



Synthesize the Structural and Optical Properties of Hybrid PMMA Nanocomposites Doped with Metal Oxides for High-performance Coating Applications for Yachts and Boats

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دراسة الخصائص البصرية والتركيبية للمركبات النانوية الهجينة من مادة
PMMA

المطعمة بأكاسيد المعادن لتطبيقات الطلاء عالية الأداء لليخوت والقوارب

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ABSTRACT

Background: The present study conducted a deep analysis of the structural and optical properties of hybrid polymer-based (PMMA) nanocomposites that were reinforced with a synergistic mixture of metal oxides (SiO₂, TiO₂, ZnO). The aim of this study was to develop advanced functional coatings capable of addressing environmental challenges. Moreover, focusing on the improvement of the physical properties of the base material for precision industrial applications.

Materials and Methods: The methodology included preparing thin films nanocomposite films by the use of a casting solution with varying oxide weight percentages. The work relied on advanced optical measurements, particularly diffuse reflectance and absorption spectroscopy, in order to obtain an accurate determination for the refractive index and optical bandgap of the prepared films.

Results: The results revealed that the incorporation of the hybrid oxides resulted in a substantial enhancement of light stability and UV shielding efficiency in comparison to the pure polymer. The measurements also approved the maintenance of a suitable level of optical transparency, demonstrating a homogeneous distribution of nanoparticles within the polymer matrix and a considerable improvement in specific optical properties.

Conclusion: The work showed that the prepared nanocomposite revealed a superior protection for yacht and boat surfaces against photocorrosion and harsh marine environmental conditions. Such results denote a significant step towards the production of high-performance functional coatings that combine protective efficiency with optical transparency. This could make them an ideal choice for modern marine applications.

Key words: PMMA; Hybrid Nanocomposites; Optical Band Gap; Structural Properties; Marine Coatings; UV-Shielding.



INTRODUCTION

Recently, studying surfaces in marine applications, has become essential to extending the operational lifespan of boats and yachts. As such structures face complex environmental challenges including heat, corrosion from seawater salinity and continuous exposure to ultraviolet (UV) radiation, which causes photodegradation, that may lead to the breakdown of polymer chains and loss of durability and gloss [1],[2]. Therefore, in this context, polymethyl methacrylate (PMMA) has been selected as one of the most important polymers that can be used as protective coatings due to its outstanding properties. The most advantages of PMMA are the high transparency that exceeds 90% of the visible spectrum, ease of synthesis and its relative chemical stability[3]. However, PMMA is fragility and poor resistance to UV radiation over extended periods make the addition of nanomaterials a pressing technological necessity to improve its properties. Therefore; doped nanocomposites that combine metal oxides with polymers offer a suitable solution to these challenges. The addition of titanium dioxide (TiO_2) and zinc oxide (ZnO) to the coating provides a high capacity for blocking ultraviolet radiation where these oxides act as semiconductors with a wide energy gap (approximately 3.2 3.37 eV), enabling them to absorb and scatter high-energy radiation before it penetrates the inner layers of the coating [4]. Additionally, titanium dioxide possesses a self-cleaning property owing to its photocatalytic activity, which helps reduce the accumulation of organic impurities on yacht surfaces [5],[6]. On the other hand, silicon dioxide (SiO_2) shows a substantial role in the development of the structural integrity of boats. It has been found that silica nanoparticles contribute to improved scratch resistance and also increased surface hardness while preserving the essential optical properties of the material. This effect is largely attributed to their refractive index being close to that of polymethyl methacrylate (PMMA), which helps to minimize or even block random light scattering that could otherwise compromise the aesthetic appearance of yachts [7],[8]. The current study aims to investigate the effects of incorporating nano-oxides ($\text{SiO}_2/\text{TiO}_2/\text{ZnO}$) on the optical properties of PMMA composites. This work has a particular emphasis that is placed on evaluating key optical parameters, including energy gap and refractive index, with an investigation of their relationship with the coating's effectiveness in improving marine surface protection. The results obtained from this research are predictable to contribute to a scientific database that supports the development of advanced coatings capable of withstanding changing marine environments [9],[10].

