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RESEARCH PAPER

Enhancement of Structural and Optical Properties of Poly (Vinyl Chloride) Films via Metals Nanoparticle

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ABSTRACT

This study focuses on the practical investigation of the structural and optical properties of (PVC-Cu) and (PVC-Al) nanocomposites, which were fabricated by Solution Casting Method at different weight concentrations including (2%, 4%, 6%, and 8%). The prepared films were characterized using XRD, FT-IR, and SEM techniques, along with an investigation of their optical properties within the spectral range of 200–1100 nm. The structural formula was confirmed by FT-IR spectra, which showed distinct absorption bands for the functional group bonds (C–Cl, C–H, C=C, O–H, C–I). The study demonstrated that reinforcing a PVC matrix with metallic nanoparticles (Cu, Al) results in a significant change in optical behaviour, characterized by increased absorbance and decreased transmittance as the addition ratios increase, along with accurate estimation of direct and indirect energy gaps. This study presents a comparative evaluation of the photocatalytic degradation processes of PVC films before and after doping with nanometals, under different irradiation conditions including ultraviolet (UV) radiation, to investigate the extent of improvement in the degradation response of the films. The study was enhanced by analyzing the surface morphology and chemical composition of the films using SEM and FT-IR techniques. The variable optical response resulting from copper and aluminium doping indicates the potential for engineering metallic nanoparticles and tailoring their properties to meet the requirements of specific practical applications.

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INTRODUCTION

Recently, numerous studies have been conducted on polymers doped with nanoparticles metal oxide as advanced alternatives for use in optical applications, including planar waveguides and optical micro-elements. [1]. The integration of nanoparticles within the polymer matrix enhances its optical, mechanical and electrical properties; as well as the ability to precisely control these properties (most notably the refractive index) by adjusting the concentration and sizes of those particles [2]. The physical properties of these nanofillers are not identical to their counterparts in the bulk state, and the resulting nanocomposites acquire unique properties that differ radically from the properties of their constituent materials. [3]. Intensive research efforts continue in the field of nanocomposites to enhance their suitability

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for various technological applications. This is achieved through diversifying filler materials, modifying preparation methods, optimizing filler quantities, and controlling the geometric and physical properties of the particles, such as size, shape, spatial orientation, and the quality of their interfacial bonding with the substrate (matrix) [4,5]. Integrating inorganic nanoparticles into the polymer matrix allows for efficient modification of its physical properties, as well as giving it new functional features that expand its range of applications [6,7]. With the rapid development of nanotechnology, it has become possible to produce a new generation of copper-based nanoparticles (CNP) that have shown antimicrobial (biocideic) properties, although there are few studies published in this field so far. [8].

Polyvinyl chloride (PVC) is considered one of the most widely used thermoplastics versatile plastic polymers in use, and it ranks second globally in terms of plastic resin production volume. [9,10]. The process of modifying polyvinyl chloride (PVC) is based primarily on dechlorination reactions, which include substitution and elimination mechanisms; and given the connection between the material's properties and its practical applications, the chemical function of PVC represents a sustainable approach to improving and developing the polymer's properties. [11].

Photodegradation of plastic polymers has recently garnered increasing research interest. Nanocomposites composed of plastic matrices and titanium dioxide (TiO_2) nanoparticles have demonstrated high efficiency as a novel technique for breaking down solid polymers under open atmospheric conditions. In this context, numerous scientific investigations have focused on studying the photodegradation mechanisms of polyvinyl

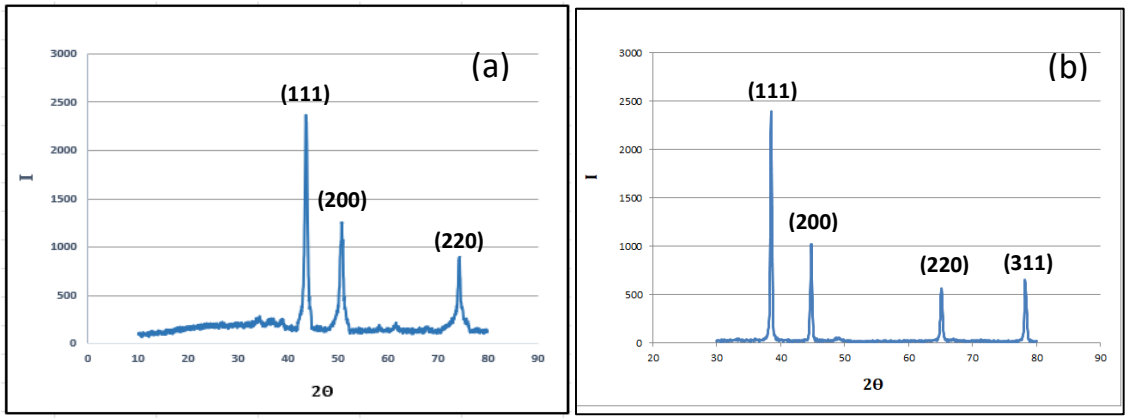

Fig. 1. XRD- patterns: (a) Cu NPs, (b) Al NPs.

