# AMORPHOUS SILICA-BASED NANOCOMPOSITE - DEPENDENCE ON QUENCHING CONDITION

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The decisive factor in obtaining high-performance nanocomposites is to determine the technological conditions that ensure their optimal structural properties. It is possible to manipulate the functional properties of nanocomposite by maintaining its composition and only by modifying the technological parameters applied during production. In this study, the influence of the temperature-time mode of crystallization on the structure and properties of amorphous nano-silica and polypropylene-based nanocomposite were investigated. XRD (Rigaku Mini Flex 600 spowder diffractometer) analysis of the structure of polymer nanocomposite shows that with the decreasing of the cooling speed, a more regular structure is formed in the morphology of the polymer matrix. Furthermore, it was found that the intensity of the photoluminescence (spectrofluorometer Varian Cary Eclips) spectrum of the nanocomposite increases with the decreasing cooling speed. This is explained by the relatively big contact area of the phases due to the formation more regular structure when the cooling time is longer, which in turn, leads to a higher intensity of the luminescence spectrum of the nanocomposite.

**Keywords:** amorphous nano-silica, quenching in liquid nitrogen, cooling rate, polymer nanocomposite, blue emission, X-ray microscopy.
**PACS:** 78.55.−m, 78.66.Jg, 61.43.Gt, 68.37.Yz, 78.70.En

## I. INTRODUCTION

Modern material science requests a new class of materials with enhanced properties that are applicable in various fields of engineering, including electronics, aerospace, security, medicine, and others [1]. The most attractive feature of nanocomposites is the synergetic effect of properties. There are many synthetic polymers with high processability, elasticity, and other characteristics that make it possible to successfully use these polymers for the production of new materials [2]. Fillers for such polymers are typically nanoparticles with specific functional properties and desirably, easy- available [3-8]. However, the characteristics of the final product are directly related to the production method, condition, proportion of components, suitability, etc. The development of the effective producing technology, and investigation of the properties of the polymer nanocomposite, depending on the type and concentration of its component, plays a vital role in the prediction of the targeted properties of this new material.

In this study, the properties of the nanocomposite based on the isotactic polypropylene and ultrafine amorphous silica nanoparticles were studied depending on their crystalline structure. To modification of the supramolecular structure of the nanocomposite, the temperature-time mode of crystallization was manipulated [9-14].

The quenching technique was used for cooling samples at different speeds. Furthermore, various modern techniques were used for the characterization of polymer nanocomposites. It was becoming clear that all properties, including intense blue emission of the nanocomposite that was related to the defects of

silica nanoparticles depend on the supramolecular structure of the polymer matrix [14-15].

## II. EXPERIMENT

All chemicals were used without any additional purification. An isotactic polypropylene polymer with a density of $0.92 g/cm^3$ at $25°C$ and molecular mass of 250,000 was pursued from Moplen company (*HF* 500 *N*, homopolymer). The melting temperature of the polymer is $162°C$. Polymer powder was solved in Toluene. Amorphous silicon dioxide $(SiO_2)$ nanoparticles with $50nm$ size were added to the polymer solution. The hot pressing method was used for the preparation of the polymer nanocomposites [16-17]. To modification of the supramolecular structure of the nanocomposite temperature-time mode of crystallization was manipulated. The quenching technique was used for cooling samples with different speeds. During slow cooling, the nanocomposite sample remained under the pressure($10MPa$) while the temperature was dropped from the melting point of polymers to room temperature. The cooling speed was $20°/min$ in this case. For producing nanocomposites through fast cooling nanocomposite samples was quenched into the liquid nitrogen and the cooling speed was $20000°/min$. The samples that are quenched into the aqua medium possess a cooling speed of $200°/min$. Difference modern techniques were used for the characterization of the polymer nanocomposite. Rigaku Mini Flex 600 XRD diffractometer was used for phase identification of the polymer nanocomposite. Diffraction patterns were obtained in the range of Bragg's angle $2\theta=10–80$. Photoluminescent properties of nanocomposite films were examined using a spectrofluorometer Varian Cary Eclipse at a wavelength range of $200–900nm$.