MATERIALS AND METHODS

• Material Preparation and Characterization

In this section, the fabrication of thin films from composite nanomaterials will be illustrated. Solution-casting was used to distribute specific weight ratios of (20-50 nm) SiO_2 , TiO_2 , and ZnO nanoparticles in a (2%) PMMA matrix dissolved in chloroform. Then, the mixture was exposed to ultrasonic treatment for a period of 90 minutes to certify a uniform nanoparticle distribution and prevent agglomeration. After that the resulting films were deposited in glass containers and then analyzed using UV-Vis diffraction spectroscopy in order to determine the refractive index (n) and experimental energy gap across the visible spectrum (400-700) nm. The resulting values are tabled below:

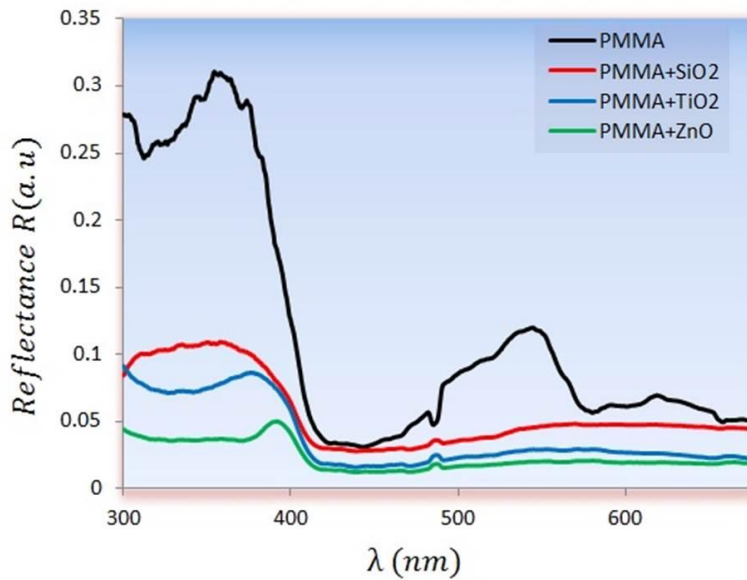


Figure (1): Diffuse reflection represents the samples used and the wavelengths between (300-700) nm.

The current results are consistent with recent studies on the effect of metallic nanoparticles on the optical properties of polymers. indicated that the introduction of metal oxides with high refractive indices leads to a decrease in reflectivity and an increase in absorption in the UV region due to enhanced omnidirectional scattering [11]. demonstrated that ZnO and TiO₂ particles impart enhanced UV-blocking capabilities to polymer composites due to their energy gap matching the UV band, which explains the greater decrease in reflectivity observed in this study compared to SiO₂ with its wider energy gap [12].confirmed that the modification of the optical response in inorganic-organic hybrid systems is directly related to the nanoload ratio and the quality of dispersion within the polymer matrix, with a homogeneous particle distribution resulting in a more stable spectral response and improved optical performance. Therefore, the current results are consistent with the theoretical and experimental framework adopted in the literature on polymer nanomaterials [13]. Using equation number 1, the refractive index of the samples and the wavelengths between them were found (300-700) nm.

$$n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}} \dots \dots \dots (1)$$

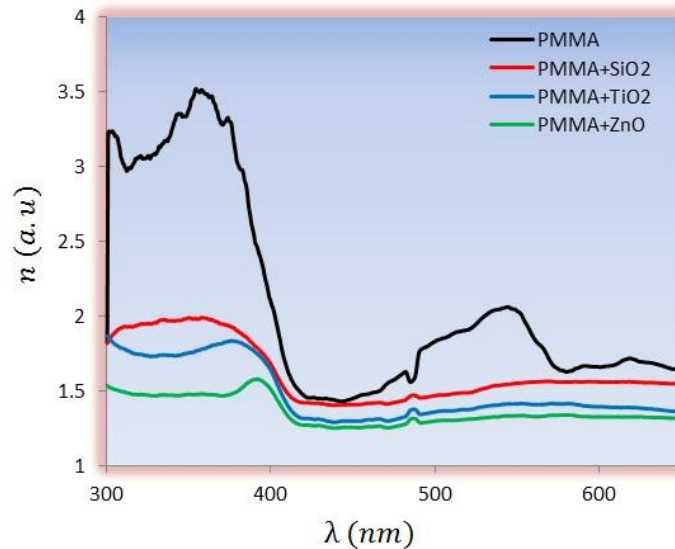


Figure (2): represents the refractive index of the samples used and the wavelengths between (300-700) nm.

