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STRUCTURAL AND LUMINESCENT CHARACTERISTICS OF LDPE MODIFIED WITH BIOFILLERS BASED ON FISH SCALES

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***Abstract*-Low-density polyethylene (LDPE)-based biocomposites containing fish scale (Fs) biofiller and iron nanoparticles were investigated with respect to their structural and photoluminescent properties. The composites were prepared with different concentrations of fish scale filler, while Fe nanoparticles were introduced as modifying additives to evaluate their influence on the optical behavior of the polymer matrix. X-ray diffraction (XRD) analysis demonstrated that thermal treatment of the fish scale biofiller increases its degree of crystallinity, indicating structural rearrangement and partial ordering of the organic-mineral components. Photoluminescence spectra of LDPE + x vol.% Fs and LDPE + x vol.% Fs + Fe composites were recorded under excitation at 342 nm. The obtained results revealed that the emission intensity strongly depends on the concentration of the biofiller and the presence of iron nanoparticles. An increase in fish scale content led to noticeable changes in the luminescence response of the composites, whereas incorporation of**

Fe nanoparticles caused a significant decrease in emission intensity. This effect is associated with enhanced nonradiative relaxation processes and possible energy transfer mechanisms induced by iron particles. The combined influence of the biofiller and metallic nanoparticles on the structural ordering and optical response of the composites was established. The developed LDPE-based biocomposites exhibit tunable luminescent characteristics and may be considered promising materials for functional polymer systems, optical coatings, and environmentally friendly polymer applications requiring controlled photoluminescent behavior.

***Keywords*: LDPE biocomposites, bionanocomposites, photoluminescence, X-ray phase analysis, fish scales, iron nanoparticles, crystallinity.**

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I. INTRODUCTION

In recent decades, polymer composites have attracted considerable attention due to their versatile applications in advanced engineering systems, optoelectronic devices, and functional materials. Their ability to combine mechanical strength, lightweight characteristics, and tunable physical properties makes them highly attractive for modern technological applications [1–3]. Among polymeric matrices, low-density polyethylene (LDPE) is widely used due to its excellent processability, chemical resistance, and relatively low cost, making it suitable for the development of composite and nanocomposite materials with enhanced functional performance.

In recent years, the incorporation of natural biofillers into polymer matrices has emerged as an environmentally friendly and sustainable approach to material design. Bio-based fillers, such as cellulose, chitin, and fish scales, are increasingly investigated due to their biodegradability, abundance, and capability to modify structural and physical properties of polymer systems [4–7]. Fish scales, in particular, possess a complex hierarchical structure composed of collagen and mineral components, which can significantly influence the internal structure and energy transfer processes within polymer composites.

Another promising direction in the development of advanced polymer systems is the incorporation of nanomaterials and metallic nanoparticles. The inclusion of nanoscale additives into polymer matrices enables precise control over structural, electrical, optical, and luminescent properties of the material [8–10]. In particular, iron nanoparticles have been shown to influence non-radiative relaxation processes and energy transfer mechanisms, leading to modification of photoluminescence behavior in composite systems. The interaction between biofillers and metallic nanoparticles creates a synergistic effect that enhances the functional characteristics of the resulting materials.

The study of photoluminescence properties in polymer-based composites has gained significant attention due to their potential applications in optical coatings, sensors, radiation converters, and light-emitting devices. Photoluminescence behavior is strongly dependent on the structural organization of the material, including crystallinity, phase distribution, and interfacial interactions between components [11–13]. Therefore, understanding the relationship between structural parameters and luminescent properties is essential for the design of functional polymer materials with controlled optical responses.

Recent advances in nanocomposite research have demonstrated that structural modifications at both micro- and nanoscale levels can be used to tailor material performance for specific applications [14–17]. Composite materials reinforced with nanoparticles exhibit improved surface properties, mechanical strength, and enhanced interaction between organic and inorganic phases. Furthermore, the use of computational and experimental approaches in materials science has facilitated deeper insights into structure–property relationships in complex polymer systems.

In addition to global research trends, studies conducted in emerging research platforms and regional journals have also contributed to the understanding of composite materials and nanostructured systems [18–20]. These studies emphasize the importance of interdisciplinary approaches combining physics, materials science, and engineering methods for the development of next-generation functional materials.

Despite significant progress in this field, the combined influence of natural biofillers and metallic nanoparticles on the structural and optical properties of LDPE-based composites remains insufficiently explored. In particular, the synergistic effects of fish scale biofillers and iron nanoparticles on crystallinity, structural ordering, and photoluminescence behavior require further investigation.

