Digest Journal of Nanomaterials and Biostructures Vol. 11, No. 2, April - June 2016, p. 365 - 372

THERMAL AND MECHANICAL PROPERTIES OF POLYMER-BASED NANOCOMPOSITES OF ISOTACTIC POLYPROPYLENE AND TITANIUM NANOPARTICLES

A. M. MAHARRAMOV, M. A. RAMAZANOV*, A. B. AHMADOVA,
F. V. HAJIYEVA, U. A. HASANOVA
Baku State University, AZ1148, Zahid Khalilov str 23, Azerbaijan Republic

Were studied thermal properties and mechanical properties of nanocomposites based on isotactic polypropylene and titanium nanoparticles. The presence of titanium in PP increases thermal stability and mechanical properties of nanocomposites. The thermal stability and mechanical properties, generally increases with increasing titanium content in polypropylene nanoparticles. The maximum growth of thermal stability is observed in the case of PP with 3% volume content of Ti nanoparticles in polypropylene matrix. The structure of nanocomposites was investigated by atomic force and scanning electron microscopy. Was revealed the relationship between the change in the thermal and mechanical properties with the change of content of nanocomposites PP + Ti. AFM studies have shown that the introduction of titanium nanoparticles in polypropylene change the supramolecular structure of polypropylene, and ordered structure is formed. Further increase of the titanium nanoparticles content leads to a polymer nanocomposite structure inhomogeneity. Thus, the histogram roughness has the value of 40-60 nm for 1% and 3% nanoparticle titanium content in polypropylene nanocomposites; for 5% Ti content - 80-100 nm. Therefore, has been found that the concentration of 1% to 3% of titanium nanoparticles content plays a central role of the adjustable structurant and further increase the content of titanium nanoparticles destroys the physical structure of the polypropylene.

(Received February 15, 2016; Accepted April 11, 2016)

Keywords: polymer, nanocomposite, polypropylene, titanium nanoparticle, supramolecular

1. Introduction

The development of composite materials based on polymers with nanoparticles of different metals is relevant in view of the need to create new materials for electronics, batteries (fuel cells),capacitors and etc. The properties of nanocomposite materials based on a polymer will depend on the size of the metal nanoparticles. In particular, these composites having a mixed electronic and ionic conductivity are considered as an active material for highly efficient fuel cells and lithium-ion batteries. Creating composites with dispersed metallic phase with dimensions of the metal nanoparticles of 1-10 nm is an urgent task, as they have a number of new properties due to excess surface energy [1].

A distinctive feature of most polymers is their low thermal conductivity, high coefficient of linear thermal expansion, and the fluidity at high temperatures, relatively low thermal and heat resistance. Thermal methods are the basic methods of research of structural relaxation processes in polymers, in particular the unfreezing of various degrees of freedom by increasing the intensity of thermal motion. When the material is heated, the frequency of vibration of the atoms and the interatomic distances increase, due to increased energy supply. Increased energy increases the average distance between atoms and the solid expands. The value of thermal expansion dependent on the energy of the interatomic distance, so polymers with weak interatomic interaction peculiar to higher spreading factors. The introduction of fillers into the polymer results in a significant

* Corresponding author: mamed_r50@mail.ru

decrease in the thermal expansion coefficients bringing together these characteristics of plastics with similar properties of metals and ceramics.

In the present work investigated thermal and mechanical properties of nanocomposites on the base PP+Ti and was revealed the relationship between the change in the thermal and mechanical properties with the change of structure of nanocomposites on the base PP + Ti.

2. Experimental part

2.1. Materials

The isotactic polypropylene (PP brand Sigma Aldrich Pcode 1001326963) has a density of 0,9 g / ml at 250C, refractive index- n20/D 1.49, transition temp - Tg -26 ° C, mol wt - average Mw ~ 250000 by GPC, autoignition temp -> 674 ° F, mp - 1890S. Nanoparticles of titanium were obtained by electroexplosive technology. Titanium nanoparticles were prepared by electroexplosive technology [2].

2.2. Methods of research

X-ray analysis

The XRD diffractograms of nanocomposites were examined by diffractometer Rigaku Mini Flex 600s using the X-ray tube with copper anode (Cu-Kα radiation, 30 kV and mA) at room temperature. Diffraction patterns were taken at a range of angles 2θ = 10-100 ° in discrete increments mode $\Delta 2\theta = 0.05$ ° and exposure time $\tau = 5$ seconds.