Figure (2) shows the change in refractive index (n) as a function of wavelength (λ) in the spectral range (300 650 nm) for pure PMMA samples and for nanocomposites prepared by adding nano-oxides (SiO_2 , TiO_2 , ZnO). Generally, all prepared samples demonstrate clear optical scattering behavior, with the refractive index gradually decreasing with increasing wavelength. Such behavior is reliable with the classical optical scattering models such as the Cauchy and Sellmeier models that describe the wavelength dependence of the refractive index owing to the interaction between electrons bound in the material and electromagnetic radiation [14]. The pure PMMA sample presents the highest refractive index values in the near-UV region and reaches reasonably high values at short wavelengths (300 – 350) nm, then decreasing significantly towards the visible region. Such performance is attributed to the increased probability of electron transitions at high energies which leads to increased electron polarization of the material and consequently a higher refractive index. For the longer wavelengths, the energy of the photons decreases, leading to a decrease in the electronic response and a lower refractive index. It has been found that when nanoparticles such as SiO_2 , ZnO and TiO_2 were added to a PMMA matrix, a relative decrease in refractive index values is observed in the comparison to the pure sample, with slight variations between different composites. This can be explained by the introduction of nanoparticles modifying the effective optical density of the composite material, as well as a change in electronic polarization resulting from the interaction between the polymer matrix and the nanoparticles. Furthermore, the scattering caused by the nanoparticles and their distribution within the polymer matrix may reduce the effective refractive index of the optical system. A relatively sharp decrease is observed in all samples near a wavelength of 400 nm, which may be related to the optical absorption edge of the composite materials, where electronic transitions occur between the valence and conduction bands. Beyond this region, the refractive index gradually stabilizes in the visible region, a common behavior in transparent polymer materials. In general, the results indicate that adding nano-oxides to PMMA modifies the optical properties of the composite, making these materials candidates for use in various optical applications such as protective coatings, optical components, and photonic sensors, where the optical properties can be controlled by the type and concentration of nanoparticles added [15].

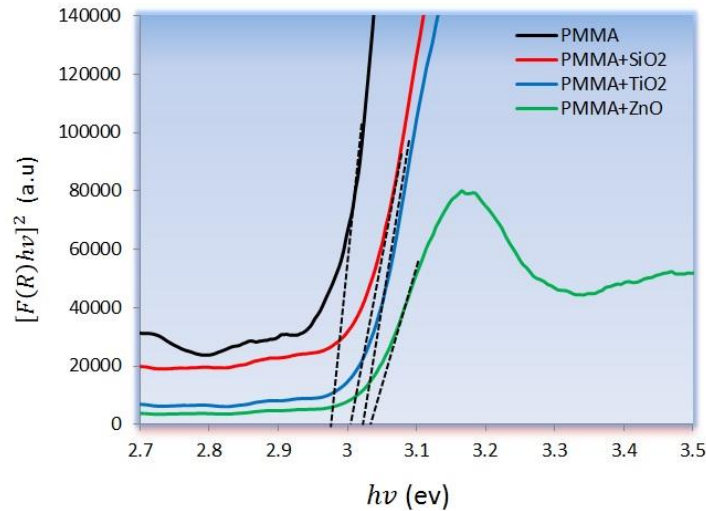


Figure (3): Represents the energy gap of the samples of polymer PMMA with added oxides (SiO_2 , TiO_2 and ZnO).

The figure shows the relationship between the photon energy ($h\nu$) in electron volts and the optical function $[F(R)h\nu]^2$, a representation based on the Kubelka–Munk theory for determining the optical band gap of the direct electron transition materials. The linear extension of the curves near the absorption edge and their projection onto the energy axis allow for the determination of the band gap (E_g) for the studied samples. The results are compared between pure PMMA polymer and polymer composites reinforced with SiO_2 , TiO_2 , and ZnO nanoparticles. From the figure, it can be noticed that pure PMMA polymer has an absorption edge located at relatively higher energies. This indicates a larger band gap compared to the composite samples. Results reveal that adding nanoparticles to the polymer matrix showed a clear change occurring in the position of the absorption edge, which tends to shift towards lower energies, indicating a relative decrease in the material's effective energy gap. Such behavior is certified to the emergence of localized energy levels within the energy gap that results from the interaction between the polymer's electronic structure and nanoparticles which leads to an increased probability of electrons transitioning from the valence band to the conduction band [16],[17]. Furthermore, the addition of TiO_2 and ZnO as nanoparticle metal oxides leads to a substantial increase in the intensity of the optical response near the absorption edge because oxides, possess high refractive indices and wide energy gaps in the range of 3.2 to 3.3 eV and granting them a high capacity for absorbing or scattering ultraviolet radiation. When these particles are distributed within the polymer matrix, they act as capable centers for interacting with electromagnetic radiation, hence improving the optical properties of the polymer composite [18],[19]. Values of the achieved energy gap for entirely samples under examination are presented in Table (2).



