

THE INFLUENCE OF SUPRAMOLECULAR STRUCTURE ON THE OPTICAL PROPERTIES OF PP + SiO₂

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This study investigates the effect of supramolecular structure on the optical properties of polypropylene (PP) composites filled with nanoquartz silicon dioxide (SiO₂). It was found that the addition of SiO₂ nanoparticles leads to a decrease in the band gap due to the formation of new trap states or structural defects. The change in the band gap is attributed to electronic interactions at the polymer–filler interface and structural rearrangement of the polymer near the surface of the nanoparticles. Cooling conditions significantly influence the supramolecular structure of the PP+SiO₂ composite, leading to variations in its optical behavior. Slow cooling promotes crystallization and causes a redshift in the absorption spectrum, while rapid cooling increases amorphousness and results in a blueshift. By tuning the band gap and the supramolecular structure, it is possible to design materials with desired optical characteristics for various applications. The reduction in band gap with increasing nanoparticle content enhances the electrical conductivity and photoactivity of the material, making it suitable for use in sensors, photocatalysts, and electronic devices.

Keywords: supramolecular structure, band gap, rapid cooling, slow cooling.

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INTRODUCTION

Polymers and polymer nanocomposites have many applications in science and technology. Using solid nanoparticles as fillers opens up new possibilities for their applications. The addition of nanoparticles in nanotechnology opens up new possibilities for their use [1]. Polymer nanocomposites show great promise in optics and optoelectronics, offering opportunities to develop new devices and technologies. They are used to create anti-reflective and protective coatings for lenses, screens, and other optical surfaces [3]. This study aims to investigate the optical properties of a polymer nanocomposite based on isotactic polypropylene (iPP) and silica. Isotactic polypropylene (iPP) was used as the polymer matrix. This material is characterized by a high degree of crystallinity due to the regular arrangement of methyl groups along the polymer backbone, which promotes the formation of a dense supramolecular packing. Such a structure is sensitive to processing temperatures and the introduction of nanofillers, making iPP an effective model system for investigating the relationship between structural organization and optical properties.

Isotactic polypropylene exhibits low intrinsic absorption in the visible range, which enables the observation of optical property changes caused by external factors without interference from the matrix itself. Its high reproducibility, resistance to thermo-oxidative degradation, and strong crystallization ability make it an optimal choice for systems focused on exploring the correlation between morphology and optical response. Nanocrystalline quartz (α -SiO₂) was used as the nanofiller in this study. It consists of nanoscale quartz crystals with a high degree of structural order. In contrast to amorphous forms of SiO₂, the nanocrystalline variant possesses a well-defined crystalline lattice, which significantly affects

its interaction with the polymer matrix and its behavior during composite formation.

EXPERIMENTAL METHODOLOGY

The main issue in nanomodification is the method of introducing and evenly distributing nanofiller particles in the polymer matrix. For the composites, isotactic polypropylene (iPP) granules with a size of 5 mm (Dema Import and Export Co. Ltd., China) and nanocrystalline SiO₂ with particle sizes of 25-35 nm and a density of 2.6 g/cm³ (Sigma-Aldrich, St. Louis, Missouri, USA) were used as the polymer matrix and nanofiller, respectively. The fabrication of the PP + SiO₂ nanocomposites was carried out by introducing nanoparticles into the polymer solution [4]. The compositions were prepared by hot pressing at the melting temperature of the polymer matrix under a pressure of 15 MPa for 4 minutes. Films with a thickness of 80 μ m were used. In this study, we investigated two crystallization modes of the polymer melt: a slow cooling rate ($\beta \approx 2^\circ/\text{min}$) and rapid cooling by placing the molten samples in an ice-water mixture ($\beta \approx 20^\circ/\text{min}$). Optical spectra in the UV and visible regions were measured using a Spekord-250 spectrophotometer. The band gap was determined from the absorption spectra of the polymer composite using the Tauc method, with curve fitting [5].