Scanning electron microscopy (SEM)

The distribution of titanium nanoparticles in the polymer matrix was studied by scanning electron microscopy (SEM, Jeol JSM-7600 F). Scanning was conducted in the SEI mode at an accelerating voltage of 15 kV and a working distance of 4.5 mm.

Atomic force microscopy

The morphology of the nanocomposites was studied using atomic force microscopy Integra-Prima (NT-MDT, Zelenograd). For the scan used special silicon cantilevers that were fabricated by plasma etching method with a radius of curvature of the needle 20 nm and the resonance frequency of 1-5 Hz. Scan size was 3 × 3 microns. The measurements were performed in the semi contact microscopy mode in air, the cantilever's fixed needle change of oscillation amplitude determined the surface topography. The rate of scanning is 1,969 Hz and the number of scanned lines of the image, is respectively 256.

Thermogravimetric analysis (TGA).

Thermogravimetric analysis of samples was conducted in a thermogravimetric analyser (TGA) Model Perkin Elmer Pyris. Nanocomposites samples were heated from 25° C to 550 ° C with a heating rate of 20^0 C/min in a nitrogen atmosphere.

Technique to study the mechanical durability of the nanocomposites on the base PP+Ti was described in work [6-8].

2.3. Synthesis of nanocomposites

Polymer composite materials were prepared as follows: isotactic polypropylene was solved in toluene at a temperature of 120^0 C. Nanoparticles of titanium added to the polymer solution at various volumetric titanium contents (1%, 3%, 5%, 7%, 10%) and stirred for an hour to obtain a homogeneous mixture. The mixture was transferred to a Petri dish and dried in a vacuum oven during the day. The thin film of nanocomposite wre obtained from these samples by hot-pressing at the melting temperature of polypropylene and a pressure of 10 MPa. Cooling the film after hot pressing was carried out in water and the cooling rate of nanocomposite films was 200 deg/min [3].

3. Results and discussion

Figure 1 shows the diffraction patterns of nanocomposites based on PP with different volume content of titanium nanoparticles. XRD diffraction patterns show that the main peaks of $35{,}27^0$ (100), $38{,}54^0$ (102), $40{,}32^0$ (101), $53{,}11^0$ (102), $63{,}09^0$ (110), $70{,}76^0$ (103), $76{,}08^0$(112) belong to the titanium nanoparticles. In this pattern, all lines can be indexed using the ICDD no. 00-001-1198 corresponding to titanium. As can be seen with increasing of titanium nanoparticle content in the polymer increases the degree of crystallinity of nanocomposites.

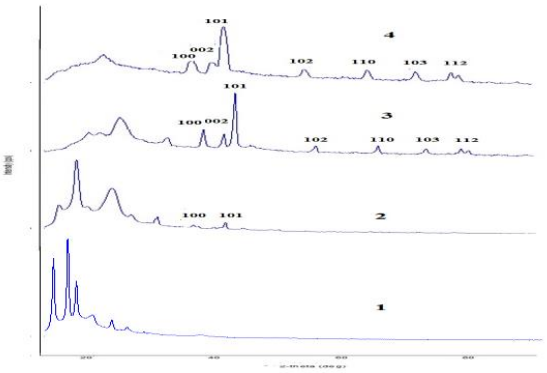

Fig. 1. XRD diffraction patterns of nanocomposites based on PP + Ti 1. PP + 3% Ti; 2. PP + 5% Ti; 3. PP +7%Ti

Figure 2 shows SEM images of nanocomposites based on PP + Ti. As can be seen from the figure 2 the increase of the volume content of titanium nanoparticles in the polymer matrix led to increasing of the number and size of nanoparticles' clusters in the PP matrix. Thus, when the volume content of Ti nanoparticles is 3% in the matrix the size is 25-70 nm, and at 7% content it is 30-90 nm (Figure 3).