Table 2: shows the energy gap values for all prepared samples.

NO.	Sample	Eg (eV)
1	PMMA 100%	3.00
2	PMMA + 2% SiO ₂	3.04
3	PMMA + 2% TiO ₂	3.07
4	PMMA + 2% ZnO	3.10

These outcomes have substantial practical applications in the field of advanced marine coatings for boats and yachts. For polymer materials, the marine environment is one of the toughest environments due to constant exposure to ultraviolet radiation, salinity and humidity, leading to the degradation of polymer chains and the loss of the coating's mechanical and surface properties. Therefore, incorporating nanoparticles such as ZnO and TiO₂ into polymers contributes to the formation of protective coatings capable of absorbing ultraviolet radiation and preventing its penetration into the inner layers, hence reducing photodegradation and increasing the coating's service life [20]. Additionally, the reports indicate that polymer coatings reinforced with nanoparticles not only act as a barrier against ultraviolet radiation but also contribute to improved mechanical properties, corrosion resistance and chemical stability in severe marine environments. This makes nanopolymer composites a promising option for developing smart marine coatings accustomed to protecting boat and yacht hulls from environmental and radiological degradation, while preserving their aesthetic and optical qualities over broadened periods [21].

CONCLUSIONS:

In current work, it has been found that the optical properties of PMMA-based nanocomposites reinforced with metal oxide nanoparticles (TiO₂, SiO₂ and ZnO) were systematically examined using diffuse reflectance spectroscopy and Kubelka–Munk theory analysis. The achieved results exhibit that incorporating metal oxide nanoparticles into the PMMA matrix considerably modifies the optical response of the polymeric system. The achieved results of Kubelka–Munk theory plots showed obvious variations in the optical band gap energy of the prepared nanocomposites compared with pure PMMA. The addition of oxide nanoparticles causes a shift in the absorption edge toward lower photon energies signifying a reduction in the effective optical band gap. This can be attributed to the formation of localized energy states within the band structure that results from the interaction between the dispersed nanoparticles and the polymer chains. This can enhance the possibility of electronic transitions between the valence and conduction bands. Moreover, the presence of TiO₂ and ZnO nanoparticles contributed to a pronounced advance in the optical absorption within the near-UV region. This behavior is associated with the high refractive index and wide intrinsic band gap of these semiconductor oxides giving them the ability to act as efficient UV-absorbing centers within the polymer matrix. Therefore, the incorporation of these nanoparticles improves the UV-shielding capability of the composite material plus develops its optical stability when it is exposed to high-energy radiation. From an application point of



view, these findings underline the potential of PMMA/oxide nanocomposites as advanced functional coatings for marine structures such as boats and yachts, as marine coatings are continuously exposed to severe environmental conditions including saline corrosion, moisture and ultraviolet radiation. Consequently, the reduction in the band gap observed and the optical absorption improvements in the developed nanocomposites denote their ability to effectively absorb and dissipate harmful UV radiation. This could be helpful in the protecting of the underlying materials from photodegradation as well as increasing the coating systems' operational lifetime. Generally, the results confirm that incorporating metal oxide nanoparticles into polymeric matrices signifies a promising strategy for developing next-generation marine protective coatings with enhanced environmental durability, optical stability and long-term performance.

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Future Work:

In order to develop a coating, some methods can be examined:

- 1- Different concentrations of the same nanomaterials with a results comparison can be assessed.
- 2- Mixing silicon dioxide nanomaterials with titanium dioxide and make a comparison with previous findings.
- 3- Mixing silicon dioxide nanomaterials with zinc oxide and evaluate results with previous results.

Conflict of interests.

There are non-conflicts of interest.

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