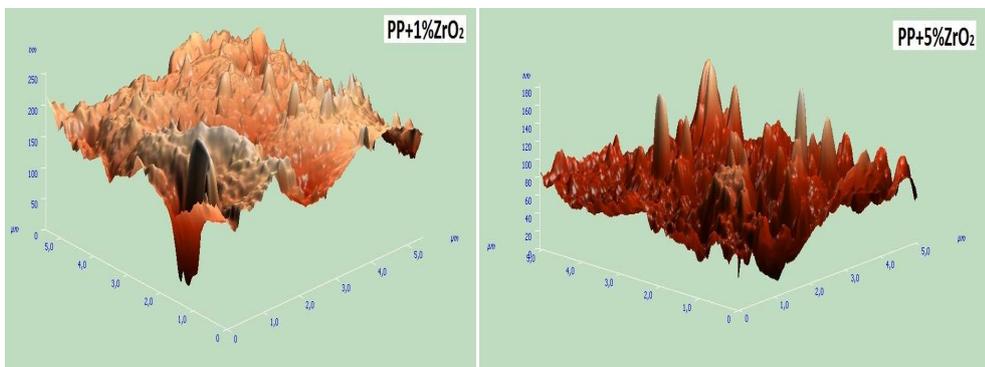


Fig. 3 - continues on next page

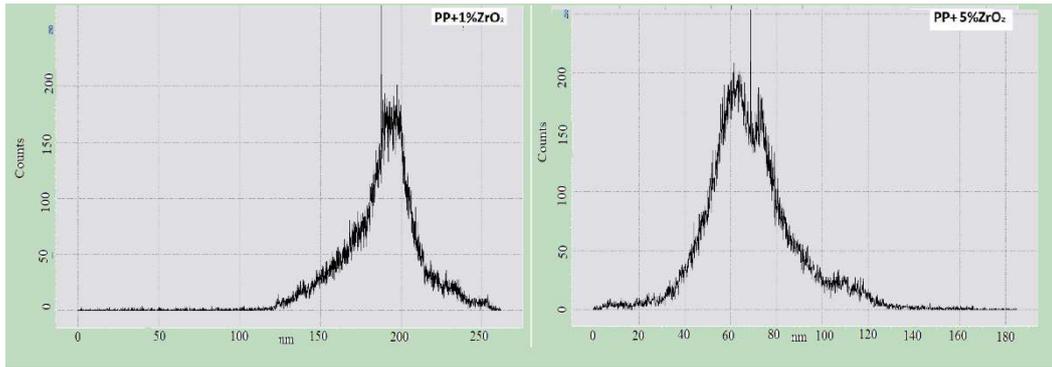


Fig 3. 3D AFM images and histograms for PP+ZrO<sub>2</sub> nanocomposite

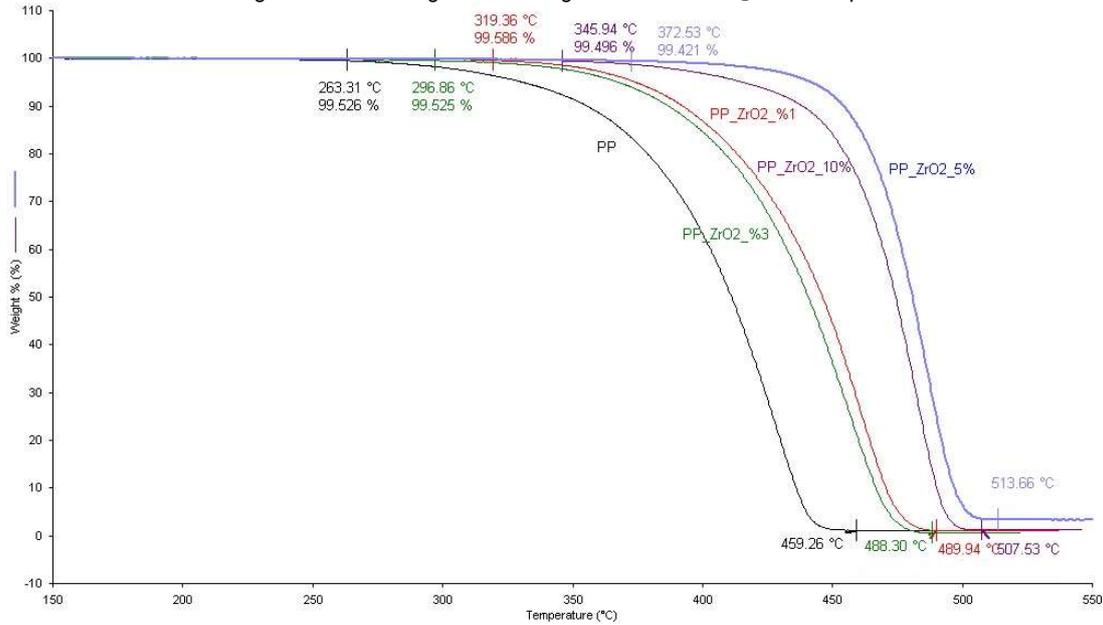


Fig. 4 -TGA curves of isotactic polypropylene (PP) and nanocomposites based on PP+ZrO<sub>2</sub>.

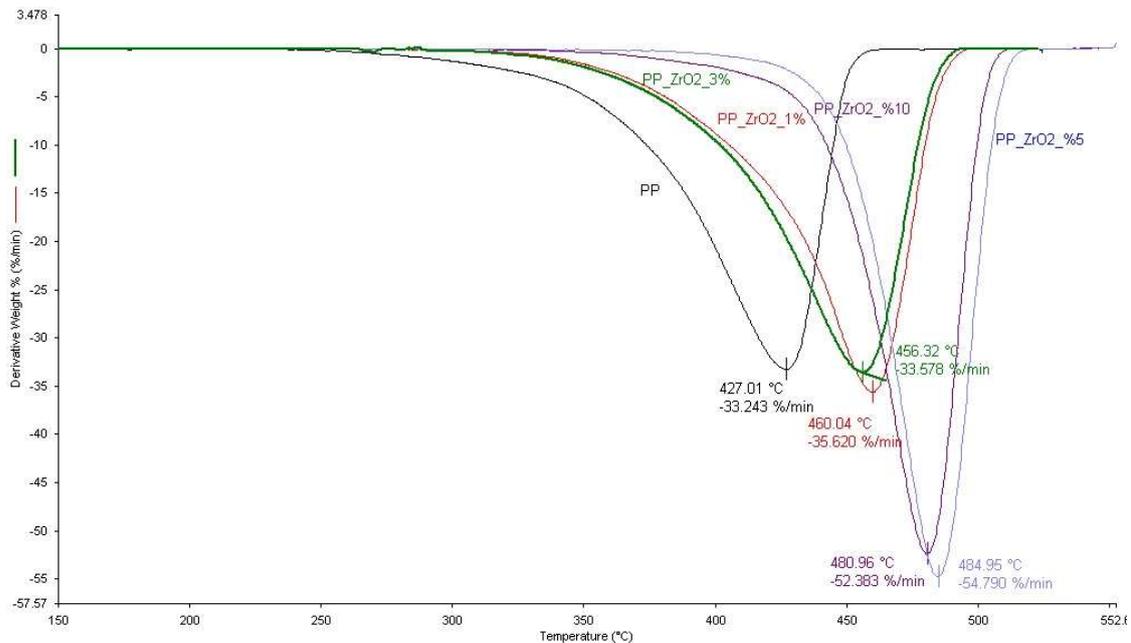


Fig. 5 -DTG curves of isotactic polypropylene (PP) and nanocomposites based on PP+ZrO<sub>2</sub>.

This paper presents the results of dynamic TGA and derivative thermogravimetry (DTG) of

polypropylene nanocomposites based on PP+ZrO<sub>2</sub>. TGA and DTG measurements were conducted

on the specimens PP and PP+ZrO<sub>2</sub> in the temperature range of 25-550 °C at a heating rate of 20°C /min. Figure 4 and 5 show the results of TGA and DTG curves of isotactic polypropylene and nanocomposites of PP+ZrO<sub>2</sub>.