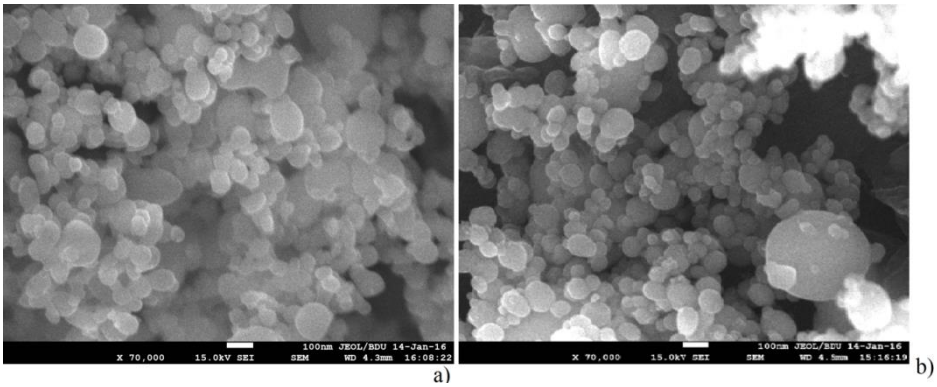

Fig. 2. SEM images based nanocomposites PP + Ti a) PP+3% Ti; b) PP + 7% Ti

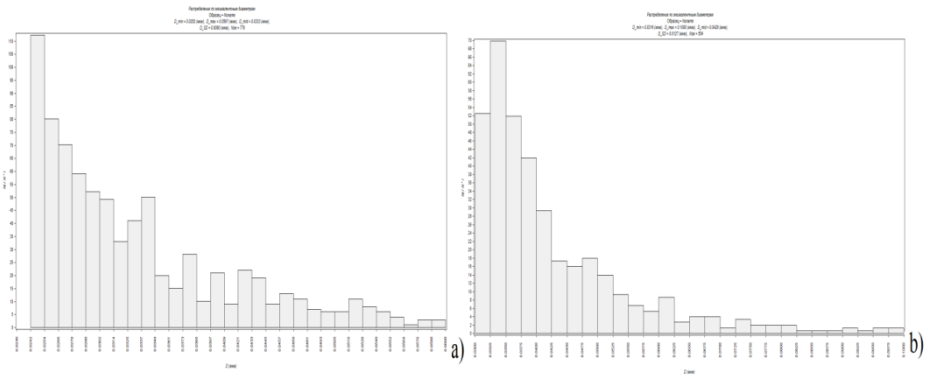

Fig. 3. Histogram size distribution of nanoparticles in the polymer matrix PP (nm) a) PP + 3% Ti; b) PP + 7% Ti

Fig. 4 shows AFM images of nanocomposites based on PP + Ti with different volume content of titanium. As seen from the figure 4 the addition of nanoparticles of titanium up to 5% of volume content in the polypropylene matrix led to formation of more ordered structure. So, the addition of 1% Ti in the polymer led to relatively orderly distribution of titanium nanoparticles, whereas nanocomposite with 3% Ti demonstrate more perfect structure. From the AFM image it is evident that a further increase of the titanium nanoparticles content in the polymer led to agglomeration phenomena in the matrix. This correlates well with the values of the average roughness of the surface of the nanocomposites. Figure 5 shows histograms of the surface roughness of the nanocomposites based on PP + Ti. Thus the average surface roughness of the nanocomposite PP + 1% Ti and PP + 3% Ti - 40-60 nm; PP + 5% Ti is 80-100 nm. From this it may be concluded that the nanocomposites have more perfect supramolecular structure, for low contents of nanoparticles, in contrast with that at high contents of nanoparticles in the polymer matrix [4].

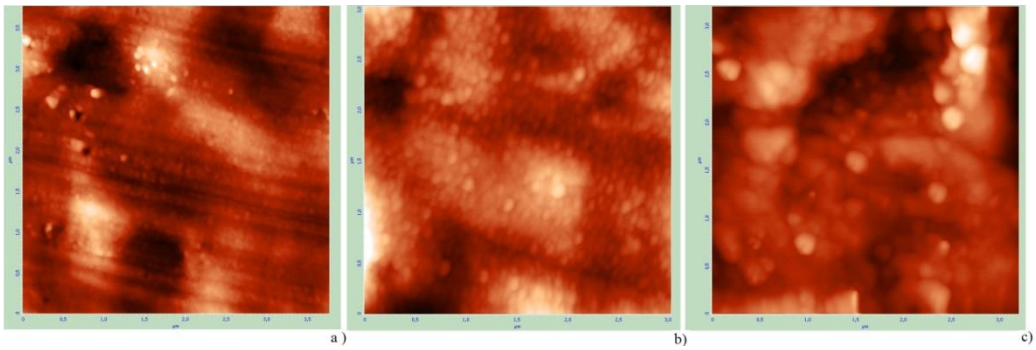

Fig. 4. AFM images nanocomposites PP + Ti depending on the volume content of titanium; PP + 1% Ti, b) PP + 3% Ti, c) PP + 5% Ti.