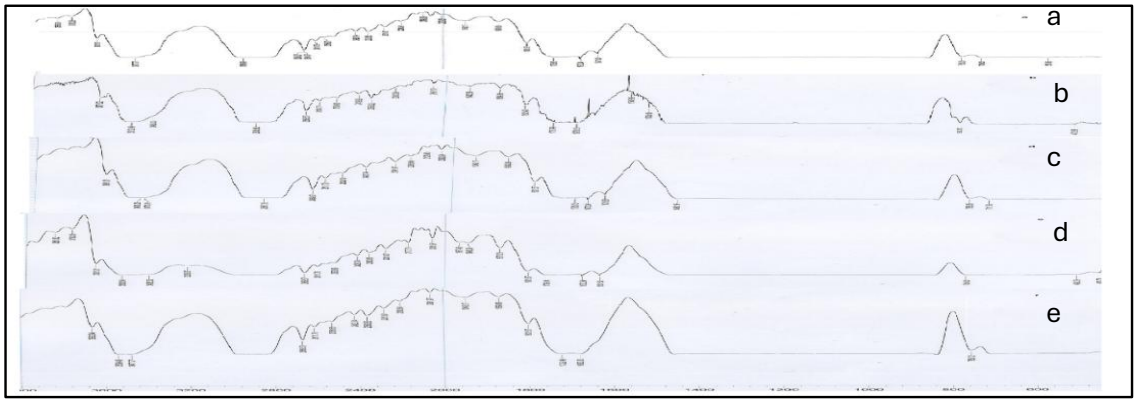

Fig. 2. (FT-IR) spectra of PVC and (PVC-Cu): (a) 0% (b) 2% (c) 4% (d) 6% (e) 8%.

chloride (PVC), polyethylene (PE) and polystyrene (PS) [12]. PVC/ZnS nanocomposites containing low concentrations of ZnS and subjected to gamma irradiation are considered suitable for use in optoelectronic devices. Thus, the significance of studying these nanocomposites lies in reducing economic costs and minimizing manufacturing challenges [13].

MATERIALS AND METHODS

At room temperature (5) g of (PVC) powder is dissolved in cyclohexanone solvent in a glass beaker using a magnetic stirrer under constant stirring. Different weight fractions of copper (Cu) and aluminium (Al) nanoparticles (0, 2, 4, 6, and 8 wt%) were added by dissolving them according to the steps described previously to prepare multiple samples. The samples were then placed in Petri dishes and allowed to dry for more than 14 days to ensure complete removal of any solvent residue. Thin films of the (PVC) were prepared using the casting method with a thickness of 0.1 mm. Finally, the optical absorption and transmission spectra of the nanocomposites (PVC-Cu) and (PVC-Al) were recorded Within the spectral range (200–1100 nm) using a computer-connected UV-Vis spectrophotometer.

RESULTS AND DISCUSSION

XRD Analysis

To study the structural properties of crystalline materials, the crystalline structure was characterized by recording the diffraction intensity as a function of Bragg's angle. The examination was performed using a copper cathode X-ray tube (Cu target) emitting radiation with a wavelength of 1.5406 Å (representing the transition line Kα), at a current of 30 mA and a potential of 40 kV. The diffraction angles survey (2θ) covered the range from 20 to 80 degrees, with a time-lapse scan rate of 4 degrees per minute. The results show a variation in nanoparticles size; the measurements recorded an average particle diameter of (58 nm) for the copper nanoparticles doped in the prepared (PVC) films, while Al was 40 nm to range. XRD Patterns of both copper and aluminium nanoparticles (Cu & Al NPs) are shown in Figs. 1a and 1b.

FT-IR Spectroscopy

(FT-IR) spectra were recorded for undoped and nanoparticle-doped polyvinyl chloride (PVC) films in the wavelength range from 400 cm^{-1} to 4000 cm^{-1}. Fig. 2a shows the (FT-IR) spectrum of the pure PVC films before copper doping (Cu), where the spectrum exhibits characteristic absorption peaks of the long polymer chains at wavenumbers 1869.08 cm^{-1}, 1942.38 cm^{-1}, 2061.97 cm^{-1}, and 3855.83 cm^{-1}. Figs. 2b-e highlight the spectral changes of (PVC) composites when doped with different weight percentages of copper (2, 4, 6, 8) %wt respectively. The spectra showed new absorption peaks for composite films within the extended range in the region.1750.57 cm^{-1}, 1672.34 cm^{-1},1548.8 cm^{-1}, 1506.46 cm^{-1}, 1460.18 cm^{-1},750.33 cm^{-1},717.76 cm^{-1}, 493.79cm^{-1}, 472.58 cm^{-1} and 439.76 cm^{-1}, which are attributed to the stretching vibrations of the covalent bonds (C=O, C=C, C–O, C–H, C–Cl and C–I) respectively. [14]. The absorption peak observed within the spectral range (2800–3000) cm^{-1} of pure (PVC) samples is attributed to the symmetric and asymmetric stretching modes of the carbon-hydrogen bonds (C–H) in the methylene groups (CH_2) [15].