## III. RESULTS AND DISCUSSION

To study the effect of crystallization mode on the structure of PP+SiO$_2$ nanocomposite samples, an X-ray diffraction analysis was conducted. Figure 1 shows the XRD pattern of nanocomposite samples depending on the crystallization mode. For all samples, the *hkl* indexes (110), (040), (130), of a phase of pure polypropylene are observed at 14,1°; 16,9°; 18,5°, respectively [18]. The X-ray spectrum of a nanocomposite obtained through quenching into the liquid nitrogen differs from that of nanocomposites obtained in the other two modes. Thus, in the samples obtained through slow cooling mode and quenching in water, two sharp diffraction patterns are observed at the 2theta angle values of 21.2° (111) and 21.8° (041) [18]. It is known that these diffraction lines are also belonging to the alpha phase of polypropylene. Observation of this pattern for samples cooled with the speed of 20°/min and 200°/min is explained in terms of the crystalline morphology of the polymer matrix. By contrast to samples obtained through quenching into liquid nitrogen for these samples, a high degree of lamellae orientation is characteristic [19-20].

Only the intensity of the emission spectrum variated depending on cooling speed. It is known that the luminescence emission of silicon dioxide nanoparticles is related to oxygen deficit centers that are located on the surface of it. The luminescence properties of nanocomposites based on SiO$_2$ depend on the features of the environment in which the particle is located and the degree of the interaction between the particle and surrounding media. Figure 2 shows the luminescence spectrum of an aqueous solution of pure SiO$_2$ nanoparticles. Figures 3 and 4 show the luminescence spectra of PP+SiO$_2$-based nanocomposite samples depending on temperature and

time mode of crystallization. The excitation wavelength was 270 *nm*. The emission spectrum of nanocomposites has been studied in the range of 300-700 *nm*. No new peaks or shifts in the luminescence spectrum of nanocomposites depending on cooling mode are recorded of PP+SiO$_2$ nanocomposite samples depending on the temperature-time conditions of crystallization. SiO$_2$ nanoparticles are known to have intense blue radiation in the range of 2.2–3.1 *eV*, in other words, 400–550 *nm*. Radiation in the 2.57 *eV* (481 *nm*) and 2.3 eV (531 *nm*) ranges are known to be due to defects on the surface of the silicon dioxide nanoparticle [21-24]. As the cooling speed increases, a decrease in the intensity of these radiation lines is observed in the luminescence spectrum of the nanocomposite. This fact is explained by changes in the supramolecular structure of the polymer with increasing cooling speed. Thus, silicon dioxide nanoparticles are uniformly distributed in the polymer alloy and play the role of structural centers for the formation of a thermodynamically regular structure. In the slow cooling mode, the spherulites formed in the amorphous phase of the polymer, and the lamellae that make them up possess enough time to form around the nanoparticles [25]. In other words, the nanoparticles take up space in the cavities of the supramolecular structure of the polymer matrix and are distributed throughout the composite.