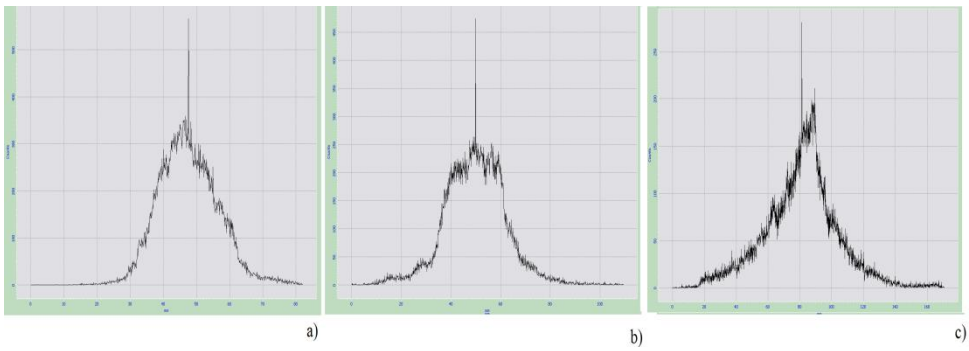

Fig. 5. Histogram of image of nanocomposite roughness PP + Ti depending on the content of titanium a) PP + 1% Ti; b) PP + 3% Ti; c) PP + 5% Ti

In the article also present the results of thermogravimetric analysis (TGA) of nanocomposites. TGA measurements of PP and PP + Ti nanocomposites were carried out in the temperature range 25-550^0 C at heating rate of 20^0 C per minute. Figure 6 shows the TGA curves for pure PP polymer and nanocomposites based on PP + Ti. For all the curves show initial point that determine of starting of weight loss. Figure 6 shows TGA of PP and PP+ Ti nanocomposites with different volume content of titanium (1, 3, 5, 10%).

In this paper presents the results of dynamic TGA and derivative thermogravimetry (DTG) of polypropylene nanocomposites based on PP+Ti. Fig. 6 and 7 shows the results of TGA and DTG curves of isotactic polypropylene and nanocomposites of PP+Ti. Figure 6 and 7 show TGA and DTG curves of PP and PP+Ti nanocomposites with different volume content of titanium (Ti) nanoparticles (1, 3, 5, 7%). 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 Fig. 7.

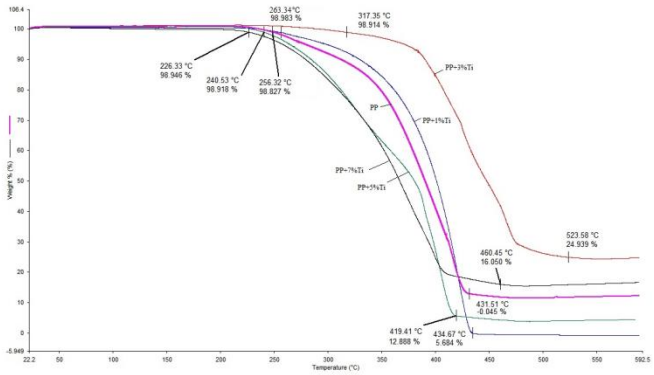

Fig. 6. TGA curves of pure polypropylene (PP) and nanocomposites on the base PP+Ti (1,3,5,7%).

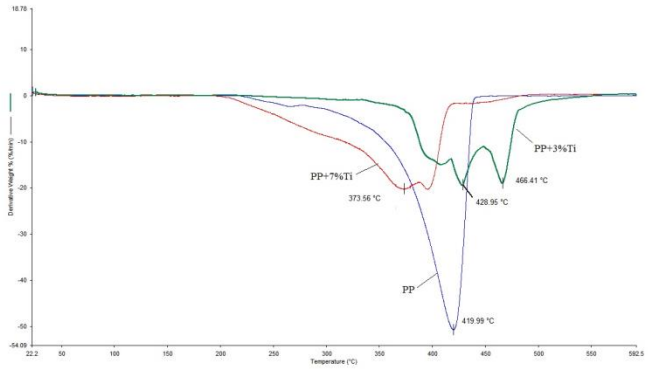

Figure 7.DTG curves of isotactic polypropylene (PP) and nanocomposites based on PP+Ti (3,7%).