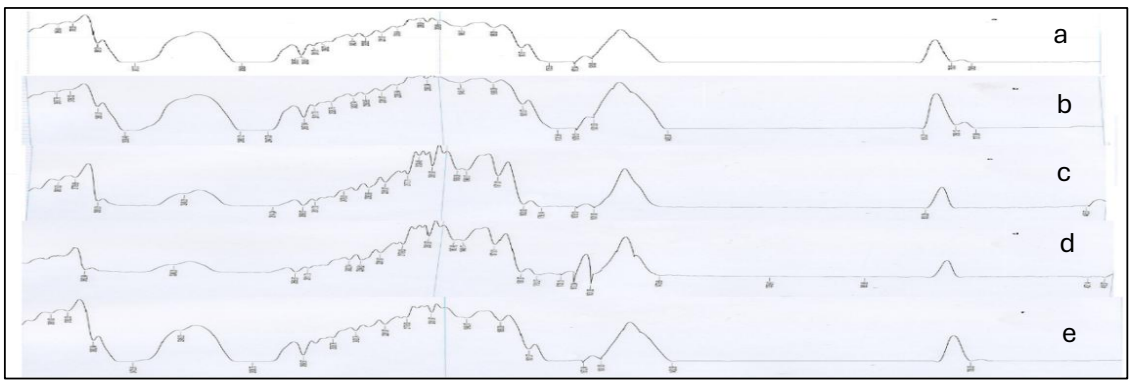

Fig. 3. (FT-IR) spectra of PVC and (PVC-Al): (a) 0% (b) 2% (c) 4% (d) 6% (e) 8%.

It was observed that with increasing dopant concentration, the band widths increased and the absorption intensity decreased in the PVC matrix. The absorption peak within the range of 3610-3855 cm^{-1} related to the bond stretching frequency (O-H) indicative of the presence of residual hydroxyl groups from the cyclohexanone solvent—almost completely disappeared in the doped films. This behavior is attributed to the process of ion exchange of basic cations (Basal Cations) coupled with the release or loss of structurally condensed water molecules. [16]. The disappearance of the absorption bands observed in the spectrum of pure films upon doping with single copper ions (Cu^{+}) is attributed to the assumption of a complex correlation/bonding between the (Cu^{+}) ions and the chlorine atoms within the PVC polymer matrix. [17]. The strong absorption band observed within the range (500 - 400 cm^{-1}) is attributed to the vibrational mode of the bond stretching (Cu–O). This result shows good agreement with values documented in previous literature and studies [18,19].

(FT-IR) spectroscopy results shown in Fig. 3a illustrate the absorption spectra of the purified (PVC) films and Fig. 3b-e after PVC-Al doped with different concentrations. Spectral analyses showed the emergence of new absorption peaks in the spectra of composite films centered in the spectral range 1803.50 cm^{-1},1672.34 cm^{-1},1473.66 cm^{-1},1456.30 cm^{-1},1209.41cm^{-1}, 955.66 cm^{-1},836.21cm^{-1}, 707.90 cm^{-1}, 418.57 cm^{-1} which could be assigned to C=O, C=N, N-H, N-O, C–O, C–H, C-I stretching vibrations respectively. Stretching frequency and indicates of (acid chlorides, amines, amides, and alkyl halides) groups; A small spectral shift is also observed at all characteristic peak positions, which is explained by the change in bond lengths. These structural changes indicate the possible attachment of aluminium ions (Al^{3+}) to hydroxyl groups (O–H) present in the side chains of the polymer molecules (PVC) [20].

(FT-IR) spectroscopy results shown in Fig. 4a illustrate the absorption spectra of pure (PVC) films before they are subjected to (UV) irradiation, (FT-IR) spectroscopy results shown in Fig. 4b illustrate the spectral changes of pure (PVC) films after exposure to (UV) irradiation, (FT-IR) results shown in Figs. 4c-e illustrate the absorption spectra of (PVC) films with (6) wt% of (Cu, Al) doped after UV irradiation. Spectral analyses showed the emergence of new absorption peaks in the spectra of nanocomposite films, centered in the spectral range(1871.01 cm^{-1}, 1797,72 cm^{-1}, 1755.28 cm^{-1}, 1626.05cm^{-1}, 1579.75 cm^{-1}, 1531.53 cm^{-1}, 1456.30 cm^{-1}, 835.21 cm^{-1}, 748,4cm^{-1},570,95 cm^{-1},491.86 cm^{-1},418.57cm^{-1}) which can be assigned to the stretching vibration patterns of the following chemical bonds: C=O, C=C, C–O, C-C, C-Cl, N-O, and C-I respectively [21] combined with the broadening of spectral bands and the decrease in absorption intensity of these bands in (PVC) composite films following ultraviolet irradiation.