In contrast, when a nanocomposite is suddenly cooled in a liquid nitrogen medium, the amorphous polymer layer around the nanoparticles crystallizes instantly, making it impossible to form a regular structure. This idea is confirmed by the explanation of the XRD description. The formation of a regular structure and the relatively large contact area of the phases explain the higher intensity of the luminescence spectrum of the nanocomposites obtained via the slow cooling mode.
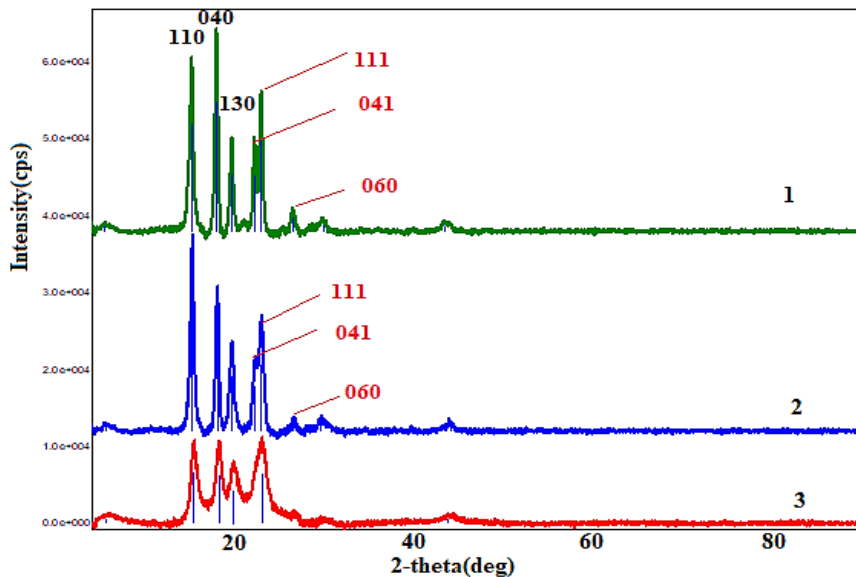


*Fig. 1.* X-ray diffraction pattern of PP+SiO$_2$ nanocomposites depending on temperature-time condition of crystallization (cooling speed)
**1.** slow cooling (20°/min)   **2.** cooling in water medium (200°/min)
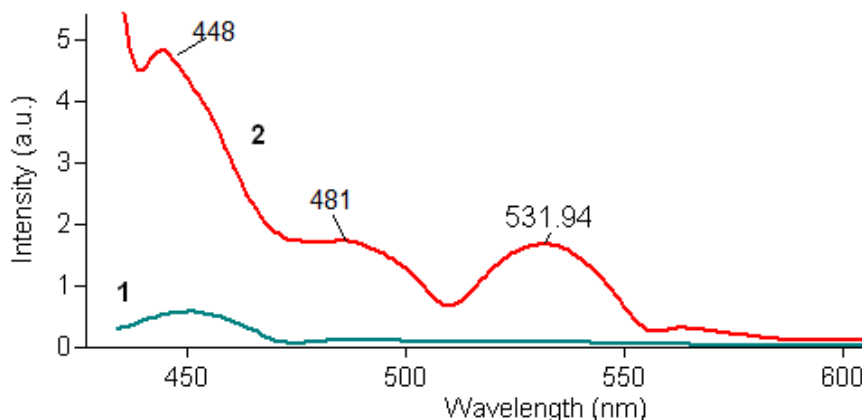**3.** cooling in liquid nitrogen medium(20000°/min)

*Fig. 2.* Pl spectrum of the water solution of the pure SiO₂ nanoparticles.
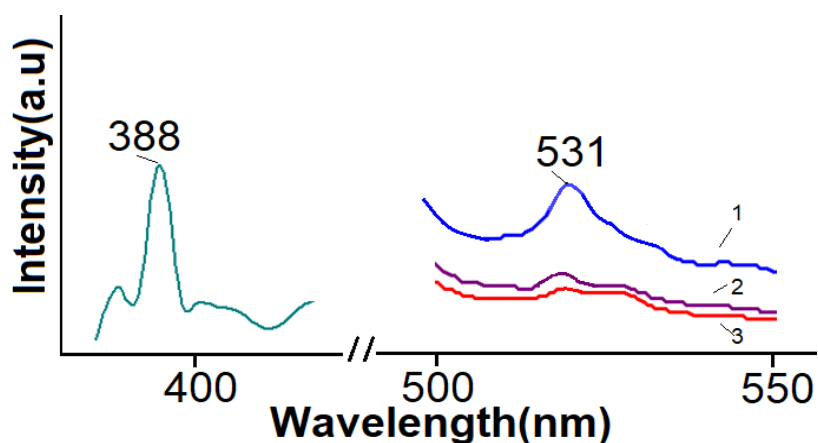1. water without silica     2. water with silica