Therefore, the aim of this study is to investigate the structural and luminescent characteristics of LDPE-based composites modified with fish scale biofillers and iron nanoparticles. Special attention is given to the relationship between composite composition, structural changes, and photoluminescence properties, in order to develop materials with controlled optical responses for advanced functional applications [21–31].

II EXPERIMENTAL METHODS

X-ray phase analysis of the composites was carried out using a URS-501 setup in an RKD-54 chamber at a counter rotation speed of 0.3°/s, a voltage of 25 10^3 V, and a current of 10^{-2} A. Diffraction maxima were recorded using a DUNKER-2D diffractometer with CuKα radiation (λ = 1.54178 Å).

Luminescence characteristics were studied using a Cary Eclipse fluorometer. A pulsed xenon lamp with an equivalent power of up to 75 kW was used as the excitation source. The optical system included a Schwarzschild collector, and spectral decomposition of the radiation was provided by Czerny-Turner monochromators. [10].

Spectra were recorded in both emission and excitation modes. It should be noted that fluorescence spectra are formed as a result of transitions from the lowest excited state, which corresponds to Kashi's law and explains the weak dependence of the spectrum shape on the excitation wavelength [11].

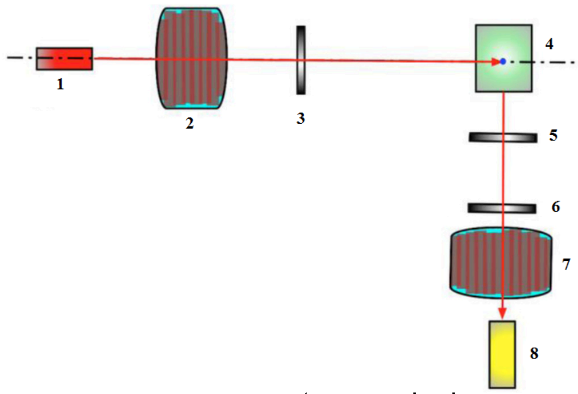
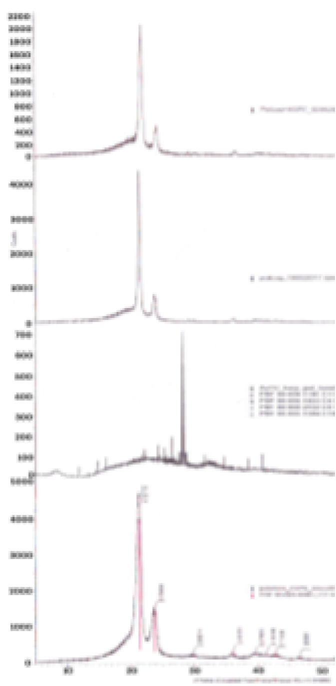


Fig.1 The Cary Eclipse operating principle: 1 - xenon lamp, 2 - monochromator, 3, 6 - lenses, 4 - 1x1 cm socket,
5 - filter, 7 - monochromator, 8 - receiver.

III RESULTS AND DISCUSSION

The structural characteristics of polymer composites are largely determined by their degree of crystallinity and the characteristics of their supramolecular organization [3,12]. X-ray phase analysis showed that the introduction of a biofiller leads to a noticeable modification of the diffraction pattern. With increasing fish scale content in the LDPE matrix, additional reflections appear, as well as changes in the intensity and width of existing peaks. This indicates a redistribution of the crystalline and amorphous phases, as well as the formation of new structural elements in the system. The quantitative assessment of the degree of crystallinity is based on the analysis of the integral intensities of diffraction maxima and the diffuse background, which makes it possible to separate the contribution of the crystalline and amorphous components [13]. Luminescence studies showed that LDPE + x% Fs composites exhibit visible emission with excitation at 342 nm. Samples with 7 vol% Fs exhibit weak peaks in the 420–480 nm range, indicating the presence of localized emission centers. With an increase in ... ol.%, the appearance of ... a (680–730 nm) is ... e associated with the ... y levels and increased ... he introduction of iron ... significant reduction in ... This effect is explained ... bability of nonradiative ... rmation of quenching centers, which is consistent with modern understanding of energy relaxation mechanisms in nanocomposites [9,14]. Thus, the obtained results indicate that changing the composition of composites allows for effective control of their structural and optical characteristics.



a)

б)

Fig. 2 X-ray phase analysis of bionanocomposites LDPE + x об.% Fs, a) x=1%,b) x =3%,
c) x=5%, d) x=7%