The exposure of pure PVC and composite films to (UV) irradiation results to degradation. The mechanism's reaction of pure (PVC) films under (UV) irradiation involves direct absorption of (UV) photons by the macromolecules of polymer (PVC), which transports them to excited states. This excitement induces chain scission, branching, and crosslinking processes within the polymer chains, as well as a series of oxidation reactions

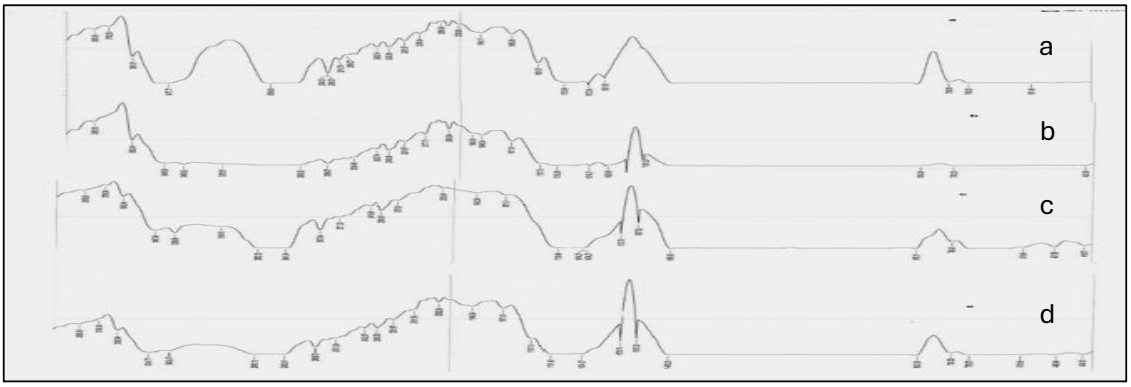

Fig. 4. (FT-IR) spectra of PVC films and doped films after UV irradiation (a), (b) PVC before and after UV irradiation (c) (PVC-Cu) film (d) (PVC-Al) film.

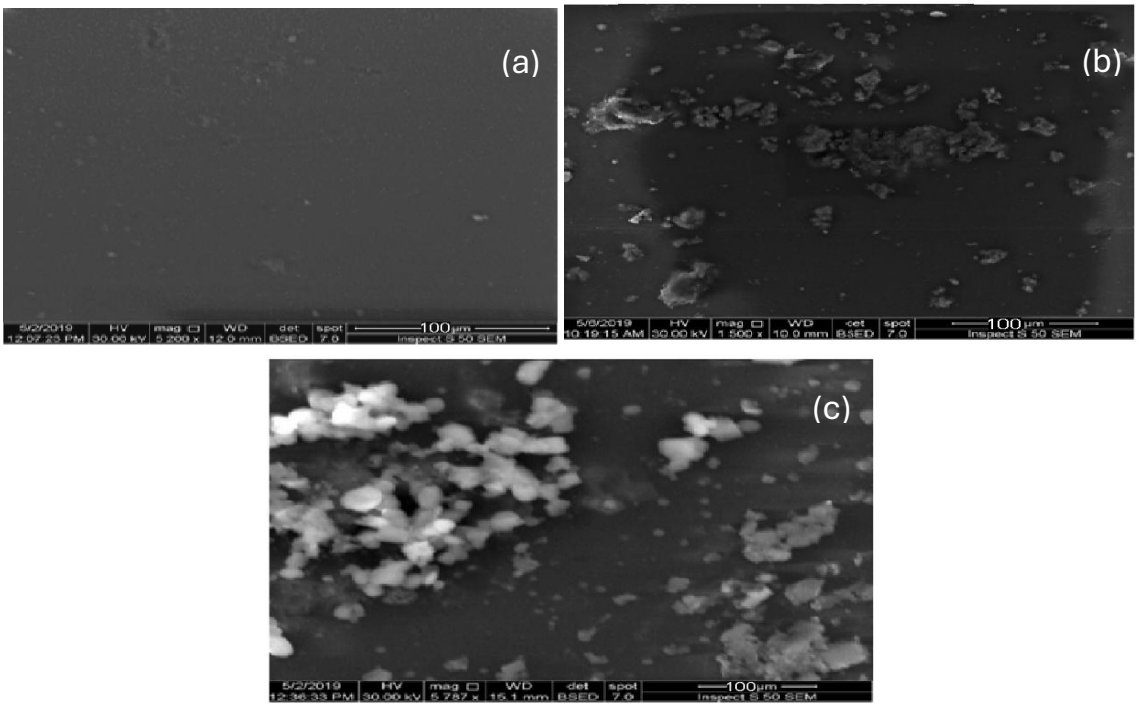

Fig. 5. SEM images of (a) PVC film (b) (PVC-Cu) film (c) (PVC-Al) film.