Figure 4 and 5 show TGA and DTG curves of PP and PP+ZrO<sub>2</sub> nanocomposites with different amount of zirconium dioxide (ZrO<sub>2</sub>) nanoparticles with 1, 3, 5, 10% by weight. For all curves, onset temperatures that denote the temperature at which the weight loss begin are determined. The temperatures corresponding to maximum decomposition were also determined from the DTG curves given in Figure 5. All results were collected in Table 1 which also contains the percentage residue mass of the samples.

zirconia nanocomposites. They observed that the presence of zirconia in PMMA slightly increased its thermal stability. They concluded that this was probably due to interactions between the zirconia and the free radicals formed during degradation which immobilized scavenged the free radicals and retarded the degradation process.

Information of the thermal phase transitions in PP and PP+ZrO<sub>2</sub> nanocomposites can be obtained from calorimetric experiments, which are given in Figure 6 and 7. The melting temperatures of nanocomposites remain almost constant. They are not affected from the presence and content of zirconium nanoparticles. The crystallization temperatures for nanocomposites are shifted to the higher temperature as ZrO<sub>2</sub>% increases. This

Table 1

The effect of ZrO<sub>2</sub> nanoparticles on thermal stability on PP.

Samples	PP	PP+1%ZrO <sub>2</sub>	PP+3%ZrO <sub>2</sub>	PP+5%ZrO <sub>2</sub>	PP+10%ZrO <sub>2</sub>
Onset Temperature (°C)	263	319	297	373	346
Max. Weight Loss Temperature (°C)	435	450	440	480	470

As can be seen in Fig. 3, for all PP-ZrO<sub>2</sub> nanocomposites, decomposition occurs in a single-step process. The presence of zirconium dioxide in PP increases its thermal stability and the thermal stability generally increases with increasing amount of zirconium dioxide. Onset of degradation of PP is 263°C whereas 5% ZrO<sub>2</sub> added PP is 373°C. Its thermal stability increases by 110°C for 5% ZrO<sub>2</sub>. Maximum improvement in thermal stability of PP occurs by the addition of 5% ZrO<sub>2</sub>. Thermal stability of PP+10%ZrO<sub>2</sub> is less than PP+5% ZrO<sub>2</sub> because of excess amount of nanoparticles beyond nano-effect. Barczewski., and et.al [8] observed that thermal stability of polypropylene-based nanocomposites filled with tetrasilanol-phenyl-silsesquioxane (phPOSS) increased in comparison to pure PP. The highest thermal stability was observed for the sample that contained 10% wt of phPOSS. Its thermal stability is increased by only 20.2 °C for 5% mass loss.

The temperature at which maximum weight loss takes place is increased by the addition of ZrO<sub>2</sub>. The increase in thermal stability of the nanocomposites is due to the strong secondary interactions (van der Waals) between the ZrO<sub>2</sub> and PP. Esthappan et. al [9] investigated the thermal stability of PP/zinc oxide (ZnO) nanocomposites. The degradation temperature of neat PP increased by 31°C with the addition of 1% wtZnO nanoparticles in PP. They also commented that the increase in thermal stability of the composites may be due to the strong interaction between the ZnO and PP.

Motaung et al [10] studied the thermal stability of poly(methyl methacrylate) (PMMA)-

indicates that ZrO<sub>2</sub> acts as a good nucleating agent and is able to shift the peak of crystallization to higher temperatures. Ren et al [11] studied different filler effects on melting and crystallization and found that weak nucleating agents are unable to shift the peak of crystallization to higher temperatures whereas strong nucleating agents can lead to a change in crystallization. Arranz-Andres et al [12] also observed that crystallization temperature is shifted to lower temperatures as Aluminum content increases for the nanocomposites based on PP and different contents of Al.

