VARIATION IN THE MECHANICAL PROPERTIES OF POLYPROPYLENE + SiO_2 DEPENDING ON ITS SUPRAMOLECULAR STRUCTURE

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The dependences of mechanical durability as a function of ultimate tensile stress has been examined for the metal oxide nanocomposite PP+SiO_2 with different supramolecular structures (SMS). It is found that the introduction of an optimal amount of nanofiller (5% SiO2) enhances the mechanical properties of nanocomposites with various supermolecular structures. The nanofiller reinforces the PP and also acts as a stabilizer in preventing the decrease in strength properties. The lifetime from mechanical stress and activation energy at different temperatures are calculated for rapidly cooled and slowly cooled nanocomposites. To break the bonds responsible for the strength of the polymer it is necessary to overcome the energy barrier U_0 the value of which depends on the nature of these bonds. It has been established that the value of activation energy U0 does not change, and the variation in mechanical strength properties is determined by the change in the structure-sensitive coefficient γ for composites with different supermolecular structures. The Zhurkov equation reveals that there is a certain mechanism by which the initial barrier U_0 is reduced by tensile forces by γσ. It should be noted that there is a close relationship between the physico-mechanical properties of polymer compositions and their supermolecular formations. Depending on the mutual arrangement of macromolecules and the degree of their ordering, different physico-mechanical indicators can be obtained even with a homogeneous polymer. It has been shown that the value of U_0 corresponds to the activation energy of chemical bonds, and the process of mechanical destruction of polymer composites occurs basically along these bonds.

Keywords: supramolecular structure, fast and slow cooling, spherulites, mechanical durability, activation energy.
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1. INTRODUCTION

Scientific and technical progress in many industries nowadays is undeniable without the use of new composite materials that are able to improve the quality and reliability indicators, increase the life time and reduce the material consumption of manufactured products. Polymer composite materials with new applications and new potential are being widely used. At present, polymer composite materials reinforced with metal oxide nanoadditives are being used extensively. With the increasing demand for the application of active polymer dielectrics ranging from microelectronics, medical diagnostics, development of various sensors and energy converters to micro- and macroenergetics, the development of the physical basis of composite dielectrics is crucial [1, 2, 3]. An essential task of modern physical science is the investigation of their mechanical durability [4, 5, 6].

Changes in the supramolecular structure (SMS) of polymers provide opportunities to create new composite materials. The change in supramolecular structure as the crystallisation time of polymer nanocomposites varies has a significant effect on their physico-mechanical, electrical, thermal and optical properties. [**7**] The effect of changing the cooling rate on the properties of polymer composites has been studied. From literature data, it was found that high crystallinity caused by slow cooling rate increases Young's modulus and yield strength, but decreases strength and fracture toughness. [9**],** In another study, the longitudinal and transverse strength of three unidirectional thermoplastic systems: carbon fiber/polypropylene (CF/PP), polyamide 6 (CF/PA6), and polyphenylene sulfide (CF/PPS) were investigated and the effect of cooling rate on strength was statistically evaluated. It is shown that the matrix modulus increases as the cooling rate decreases; the degree of crystallinity also increases [10] , in another research paper investigating carbon fiber/PEEK.It was shown that strength decreased with increasing cooling rate; tensile strength and Young's modulus of the PEEK resin decreased, while ductility increased with increasing cooling rate due to its dominant effect on crystallinity and spherulite size [11] .Thus there is considerable interest in controlling the crystallinity of polymers in the presence of additive nanoparticles by selecting the "right" size, shape and volume fraction Therefore, it is extremely important to reveal the effects of size and volume fraction of additives on the crystallization of nanocomposite polymer systems. From the above literature data, the change in mechanical properties of isotactic polypropylene with nanoquartz additives in different crystallization regimes has not been sufficiently investigated. This, it can be concluded that studying this problem is of scientific and practical interest. There are several ways to change the SMS of polymers. In some cases, changes in SMS were achieved by uniaxial or biaxial orientation, by high pressure action in combination with shear deformation, or by introducing different kinds of fillers with various dispersion. The proposed work presents the investigation results of the mechanical durability of polymer nanocomposites with various SMSs. The SMS features also affect the destruction rate and the formation of acid-containing groups. The SMSs of polymer composites were adjusted by changing the temperature-time regime of