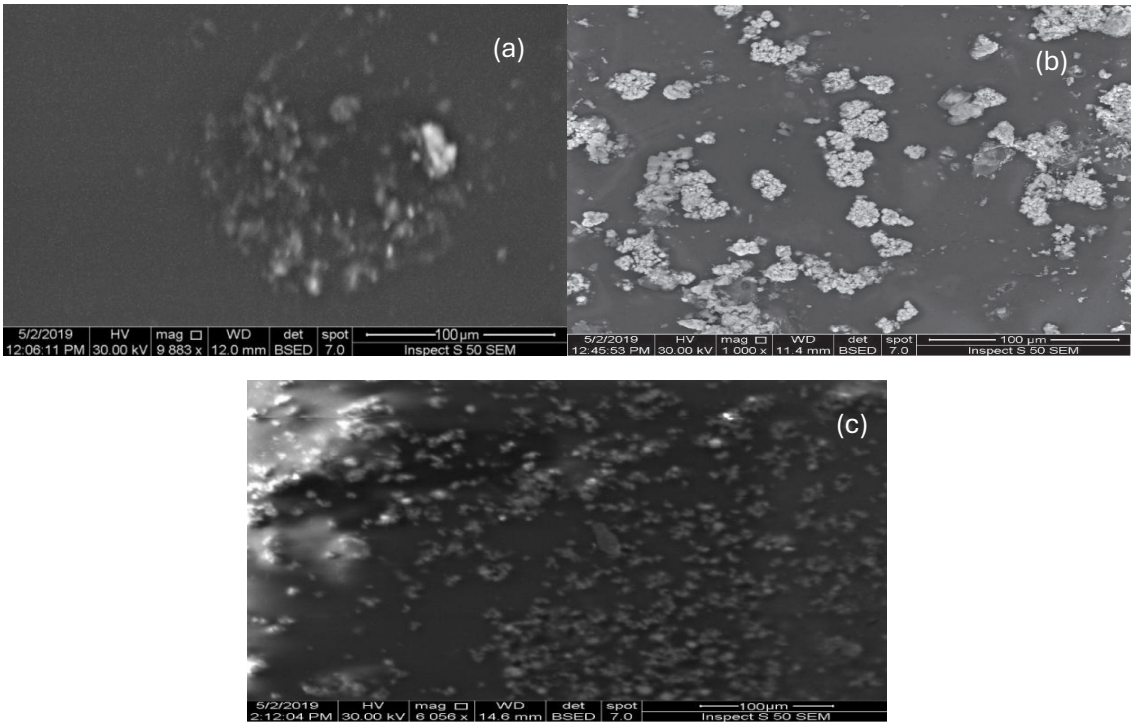

Fig. 6. SEM images of (a) PVC film under UV (b) (PVC-Cu) under UV (c) (PVC-Al) under UV.

[22]. Photocatalytic degradation is the central reaction in composite films, a process that differs radically from the photolytic degradation pathway of pure PVC films. The sequential reaction in composites leads to chain scission coupled with oxygen incorporation, resulting in the formation of intermediates rich in carbonyl and carboxyl groups. These intermediates then undergo advanced photocatalytic oxidation, ultimately being converted to carbon dioxide (CO_2) and water (H_2O) by the active role of reactive oxygen species (ROS) [23].

SEM Analysis

(SEM) images of the surface morphology of the nanocomposite films show granular groups and spherical particle aggregates that are randomly distributed and densely extended over the surface of the films. The image shown in Fig. 5a illustrate the surface morphology purified (PVC) film, (SEM) images shown in Figs. 5b and 5c illustrate the surface morphology and structural distribution (PVC) films doped with (Cu) and (Al) nanoparticles, respectively. Morphological observations of the sample surfaces showed a structural shift towards a hexagonal shape, coupled with crystalline growth on the surfaces of the polymer films following drying and the occurrence of a photo-crosslinking reaction; where increasing the concentration of the grafting material within the (PVC) matrix