This means that the inclusion of the Al nanoparticles postpones the capability of ordering in the iPP polymeric chains in these nanocomposites [12]. The % crystallinity-of PP and PP+ZrO<sub>2</sub> nanocomposites calculated by using Eq. 1 are given in Table 2. For crystallinity determinations, a value of 165 Jg<sup>-1</sup> has been taken as enthalpy of fusion of a perfect crystalline PP. As can be seen from Table 2, crystallinity is not significantly affected with increasing of ZrO<sub>2</sub> content.

$$\% \text{ Crystallinity} = \frac{\Delta H_{\text{sample}}}{\Delta H_{\text{sample}}^0} \times 100 \quad \text{Eq. 1}$$

For forecasting of life time of nanocomposite PP+ZrO<sub>2</sub>, as well as defining the kinetic process occurring in this system, the power dependence of mechanical durability lgT<sub>σ</sub> (σ) have been studied.

Mechanical durability test has been carried out on device that allows providing the discontinuous stress during the whole period of experiment.

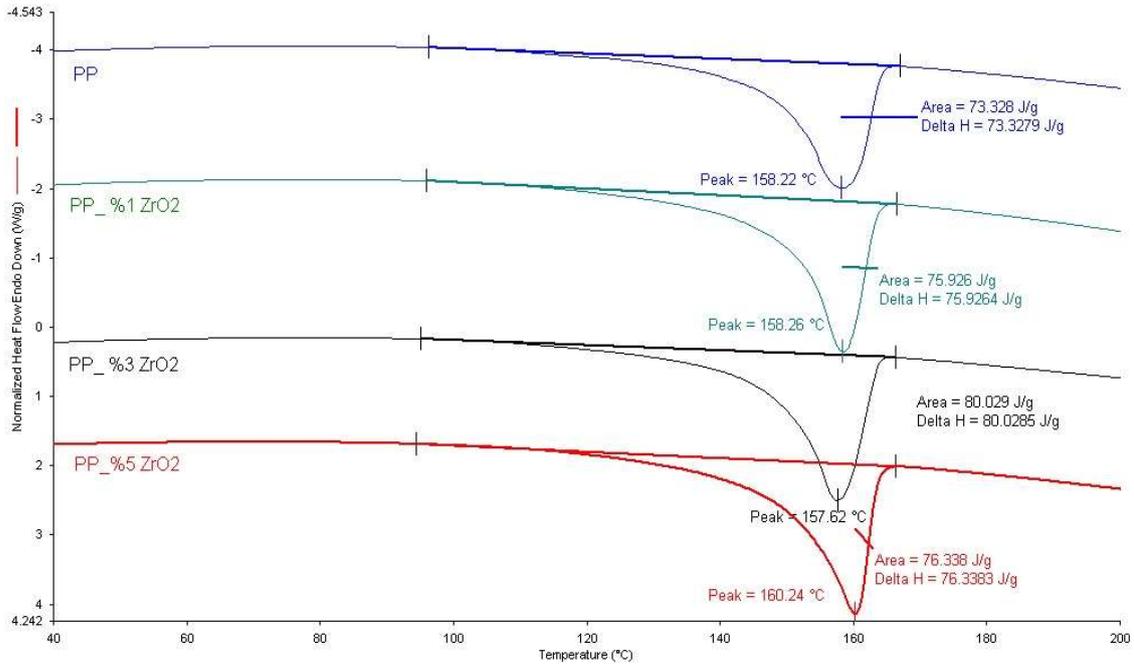


Fig. 6 -The melting temperatures and  $\Delta H_{\text{melting}}$  for PP and PP+ZrO<sub>2</sub> nanocomposites obtained by DSC.