The X-ray diffraction patterns of the studied composites reveal characteristic diffraction peaks corresponding to the crystalline phase of LDPE. With increasing biofiller content, not only do the peak intensities change but they also broaden, indicating a decrease in crystallite size and increased structural heterogeneity. The X-ray diffraction patterns of the studied composites reveal characteristic diffraction peaks corresponding to the crystalline phase of LDPE. With increasing biofiller content, not only do the peak intensities change but they also broaden, indicating a decrease in crystallite size and increased structural heterogeneity. It should be noted that the increase in crystallinity with the introduction of filler is associated with limited mobility of macromolecular chains and the formation of a denser packing of segments. At the same time, the observed broadening of the peaks indicates a decrease in the degree of perfection of the crystalline regions. Thus, the biofiller has a dual effect: on the one hand, it initiates crystallization, on the other, it leads to the formation of a defective structure.

Fig. 3 Luminescence spectra of the LDPE biocomposite +7 vol.% Fs (a) and the LDPE bionanocomposite
+7 vol.% Fs +3 vol.% Fe (b)

Analysis of the luminescence spectra shows that the radiative properties of the composites are formed due to localized energy states associated with both the organic matrix and the biofiller. Emission observed in the 420–480 nm range may be related to π–π* and n–π* electron transitions in the organic components of fish scales. The presence of multiple peaks indicates energetic heterogeneity of the system and the existence of various luminescence centers. As the filler concentration increases, new energy levels are formed, manifested by the appearance of long-wavelength maxima (680–730 nm). This may be due to:

- strengthening of interphase interactions,
- formation of charge traps
- increasing the probability of energy transfer between components

The shift of the maxima to the long-wavelength region indicates a decrease in the transition energy and an increase in the degree of delocalization of excited states. The introduction of iron nanoparticles leads to a

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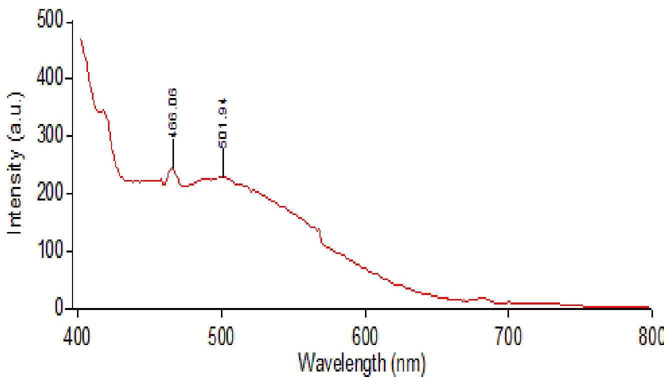

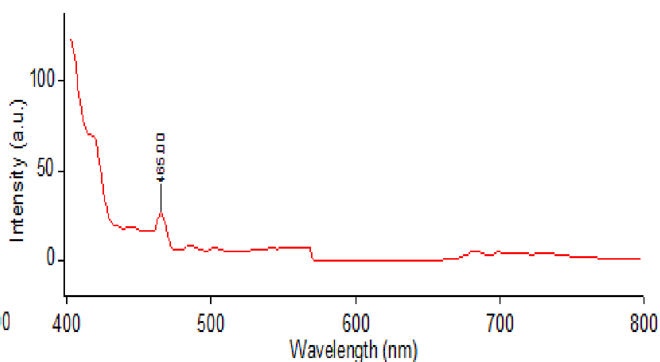

recombination centers or energy acceptors, leading to luminescence quenching. In addition, the presence of metal particles contributes to:

- increasing the probability of energy transfer via the Förster mechanism,
- strengthening of interphase interactions,
- the emergence of additional defective conditions.

As a result, there is a redistribution of excitation energy in favor of non-radiative processes. The observed dependence of the luminescence intensity on the filler concentration is nonlinear, which indicates competition between radiative and non-radiative processes.

IV CONCLUSION

The results demonstrate that the incorporation of a fish scale–based biofiller significantly influences the supramolecular structure of low-density polyethylene. The observed changes indicate a redistribution between crystalline and amorphous phases, as well as the formation of a more ordered structural arrangement. It has been established that the optical properties of the composites, particularly their photoluminescence behavior, are governed by both the composition of the system and the nature of interfacial interactions. Increasing the concentration of the bio-based filler leads to the formation of new energy states and the emergence of additional emission centers. The introduction of iron nanoparticles has a pronounced impact on the relaxation processes of excited states, increasing the probability of non-radiative transitions and consequently reducing luminescence intensity. This effect is associated with the formation of energy transfer pathways and quenching centers within the composite structure.

Overall, controlled variation of composition and structure enables targeted tuning of the structural and optical properties of these materials, highlighting their potential for advanced functional applications

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