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crystallization. A non-polar isotactic polymer-polypropylene was chosen to be a matrix. The choice of PP is conditioned by its low cost, manufacturability, prevalence and good dielectric properties.

2. EXPERIMENTAL DETAILS

Isotactic PP granules with size of 5 mm (Dema Import and Export Co. Ltd., China), density of 0.92 g/cm^3, a molecular weight of 300–700 thousand and a specific volumetric electrical resistivity of 10^{14}–10^{15} Om.m were used as a polymer matrix for the composites. SiO2 nanokvarts metal oxide with a particle size of 20-25 nm (Sigma-Aldrich, St. Louis, Missouri, USA), density 1.96 g/cm³, molecular weight 60 g/mol was used as filler. The shapes and sizes of the nanoparticles can be determined from the TEM images (Fig1).

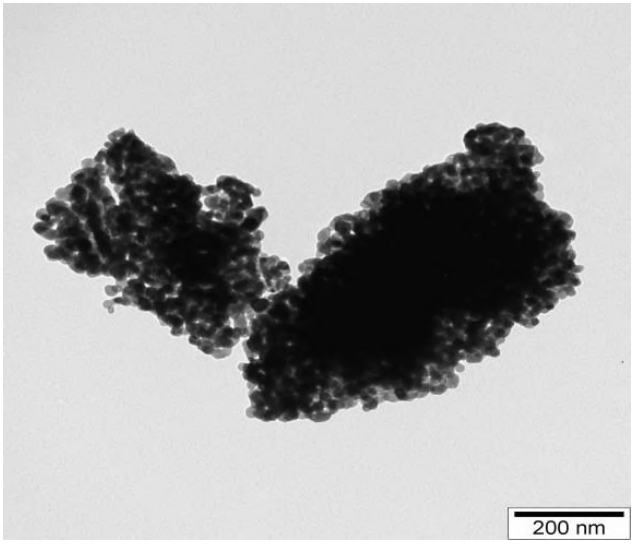


Fig1. TEM Images of Silica SiO_2 nanoparticles.

From the images, it can be seen that the silica SiO2 nanoparticles have spherical shape and the size varies from 20-30 nm. SiO_2 nanoparticles have a spherical shape, which facilitates their uniform distribution within the iPP matrix, reducing the risk of defects. This morphology enhances adhesion between the polymer matrix and nanoparticles, contributing to the structural stability of the composite. Additionally, the small particle size increases the surface area for interaction, promoting the formation of stronger interfacial bonds.

To achieve uniform dispersion of the filler in the volume of the polymer matrix, in our case, obtaining of nanocomposites based on PP+SiO_2 was carried out by introducing the nanoparticle into the polymer solution [12]. Polypropylene was dissolved in toluene at a temperature of 170°C. SiO2 nanopowders were then added to the original liquid system without cooling the polymer solution, at the same temperature Nanocomposite samples with different SMSs were obtained by hot pressing method at PP melting temperature and 10 MPa pressure for 3 minutes. They were obtained in two modes of polymer melt crystallization: in a slow mode (β≈2 deg/min) and by placing molten samples in an ice-water mixture (β≈20 deg/min). The thickness of the nanocomposites was 70-100 μm. The filler concentrations were 1 vol%, 3 vol%, 5 vol%, 7 vol% and 10 vol%. An ISO/R527 instrument (the Zwick-Roell Group, Germany) has been used to measure the mechanical durability of the polymer composites. Samples was dispersed in distilled water and a drop was placed on a carbon coated copper square mesh grid (Electron Microscopy Science, USA). Nanoparticles examples were examined under the Transmission Electron Microscope JEM-1400 (JEOL, Japan) at a voltage of 80–120 kV. Measured photographic magnification was in the range of 200–1000 times, and for this purpose, a universal microscope of the Axio Imager series, (Germany) which can operate with transmitted and reflected light, was used. Atomic force microscopy (AFM) studies were per formed by Ntegra Prima NT-MDT microscope(Russian)