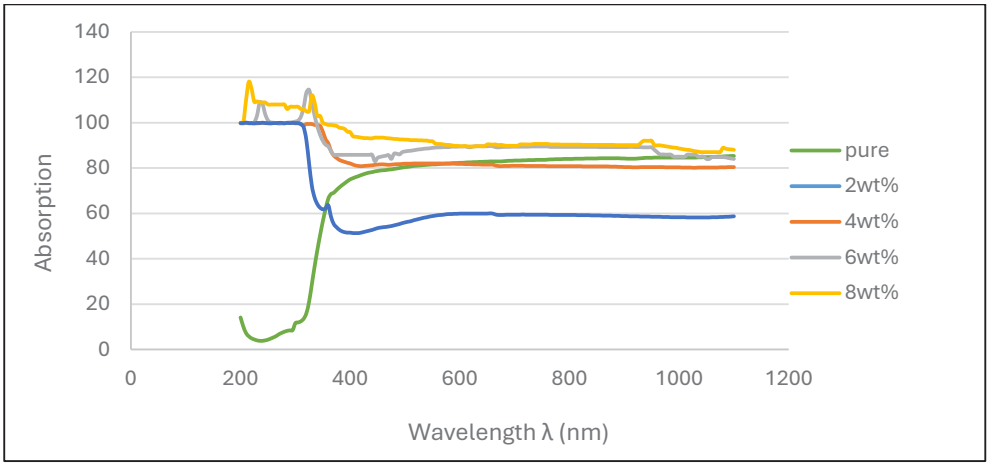

Fig. 7. Absorption of pure PVC and (PVC-Cu) films.

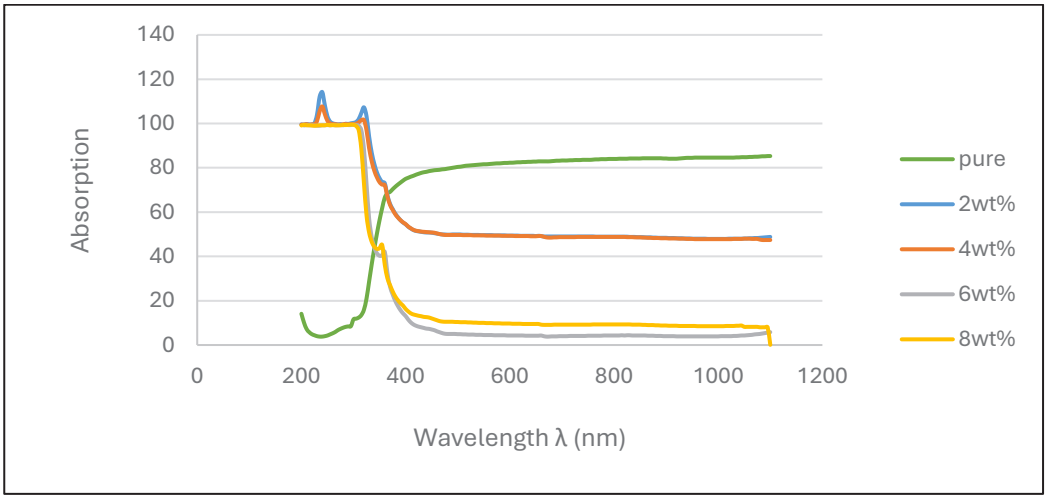

Fig. 8. Absorption of pure PVC and (PVC-Al) films.

significantly enhances the polymer's stability. [24].

Fig. 6a shows that the surface topography of pure (PVC) films was characterized by smoothness and glossiness under UV irradiation. In contrast, SEM images in Figs. 6b and 6c show the surface structure of copper (Cu) and aluminium (Al) doped (PVC) films after photo-exposure, respectively. Microscopic observations revealed the formation of randomly distributed microcavities across the surface; these surface cavities formation is attributed to the volatilization and emission of vinegary volatile products associated with the photo-degradation of the polymer matrix. [19]. The emission and formation of cavities on the surfaces of (PVC) composite films are observed at a higher rate compared to pure PVC films. This morphological phenomenon implies that generated the active oxygen species (ROS) on the surface have permeated and diffused within the (PVC) matrix, resulting in its structural degradation.

Optical Analysis

The optical absorption and transmittance spectra of pure and nanoparticle-doped) PVC films

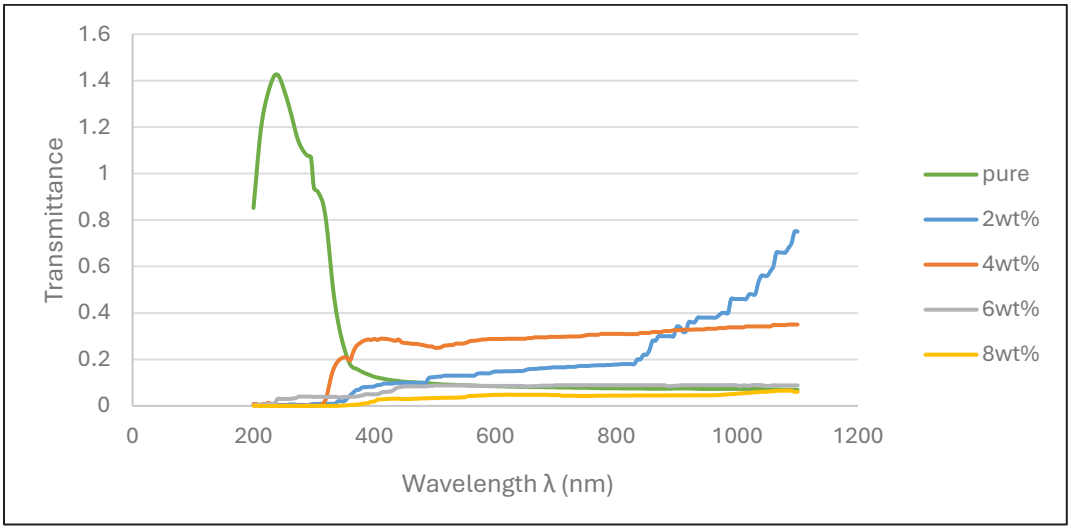

Fig. 9. Transmittance of pure PVC and (PVC-Cu) films.