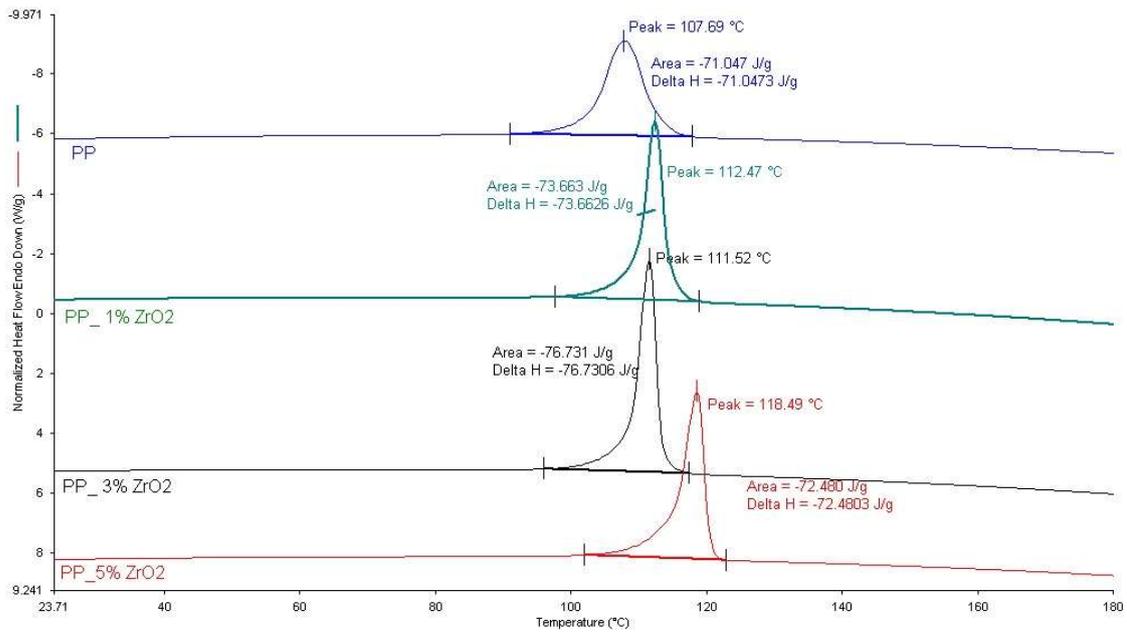


Fig. 7- The crystallization temperatures and  $\Delta H_{\text{crystallization}}$  for PP and PP+ZrO<sub>2</sub> nanocomposites obtained by DSC.

Table 2

Determination of crystallinity (%) of PP and PP+ZrO<sub>2</sub> based polymer nanocomposites.

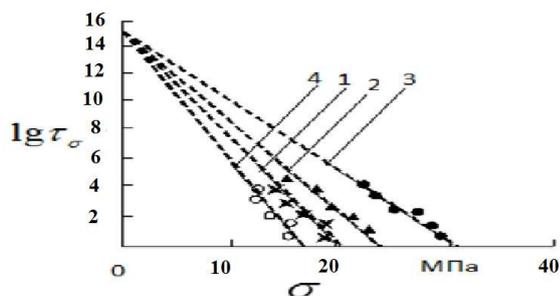
Samples	PP	PP+1%ZrO <sub>2</sub>	PP+3%ZrO <sub>2</sub>	PP+5%ZrO <sub>2</sub>
Crystallinity (%)	44.4	46.0	48.5	46.2

The influence of ZrO<sub>2</sub> nanoparticles concentration on mechanical durability in polypropylene of PP+ZrO<sub>2</sub> composites was studied. The Figure 8 demonstrate the dependence of logarithm of mechanical durability  $\lg T_{\sigma}$  ( $\sigma$ ) on mechanical stress  $\sigma$ . It is known that change of

mechanical durability of polymer and the composite on its basis obey the following rule, i.e.

$$\tau_{\sigma} = Ae^{-\alpha\sigma} \quad (\text{Eq. 2})$$

Where A and  $\alpha$ -are the parameters depending from the nature of mater and temperature.



**Fig. 8** - Dependence of logarithm of mechanical durability  $\lg \tau_{\sigma}(\sigma)$  on mechanical stress  $\sigma$  for various volumes content of  $ZrO_2$  for nanocomposite  $PP+ZrO_2$ : 1.PP, 2. PP+1%  $ZrO_2$ , 3.PP+5%  $ZrO_2$ , PP+10%  $ZrO_2$ .

It is known from literature [13], that temperature-strength dependence of mechanical durability of various solid compounds, including polymers and composites expressed by Jurkov formula:

$$\tau_{\sigma} = \tau_0 e^{\frac{U_0 - \gamma \sigma}{RT}} \quad (\text{Eq. 3})$$

Where coefficients  $\tau_0$ ,  $U_0$  и  $\gamma$  are the parameters defining mechanical durability properties of tested material.