3. RESULTS AND DISCUSSIONS

Dependences of mechanical durability $\lg\tau_\sigma$ as a function of ultimate tensile stress σ at constant room temperature for slow and fast cooled PP samples containing different SiO_2 additives are presented in semi-logarithmic coordinates in Fig. 2 (a and b). It can be seen from the figure that in all cases $\lg\tau_\sigma$ is linearly decreasing depending on σ, hence the exponential equation is met [13].

$$\tau_M = Aexp(-\alpha\sigma) \quad (1)$$

Where A and α are the parameters that identify the mechanical strength properties of the material, and they depend on the nature of the material under investigation and the durability test temperature. $A = \tau_0 exp\frac{U_0}{RT}$ (2) and $\alpha = \frac{\gamma}{RT}$ (3)

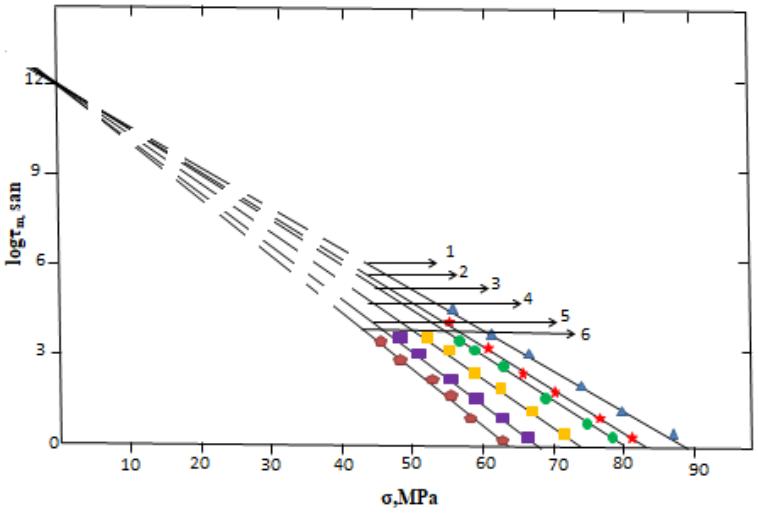


Fig. 2. Force dependences of the mechanical durability of FC samples made of PP and its composites at a temperature of 293 K: 1 - PP+5% SiO_2; 2- PP+7% SiO_2; 3- PP+3% SiO_2; 4 - PP+1% SiO_2; 5- pure PP; 6-PP+10% SiO_2