*Fig. 3.* PL spectrum of PP+SiO₂ nanocomposites depending on temperature-time condition of crystallization (cooling speed).
$\lambda_{Ex}=270nm.$ $\lambda_{Em}=531nm.$
1) slow cooling (*20°/min* ), 2) cooling in water medium (*200°/min*),  3) cooling in liquid nitrogen medium(*20000°/min*)
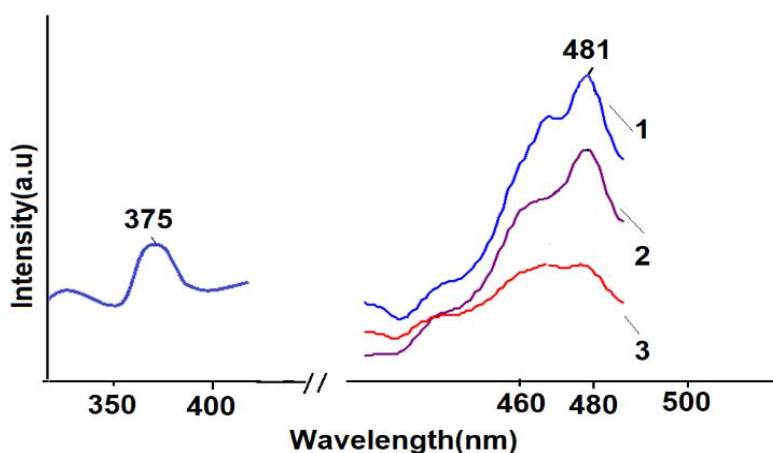


*Fig. 4.* PL spectrum of PP+SiO₂ nanocomposites depending on temperature-time condition of crystallization (cooling speed).
$\lambda_{Ex}=270nm.$ $\lambda_{Em}=481nm.$ 1) slow cooling (20°/*min*); 2) cooling in water medium (200°/*min*); 3) cooling in liquid nitrogen medium(20000°/*min*)