RESULTS AND DISCUSSION

Figure 1 shows the absorption spectra for the composite. As seen from the figure, the absorption peak is located in the short-wavelength region, which may be associated with the presence of unsaturated (ethylene and carbonyl) groups in the structure of the blend. The peak shifts towards longer wavelengths with an increase in the nanofiller content, indicating a

reduction in the band gap, an increase in the amorphous structure of the films, and an improvement in the semiconducting behavior of the obtained films. Figure 2 shows the changes in the band gap width for the nanocomposite. According to the Tauc theory:

$$\alpha h\nu = B(h\nu - E_g)^P \quad (1)$$

where: α is the absorption coefficient, $h\nu$ is the photon energy, E_g is the optical band gap, B is a frequency-independent constant determined by the material and the type of optical transition (direct or indirect), P is the exponent related to the density of states distribution, which can take values of 1/2, 3/2, 2 or 3, depending on the nature of the electronic transition.

As seen from the figure2, the band gap of the pure polymer is larger than that of the nanocomposite. The doping of nanooxides affects the transmission band of the polymer structure. As the concentration of the nanofiller increases, the optical gap decreases. Therefore, effective control of the transmission band can be achieved by introducing a specific concentration of nanofiller into the polymer matrix. This is explained by the fact that nanoparticles can interact with the polymer matrix, altering the local distribution of electronic states. Such interaction can modify the energy of electronic transitions in the

composite, which also influences the band gap. Size effects (quantum size effects) can alter the energy levels in nanoparticles, which in turn affects the optical properties of the composite. For SiO_2 nanoparticles, a decrease in size leads to an increase in the binding energy and, as a result, a reduction in the band gap [6] For composites with nanocrystalline silicon dioxide (SiO_2), the most characteristic optical transition type is indirect. This is due to the features of the SiO_2 crystalline structure and the energy states in its forbidden zone. Nanocrystalline particles have an ordered crystalline lattice, which generally leads to indirect transitions. In this case, electrons not only need to absorb a photon but also transfer momentum through the crystal lattice, making such transitions less likely and requiring additional interactions. Thus, for composites with nanocrystalline SiO_2 , an indirect optical transition is characteristic, and the nanoparticle size has a significant impact on their optical properties. These data could be useful in the development of materials with tailored optical characteristics for various applications. The change in the supramolecular structure of the composites has a varying impact on their optical properties due to differences in the distribution of crystalline regions and interfacial boundaries.

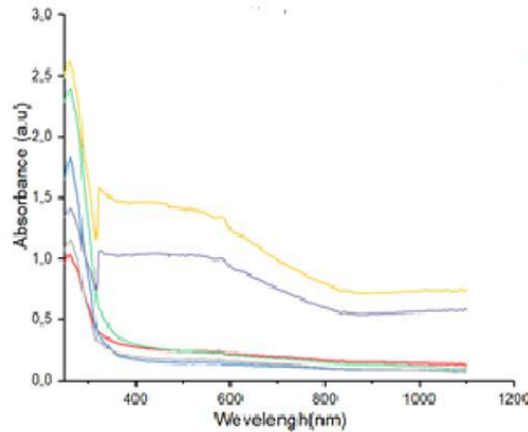


Fig.1. Absorption spectra of PP + nano quartz silicon dioxide composites – PP, – PP+1% SiO₂, – PP+3% SiO₂, – PP+5% SiO₂, – PP+7% SiO₂, – PP+10% SiO₂

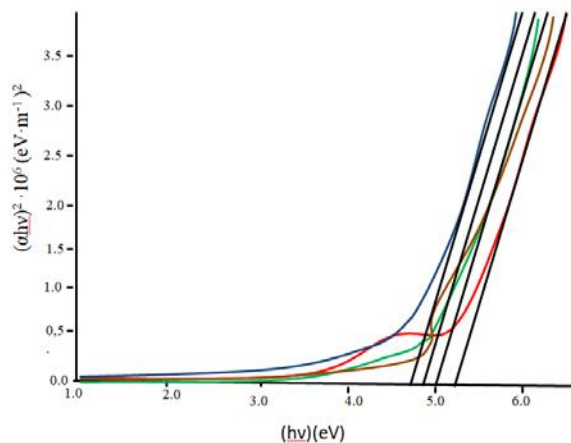


Fig. 2. Band gap variation in PP + nanocrystalline SiO₂ composite –PP, -PP+3% SiO₂, -PP+5% SiO₂, -PP+10% SiO₂