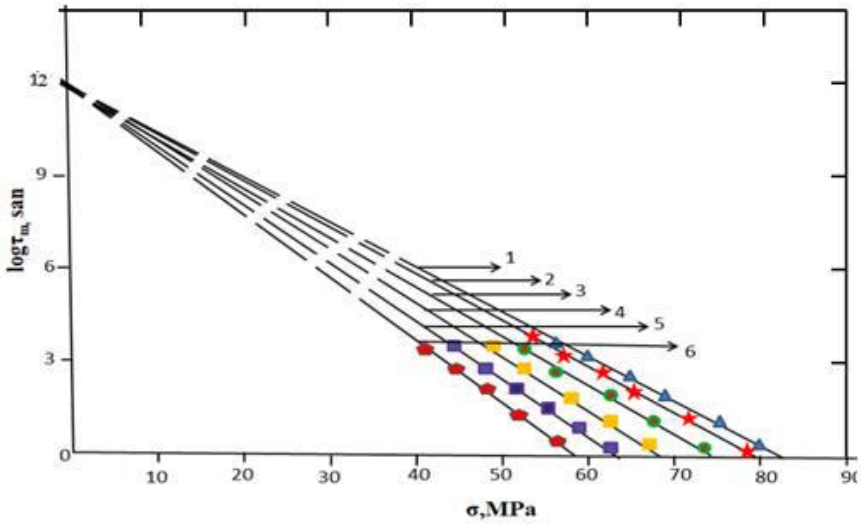


Fig.3. Force dependences of the mechanical durability of SC samples made of PP and its composites at a temperature of 293 K: 1 - PP+5% SiO_2; 2- PP+7% SiO_2; 3- PP+3% SiO_2; 4 - PP+1% SiO_2; 5- pure PP; 6-PP+10% SiO_2

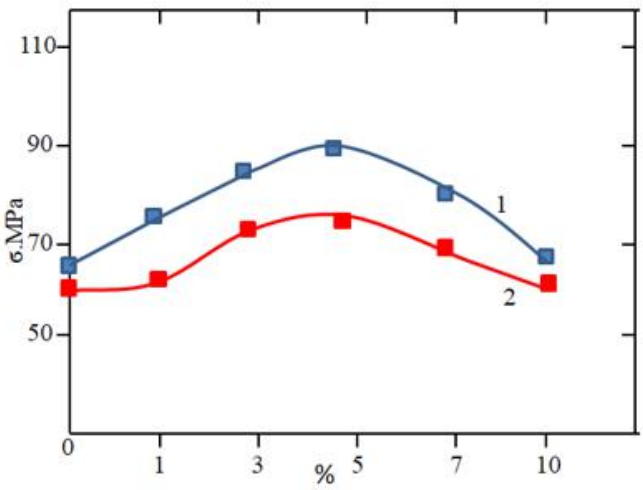


Fig. 4. Dependence of the mechanical strength of PP+5%SiO_2 as a function of the nanoadditive content at a temperature of 293 K. 1 - FC samples, 2 - SC samples.

Thus, if the increase in mechanical strength of PP with the introduction of 5% SiO_2 is 29% with fast cooling, then with slow cooling, all other conditions being equal, the increase in strength is 19%. While further increase in the amount of nanoadditive leads to a decrease in the mechanical strength of FC samples, it is always greater than that of SC samples [14]. The character of change in mechanical strength depending on the amount of nanoadditive is remarkable. This is associated with the nature of the supramolecular structure of the polymer, and the nanoadditive plays a significant role [15]. A characteristic feature of polymeric materials is the diversity of SMSs and the relative ease of transition of one structural form into another [16]. The major strength characteristics change very dramatically with changes in the SMSs of composites. Increasing the cooling rate of nanocomposites leads to a decrease in the crystallization degree. The degree of crystallinity decreases when the composites are rapidly cooled, and the relaxation of internal stresses also decreases [17]. Obviously, in the slow cooling regime of composites, spherulites grow large; however, they can also create regions of high brittleness at the boundaries between crystallites. The boundaries of the spherulites become stress concentration sites, leading to the formation of cracks under mechanical loading. Although large spherulites increase the crystallinity of the material, they may be less resistant to impact and tensile loading. However, when composites are cooled rapidly, the spherulites do not have time to grow large, making the structure more homogeneous and reducing the number of weak zones (spherulite boundaries).This increases the strength of the material because the fine crystalline structure better distributes mechanical loads.