*Fig. 5.* Frequency dependence of the dielectric constant of PP+SiO$_2$ nanocomposites depending on temperature-time condition of crystallization (cooling speed). $\lambda_{Ex}$=270nm. $\lambda_{Em}$=481$nm$.
1) slow cooling (20°/min); 2) cooling in water medium (200°/min); 3) cooling in liquid nitrogen medium(20000°/min)
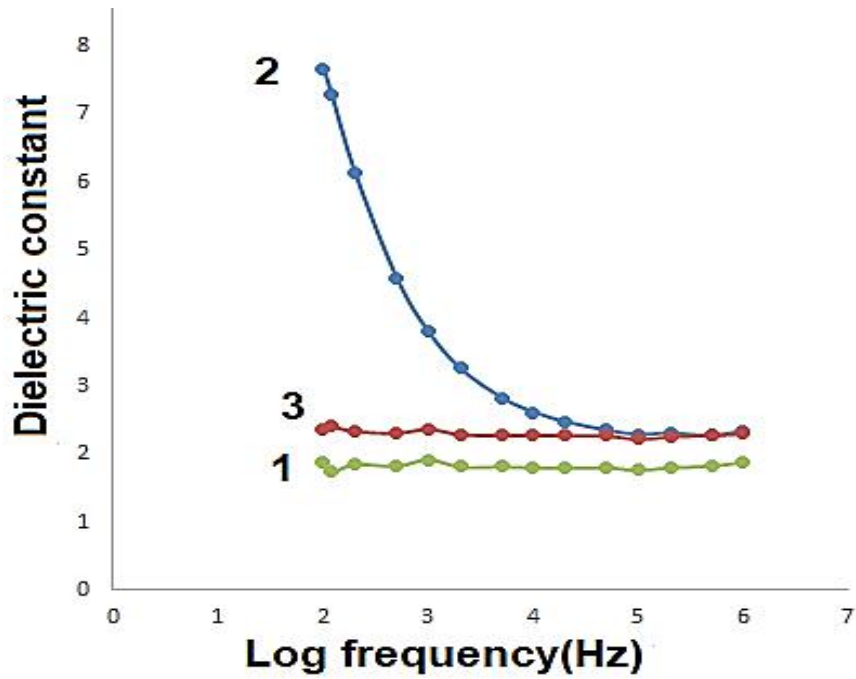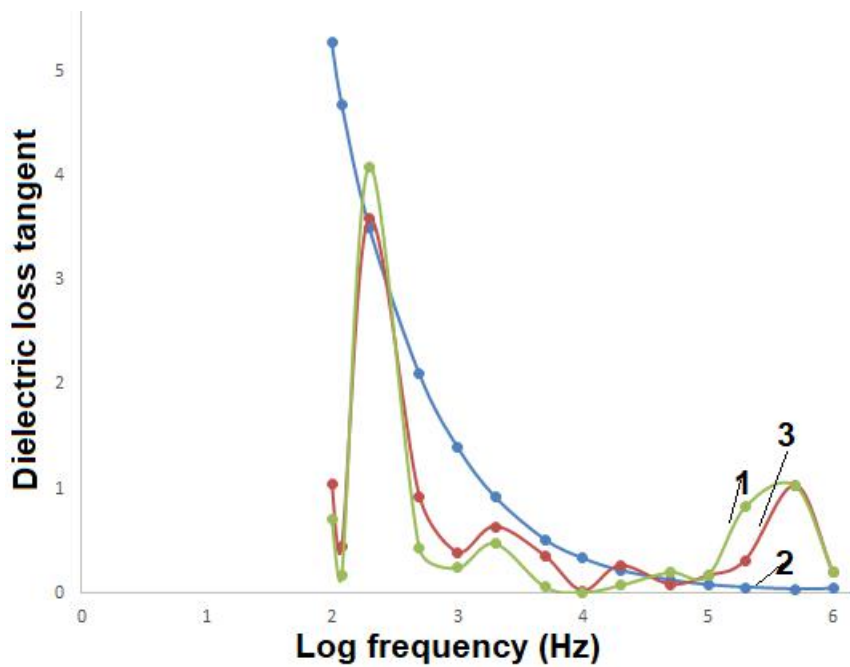


*Fig. 6.* Frequency dependence of the dielectric loss tangent of PP+SiO$_2$ nanocomposites depending on temperature-time condition of crystallization (cooling speed). $\lambda_{Ex}$=270nm. $\lambda_{Em}$=481$nm$.
1)slow cooling (20°/$min$);  2) cooling in water medium (200°/$min$); 3) cooling in liquid nitrogen medium(20000°/$min$)

The electrophysical properties of PP+SiO$_2$ nanocomposite samples depending on the temperature-time conditions of crystallization were considered. Figure 5 shows the frequency dependence curves of the dielectric constant of PP+SiO$_2$ nanocomposite samples. As can be seen from the figure, the value of the dielectric constant for samples obtained by the slow cooling (20°/$min$) is relatively lower than for samples produced through quenching into the liquid nitrogen (20000°/$min$) and aqueous media (200°/$min$). This is due to the supramolecular structure of the polymer nanocomposite [26-27]. A decrease in the proportion of the amorphous phase in the polymer matrix results leads to a reduction in the number of relaxing segments. The value of the dielectric constant is also low because the structural elements that can participate in the relaxation process in the samples obtained through slow cooling are less than those of samples obtained by the other two modes. The dielectric constant of a nanocomposite

sample obtained in an aqueous medium decreases with increasing frequency. The values of the dielectric constant for nanocomposites obtained via quenching into the liquid nitrogen and aqueous media in the high-frequency range (105-106$Hz$) overlap. The change in the value of the dielectric loss tangent in the high-frequency region depending on the cooling speed of the samples demonstrates good consistency with the frequency dependence of the dielectric constant of these samples (fig 6). Thus, most dielectric losses are observed for samples produced through slow cooling mode.

It can be concluded that all properties including intense blue emission of the nanocomposite, that was related to the defects of silica nanoparticles depend on the supramolecular structure of the polymer matrix.

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