$\tau_0$  - constant, independently from the type of solid matter, state of matter, and its value is the same with period of its atom thermal oscillation solid state, i.e.  $\tau_0 \approx 10^{-12} - 10^{-13} \text{sec}$ .

$U_0$  - activation energy of thermal destruction of polymers,

$\gamma$  - structural-sensitive coefficient,  $\sigma$  - mechanical durability [14,15].

The comparison of (Eq.2) with (Eq.3) reveals,

$$A = \tau_0 e^{\frac{U_0}{RT}} \quad \text{and} \quad \alpha = \frac{\gamma}{RT} \quad (\text{Eq. 4})$$

Taking into consideration that the R-universal gas constant,  $\tau_0 = \text{const}$ , then for  $T = \text{const}$  with the formula (Eq.4) it follows that  $A = \text{const}$ . In other words, the constancy of the parameters A, as seen from the formulas mean value  $U_0 = \text{const}$ . This means that the activation energy of the process of mechanical destruction of compositions based on  $PP+ZrO_2$  is  $U_0$ . Logarithm formula (Eq. 2) and plot  $\log \tau_{\sigma} = f(1/T)$  and from tilt we can calculate  $\gamma$ -sensitive structural factors.

It is found that regularity of mechanical durability change obey the rule. It was experimentally shown that increasing of volume content of  $ZrO_2$  leads to change of mechanical

durability of nanocomposite  $PP+ZrO_2$  with extremum. The concentration of  $ZrO_2$  up to 5% increase durability, and more that 5% decrease it. It should be noted that equation (2) fulfilled till threshold of  $ZrO_2$  nanoparticles filler in the polymer. At higher threshold of  $ZrO_2$  nanoparticles filler, the continuity of polymer matrix disrupted and system passes from ordered continuous structure to friable. From Figure 8 calculated the value of structural-sensitive coefficient  $\gamma$  for samples  $PP+ZrO_2$ , prepared with different volume content of nanoparticles.

In Table 3 structural – sensitive coefficient  $\gamma$  for samples  $PP + ZrO_2$  is given

As can be seen in Table 3, structural-sensitive coefficient  $\gamma$  for samples  $PP+ ZrO_2$  with increasing of concentration up to 5% decreases and then increases. These results prove that  $ZrO_2$  nanoparticles with concentration up to 5% serves as nucleation centers whereas further increasing of nanoparticles concentration leads to destroying of physical structure of polypropylene. The volume content of  $ZrO_2$  up to 5% leads to more ordered structure and as sequence it leads to increasing of mechanical durability.

#### 4. Conclusion.

The AFM studies show that a change in upper molecular structure of polypropylene as well as a chipping of structure elements of surface morphology occur with addition the nanosize powder to the polymeric matrix. Thermal properties and mechanical properties of nanocomposites based on isotactic polypropylene and zirconium dioxide nanoparticles have been studied. The presence of zirconium dioxide in PP increases its thermal stability and mechanical properties of nanocomposites. The thermal stability and mechanical properties generally increases with increasing amount of zirconium dioxide. Improvement in thermal stability of PP occurs by the addition of 5%  $ZrO_2$ . It was experimentally shown that increasing of volume content of  $ZrO_2$  changes the mechanical durability of nanocomposite  $PP+ZrO_2$  with extremum, i.e. the concentration of  $ZrO_2$  up to 5% increase durability, and more than 5% decrease it. These results prove that  $ZrO_2$  nanoparticles with concentration up to 5% are the centers of structure nucleation, and further increasing of nanoparticles concentration leads to destroying of physical structure of polypropylene.

**Table 3**

Values of structural-sensitive coefficient  $\gamma$  for samples  $PP+ZrO_2$ , prepared with different volume content of nanoparticles.

Concentration of $ZrO_2$ in PP, %	0	1	5	10
structural-sensitive coefficient, $\gamma, \frac{kCal \cdot mm^2}{mol \cdot kg}$	0.54	0.49	0.42	0.52

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Coronamentul cu care se termină cupola (pg. 85 - Nicolae St.Noica - ATENEUL ROMÂN ȘI CONSTRUCTORII SĂI)