From the TGA curve it is clear that the PP begins to decompose at temperatures 256.82^0 C with a continuous weight loss of up to 431.52^0 C. After 431.52^0 C as seen from the TGA curve corresponds to a gradual weight. After addition of 1% Ti nanoparticles the decomposition temperature for nanocomposites shifted toward higher temperatures and is 263.34^0 C with continuous weight loss up to 434.67^0 C; whereas addition of 3% Ti nanoparticles the decomposition temperature for the nanocomposites shifted to temperature 317.35^0 C with continuous weight loss up 523.58^0 C.

Further increase of the Ti content in the polymer matrix of polypropylene decomposition temperature shifts to lower temperatures. So at 5% Ti content the decomposition temperature for the nanocomposites is 240,53^{0}C with a continuous weight loss of up to 419.41^{0}C, and for 7% Ti

decomposition temperature for the nanocomposites is 226.33^0 C with a continuous weight loss of up to 460.45^0 C.

Consequently, it was found that the addition of 1% to 3% volume content of titanium nanoparticles in a polymer matrix increases the thermal stability of polypropylene polymer. A further increase the titanium content in the matrix decreases the thermal stability of polypropylene. With the introduction of nanoparticles volume content of 1% -3% titanium the decomposition temperature is shifted to higher temperatures (up to 62^0 C) in comparison with pure polymer.

All the results of thermogravimetric analysis of PP and PP + Ti samples are shown in Table 1. Table 1 includes the temperature ranges for the various stages of decomposition of pure PP and PP-based nanocomposites + Ti.

Table 1. Effect of titanium nanoparticles on polypropylene thermostability.

Samples	PP	PP+1%Ti	PP+3%Ti	PP+5%Ti	PP+7%Ti
Initial decomposition temperature (^{o}C)	256	263	317	241	226
Half decomposition temperature (^{o}C)	420	409	466	396	374
Final decomposition temperature (^{o}C)	432	435	524	419	460

These experimental results shows that at 1% to 3% of titanium nanoparticles content they act as structurant in the polymer matrix, and in our opinion at low concentration of titanium nanoparticles they are able strongly interacts with the molecules of polypropylene.

In order to predict expiration date of nanocomposites and interfacial interactions of PP + Ti, as well as for the study of kinetic processes occurring in these systems, has been studied mechanical durability of the power based on $\lg\tau_\sigma(\sigma)$. Testing of mechanical performance in equipment that allows to ensure the constancy of the rupture stress during the experiment.

Has been studied the effect of the Ti nanoparticles' concentration on the mechanical durability of PP + Ti nanocomposite. Figure 8 shows the dependence of the logarithm of the mechanical durability $\lg\tau_\sigma$ (σ) on the mechanical stress σ. It was found that the change of the mechanical durability is subject to the following regularity [5]. i.e. the following equation:

$$\tau = \tau_0 \cdot e^{\frac{U(\sigma)}{kT}} = \tau_0 \cdot e^{\frac{U_0 - \gamma\sigma}{kT}} \quad (1)$$

τ_0- constant, regardless of the type of solid body, the state of the material, and its value coincides with the period of own thermal vibrations of atoms in solids. U_0- the activation energy of the process of thermal degradation, γ - structural-sensitive factor, σ- mechanical strength of the material.

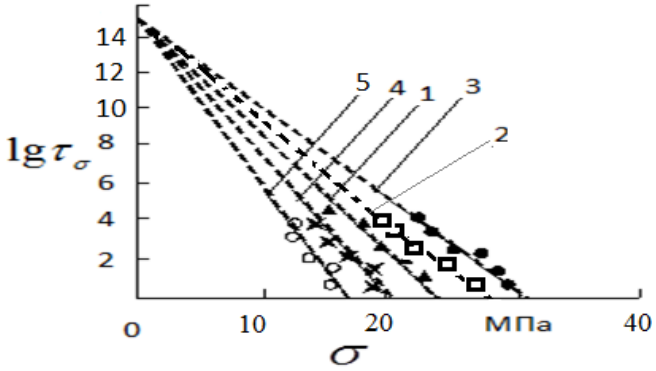

Fig. 8. Dependence of the logarithm of the mechanical durability $lg\tau_\sigma$ from σ at different Ti nanoparticles contents for nanocomposite PP + Ti. 1. PP, 2. PP + 1% Ti, 3. PP + 3%Ti, 4. PP +5% Ti, 5. PP + 7% Ti