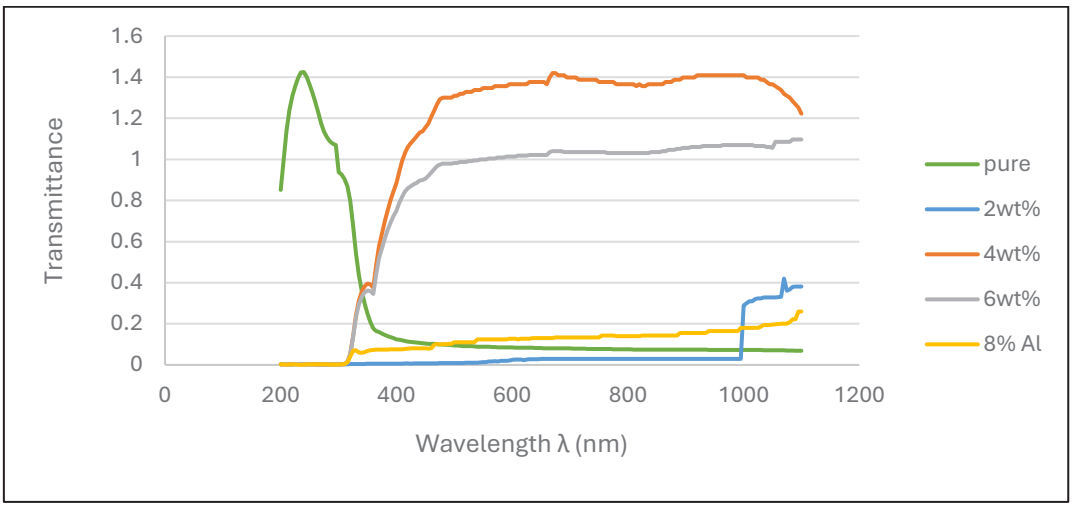

Fig. 10. Transmittance of pure PVC and (PVC-Al) films

were performed using (UV-Vis-NIR) spectroscopy in the wavelength range of 200 to1100 nm, as shown in Figs. 7 and 8. The spectral curves show that the absorbance is highest for all films near the fundamental absorption edge at 200 nm, with a marked increase in intensity as the doping concentration increases. This is followed by a spectral response in which the absorbance gradually decreases with increasing wavelength, consistent with Beer-Lambert's Law [25,26], the optical absorption mechanism involves electron excitation and transition from lower to higher energy levels as a result of absorbing incident photons; this spectral behavior is an indication of a chemical/physical interaction between the polymer matrix (PVC) and the nanoparticles.

Figs. 9 and 10 show that the optical transmission spectra show an upward trend with increasing wavelength, while the transmission values decrease steadily with increasing doping concentration in the (PVC-Cu) and (PVC-Al) nanocomposites. This spectral behavior is

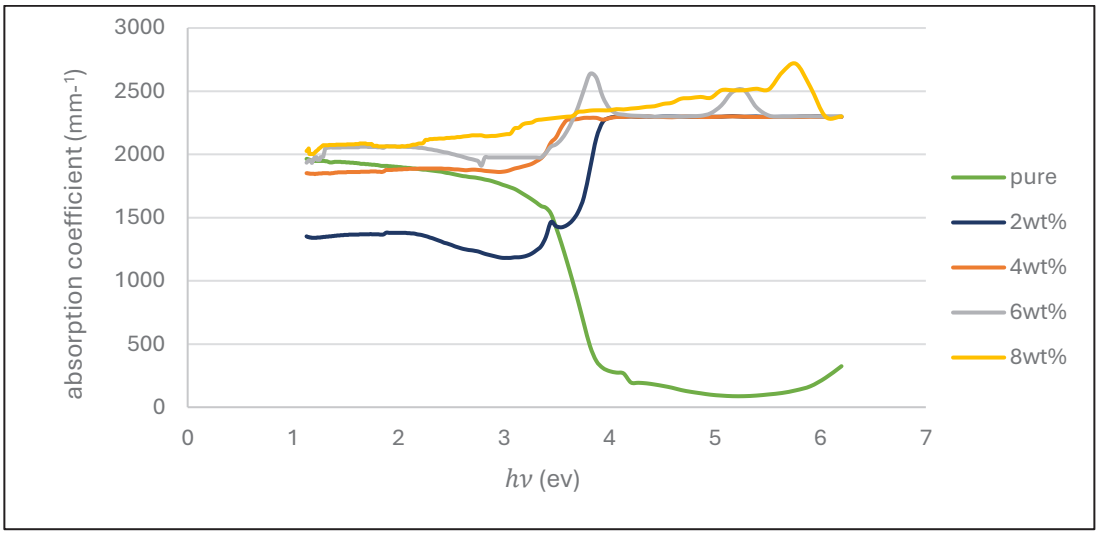

Fig. 11. Relationship between (α) vs. (hv) of PVC and (PVC-Cu) films.