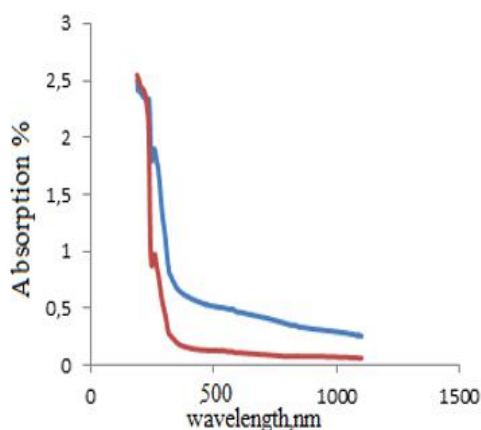


Fig.3. Absorption spectrum of PP +5%SiO₂ under different cooling conditions. PP+5%SiO₂ spectra recorded during rapid cooling, PP+5%SiO₂ spectra recorded during slow cooling

Figure 3 shows the absorption spectrum of PP + 5% SiO₂ under different cooling conditions. As seen from the figure, these spectra differ. Nanocrystalline silicon dioxide (SiO₂) affects the optical properties by changing the structural states, which can explain the differences in the cooling results. Slow cooling leads to higher crystallinity and a shift towards longer wavelengths, whereas rapid cooling increases amorphousness and defects, shifting the spectrum towards shorter wavelengths. In the composite, slow cooling promotes higher crystallinity and, consequently, greater light absorption. This difference can be explained by the varying nature of the interaction between nanoparticles and the polymer matrix, their size effects, and changes in the supramolecular structure under different cooling conditions. Changes in the supramolecular structure of the composite significantly influence its optical properties due to the rearrangement of polymer chains and the distribution of crystalline and amorphous regions. Slow cooling promotes the formation of larger crystalline domains, leading to a more ordered polymer structure that enhances light absorption and

improves the semiconducting behavior of the composite. On the other hand, rapid cooling increases the amorphous fraction and introduces more defects, shifting the absorption spectrum to shorter wavelengths. These defects play a crucial role by introducing additional energy states within the forbidden zone, which facilitates electronic transitions. Moreover, the interaction between the polymer matrix and the nanofiller can modify the packing density and the overall morphology of the composite, further influencing the optical characteristics.

CONCLUSIONS

Thus, with small additions of SiO₂, the width of the forbidden zone decreases due to the appearance of new traps or defect states. The change in the forbidden zone width of the PP+SiO₂ composite is caused by: electronic interaction at the phase boundary, as well as structural rearrangement of the polymer at the nanoparticle surface. Changes in the cooling regime affect the supramolecular structure of the PP+SiO₂ composite, leading to differences in optical properties. Slow cooling promotes crystallization and shifts the spectrum toward longer wavelengths, while rapid cooling increases amorphousness and causes a shift toward shorter wavelengths. By altering the width of the forbidden zone and the supramolecular structure of the composite, materials for various applications can be obtained. The change in the forbidden zone of the composite with the addition of a nanoparticle percentage makes it more conductive or photoactive, which is useful for materials in sensors, photocatalysts, and electronics. Reducing the width of the forbidden zone expands the light absorption spectrum, which is used in sensors, UV detectors, and photocatalysts for water/air purification. The activity under visible light makes such composites promising for environmental technologies. The PP+SiO₂ composite with altered supramolecular structure is a multifunctional material used in electronics, construction, etc.

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