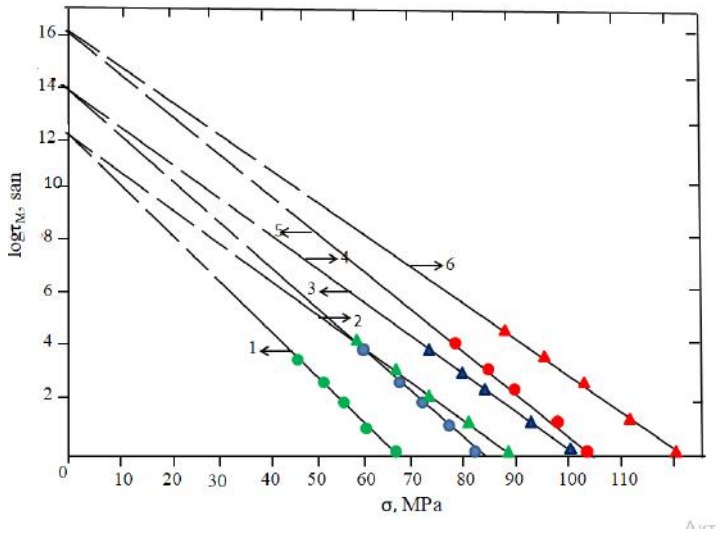


Fig. 5. Dependences of mechanical lifetime ($\log\tau_M$) of PP+5%SiO_2 nanocomposites at different temperatures as a function of the mechanical stress (σ): 1,3,5 ~ PP; 2,4,6 ~ PP+5% SiO2; 1,2 ~ 293K; 3,4 ~ 223K; 5,6 ~ 203K.

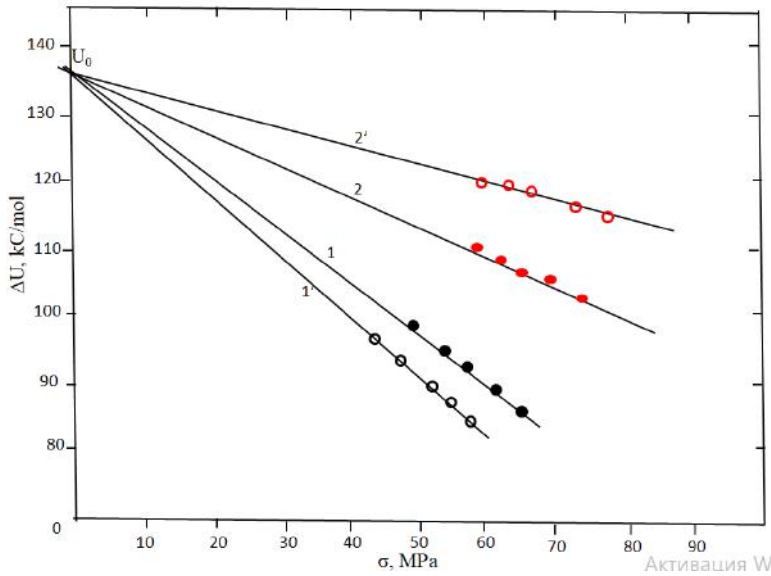


Fig. 6. Dependences of the activation energy as a function of the mechanical destruction process of FC and SC samples for PP and PP+5% SiO_2 composite. 1 and 2 - for PP and PP+5% SiO_2 composite obtained in FC mode; 1′ and 2′- for PP and PP+5% SiO_2 composite obtained in SC mode

As the figure shows, an increase in the mechanical strength of the nanocomposites is observed at lower temperatures. This can be explained by the weakness of thermofluctuation processes at low temperatures. Mechanical destruction differs from each other as they occur at high and low temperatures. Thus, mechanical destruction at higher temperatures is due to structural relaxation. In the low temperature regions, the rate of structural relaxation decreases, being understood as the relaxation of the energy of the internal degrees of freedom of the molecule.