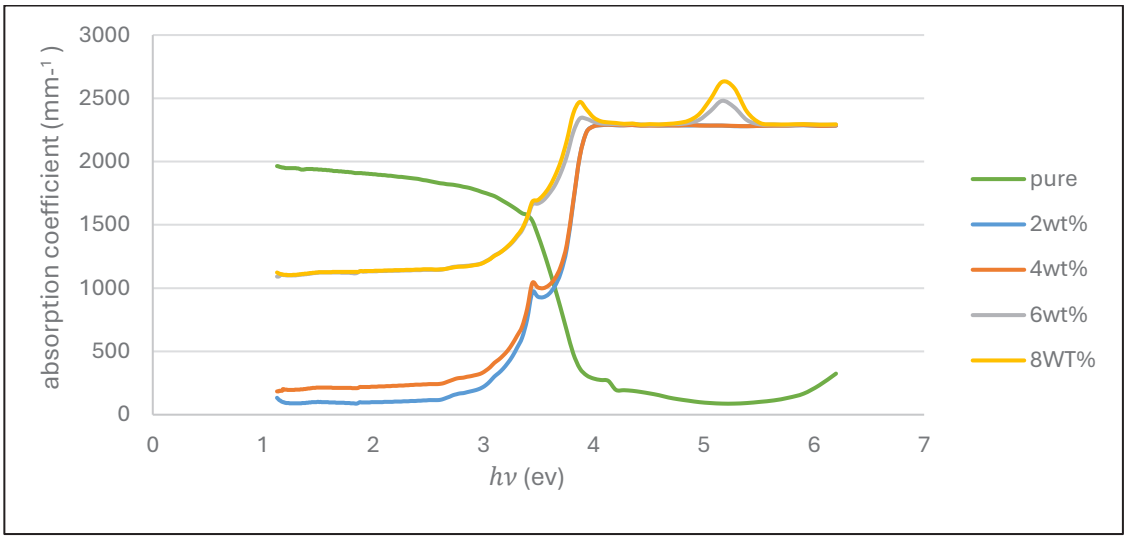

Fig. 12. Relationship between (α) vs. (hv) of PVC and (PVC-Al) films.

attributed to the fact that increasing the doping ratio leads to a higher density of localized states within the band gap, which in turn reduces the optical transmission [26,27].

Figs. 11 and 12 illustrate the graphical relationship between the optical absorption coefficient (α) and the incident photon energy (hv) of pure and doped (PVC) nanofilms. Calculating the optical absorption coefficient helps determine the mechanism and physicochemical nature of the electronic transitions occurring between between the filled valence band and the empty conduction band of the polymer; is the fewer at high wavelength and low energy when the values of absorption coefficient is low ($\alpha < 10^4 cm^{-1}$) in this case indirect electronic transitions [28]. The optical absorption coefficient (α) can be expressed mathematically and its value determined based on the Beer-Lambert law. [29]:

$$\alpha = 2{\cdot}303A/t \quad (1)$$

where A: the Optical absorbance of the film (unit-free) and t: the thickness of the polymer film is measured in units (cm).

CONCLUSION

The results indicate that:

Copper (Cu) and aluminium (Al)-based nanofillers show a clear effect when incorporated into a polyvinyl chloride (PVC) matrix; this grafting resulted in improved and enhanced physical properties of the composite, particularly its response and optical properties.

The incorporation of nanoparticles results in a significant decrease in optical transmittance and a corresponding increase in absorbance values for PVC films across various wavelength ranges, particularly in the UV-Vis region. This spectral response is attributed to the intrinsic properties of nanoparticles, namely the mechanisms of optical scattering and absorption.

The values of the optical absorption coefficient (α) change as a function of the incident photon energy (hv); and the absorption coefficient values register levels below $10^4 cm^{-1}$, which is physical evidence of the dominance of indirect electronic transition mechanisms within the material.

(SEM) results showed that when doped with copper and aluminium nanoparticles, morphological changes occur in the structure of the PVC film; the surface nature changes to a hybrid structure that combines amorphous and crystalline regions.

The results of (FTIR) showed the appearance of absorption bands that oscillate between strong and weak, which is evidence of the presence of diverse vibrational modes, including bending and stretching vibrations, of the chemical bonds within the composite.

Photo degradation nanocomposites films occurred at faster rate than the pure films under UV irradiation.

CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this manuscript.

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