It was found that the regularity of change of the mechanical durability is subject to the law (1). It was shown experimentally that with increasing of volume content of Ti nanoparticles the mechanical durability of nanocomposite PP + Ti is changed with an extremum, i.e. at 3% concentration the durability increases and then decreases. Note that equation (1) is performed to a threshold Ti content in polymer nanoparticles. Filling above the threshold broke the continuity of the polymer matrix, i.e. the system passes from orderly continuous to loose structure. From figure 8 calculated value of a structurally sensitive factor γ for the nanocomposite samples PP + Ti, at different volume content of titanium nanoparticles. Table 2 shows the values of structure-sensitive factor γ for the nanocomposite PP + Ti.

Table 2. Values of structure-sensitive factor γ for the nanocomposite PP + Ti

Ti nanoparticles in PP, %	0	1	3	5	7
Structure-sensitive factor, γ	0,54	0,49	0,42	0,45	0,57

Table 2 shows that the structure-sensitive factor decreases with increasing concentrations up to 3% and then at higher concentrations increases. These results indicate that at 3% volume content of Ti nanoparticles, they act as structurant and further increases of the nanoparticles concentration destroys the physical structure of the polypropylene. The 3% volume content of Ti nanoparticles creates a more ordered structure, i.e. increases interfacial interactions, and this led to an increase $lg\tau_\sigma$ (σ) [6-8]. These experimental results are well correlate with results Figure 6.

4. Conclusion

Were studied thermal properties and mechanical properties of nanocomposites based on isotactic polypropylene and titanium nanoparticles. The presence of titanium in PP increases thermal stability and mechanical properties of nanocomposites. The thermal stability and mechanical properties, generally increases with increasing titanium content in polypropylene nanoparticles. The maximum growth of thermal stability is observed in the case of PP with 3% volume content of Ti nanoparticles in polypropylene matrix. The structure of nanocomposites was investigated by atomic force and scanning electron microscopy. Was revealed the relationship between the change in the thermal and mechanical properties with the change of content of nanocomposites PP + Ti. AFM studies have shown that the introduction of titanium nanoparticles in polypropylene change the supramolecular structure of polypropylene, and ordered structure is formed. Further increase of the titanium nanoparticles content leads to a polymer nanocomposite structure inhomogeneity. Thus, the histogram roughness has the value of 40-60 nm for 1% and 3%

nanoparticle titanium content in polypropylene nanocomposites; for 5% Ti content - 80-100 nm. Therefore, has been found that the concentration of 1% to 3% of titanium nanoparticles content plays a central role of the adjustable structurant and further increase the content of titanium nanoparticles destroys the physical structure of the polypropylene.

References

[1] Abel Maharramov, Mahammadali Ramazanov, Mohammad Reza Saboktakin Advanced Nanocomposites Types, Properties and Applications Nova Publisher, Nyu York, 2013, 334 p.
[2] A.D.Pomogaylo, A.S.Rozenberg, I.E.Uflyand. Metal nanoparticles in polymers. Publ: Chemistry, 2000, p.671
[3] A.M.Magerramov, M.A.Ramazanov, F.V.Hajiyeva, V.M.Guliyeva Journal of Ovonic Research **9**(5), 133 (2013)
[4] A.M.Maharramov, M.A.Ramazanov, F.V.Hajiyeva J. Chalcogenide Letters **11(**4), 175 (2014)
[5] H.S. Ibragimova, M.A.Ramazanov, S.A. Abasov, Optoelectron. Adv. Mater. – Rapid Commun. **2(**9) 54 (2008).
[6] M.A. Ramazanov, S.A. Abasov, H.S. Ibragimova j.Fizika, 2008, XİV № 3, p. 25
[7] M.A. Ramazanov, Sh.V. Mamedov, U. Lencer, S. Bolical, Turkish journal of Physics, **23**(3), 511 (1999).
[8] V. N. Bogomolov, D. A. Kurdyukov, L. S. Parfen'eva, I. A. Smirnov, H. Misiorek, A. Jezowski Journal Solid State Physics, **47(4**), 769 (2005)