These dependencies are represented by the well-known Zhurkov's equation [18].

$$\tau_M = \tau_0 \exp\left(\frac{U_0 - \gamma\sigma}{RT}\right), \quad (4)$$

where $\tau_м$ is the time from load application to destruction (durability), τ_0 is a constant, numerically close in the period of thermal vibrations of atoms (10^{-12}-10^{-13} sec.), U_0 is the activation energy of the elementary act of the destruction process in the absence of stress, close in value to the sublimation energy for metals and to the energy of mechanical bonds for polymers, σ is stress, γ is structure-sensitive coefficient, coefficient proportional to the overvoltage at interatomic bonds (compared to the average stress in the sample). R is the universal gas constant, T is the absolute temperature in °K. According to the graphs, U decreases linearly as a function of σ both for the initial PP and for PP+5% SiO_2 composites obtained under FC and SC modes and is expressed by the equation

$$U = U_0 - \gamma\sigma \quad (5)$$

the value of U was calculated from formula (4), writing it in the form

$$U = 2{,}3RT(lg\tau_m - lg\tau_0) \quad (6)$$

Figure 6 depicts the dependences of activation energy as a function of the mechanical destruction process of FC and SC samples for PP and PP+5% SiO_2 composite. It is clear from the graph that the value of U_0 is constant for all cases and does not depend either on the crystallization mode or on the introduction of the SiO_2 additive into the polymer [19]. The treatments carried out (different cooling rates and introduction of nano additives), however, have effects on the value of the γ coefficient and the mechanical strength (durability) of the PP. First of all, it should be noted that the invariability of the value of τ_0 is understandable, since it is a universal constant. The constant value of the initial energy barrier U_0 at different treatments, especially at the introduction of nanoadditive into PP gives us reason to suppose that the destruction of PP before and after treatment, particularly at the introduction of additive is mainly by the same chemical bonds [20]. The change in the structure-sensitive coefficient γ is due to the fact that, obviously, there is a distribution of external mechanical stress over macromolecules. Otherwise, the introduction of nanoadditive does not change the chemical bonds themselves, but the conditions of their rupture, changing for instance the level of load on the load-bearing bonds. As well as changes in the structure-sensitive coefficient γ can be related to changes in the SMSs of the polymer. In accordance with the kinetic thermofluctuation theory of S.N. Zhurkov, material destruction occurs due to the rupture of chemical bonds, which is caused by the joint action of the energy of thermal motion of molecules and some external force (mechanical load, electric field strength, etc.). Direct rupture of a chemical bond, weakened by the action of external loads, is due to fluctuations in the kinetic energy of the thermal vibrational motion of atoms or molecules.

Figure 7 shows micrographs of PP+5%SiO_2 composites obtained during rapid cooling (a) and slow cooling (b). Micrographs of PP+SiO_2 composites obtained after slow and fast cooling show significant differences in structure. These differences are due to the processes of crystallization and aggregation of particles that occur at different cooling rates. In the slow cooling regime, the composites have time to form large and well organized crystallites (spherulites) [21].This leads to the appearance of a structure with well-defined spherulite boundaries in micrographs. The boundaries of large spherulites represent weak zones where stresses are concentrated under mechanical loading. These boundaries promote cracking, which reduces the strength of the material.

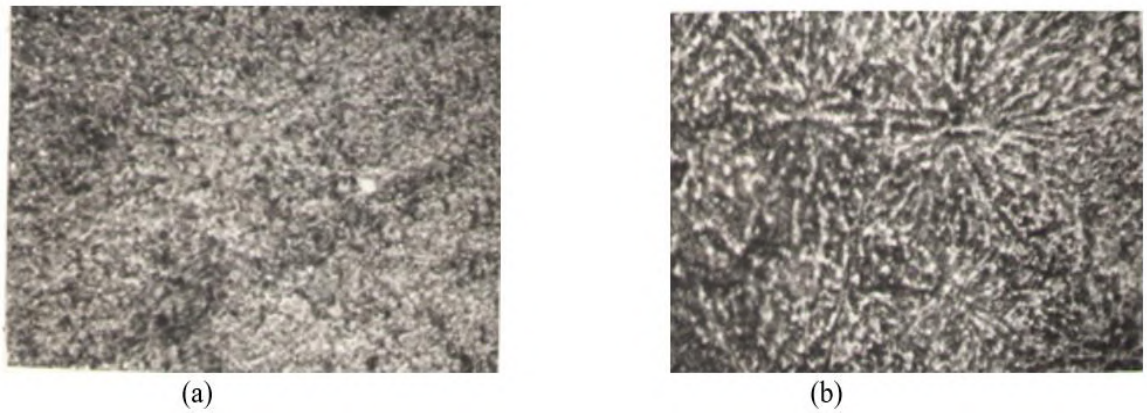
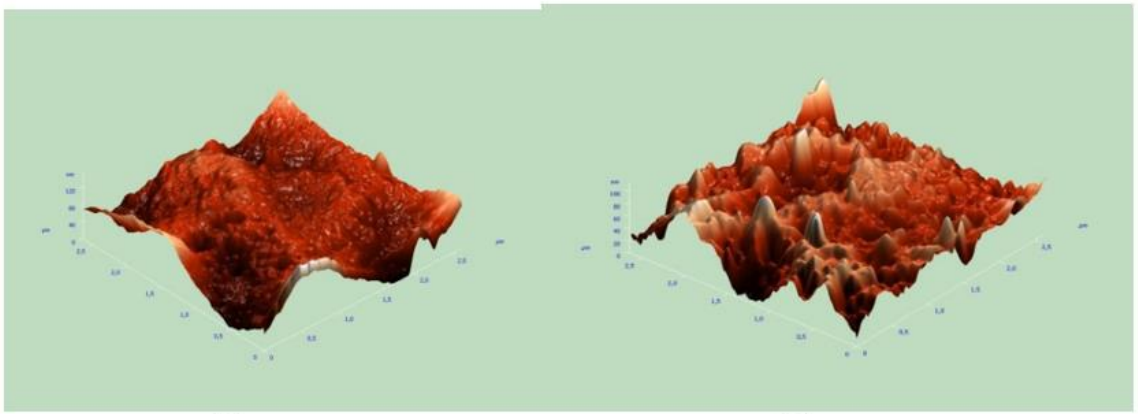


Fig. 7. Micrographs of PP+5%SiO_2 composites obtained during rapid cooling (a) and slow cooling (b)



(a) (b)

Fig. 8. AFM images of PP + 5% SiO_2 composites obtained under different cooling conditions:
(a) Composites obtained under rapid cooling (BO).
(b) Composites obtained under slow cooling (MO).

Based on the presented AFM images, the following observations can be made:

The first image (a), characterized by smoother transitions and less pronounced roughness, corresponds to a fine-spherulitic structure formed under rapid cooling. Rapid cooling results in the development of small spherulites, leading to a smoother and more uniform surface without sharply defined structural boundaries.

The second image (b), displaying sharp protrusions, high roughness, and pronounced peaks, corresponds to a coarse-spherulitic structure formed under slow cooling. Slow cooling promotes the growth of larger spherulites, resulting in noticeable granularity and well-defined structural boundaries, along with a distinct surface relief.

In contrast, under the rapid cooling regime, the composites exhibit uniformly distributed small spherulites (lighter-colored regions with smaller boundaries) and a homogeneous structure without visible microcracks.

CONCLUSION

Consequently, in summary, it can be assumed that the introduction of 5% SiO_2 nanoadditive into PP results in an increase in the mechanical durability of the polymer obtained in FC and SC crystallization modes, i.e. it is a stabilizing factor. On the basis of temperature-force dependences of mechanical durability of FC and SC of samples of initial PP and PP+5%SiO_2 composite, the kinetic parameter of mechanical destruction has been determined and it has been shown that the activation energy of this process remains unchanged, the observed changes have been reflected in the structure-sensitive coefficient γ. It has been found that the mechanical strength of composites obtained in FC mode is greater than the strength of composites obtained in.SC mode, which is explained by the size of spherulites for these structures.

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