



Influence of a binary phase ZnO–CuO on the structural and reflectance properties of poly-ε-caprolactone based nanocomposites

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ABSTRACT

The binary phase metal oxide of ZnO and CuO (BPMO-ZC) nanopowders were synthesized by the chemical bath deposition. The BPMO-ZC nanopowders were distributed through the poly-ε-caprolactone (PCL) matrix by solution casting. The effect of the BPMO-ZC on the structure, thermal and reflectance properties of PCL was investigated. The X-ray diffraction (XRD) confirmed the combined hexagonal wurtzite and cubic forms of the respective ZnO and CuO nanomaterials as well as an orthorhombic form of the semi-crystalline PCL nanocomposite films. Morphology included aggregated particles with heterogeneous distribution. Differential scanning calorimetry (DSC) showed that the degree of crystallinity of nanocomposites films increased in the presence of the nanopowders. Nanocomposites displayed poor thermal stability compared to PCL, but improved residue. Reflectance measurement revealed that the absorption edges of PCL shifted to higher wavelength with the addition of ZnO–CuO.

1. Introduction

Recently, research has focused more on individual pure zinc oxide (ZnO) and copper oxide (CuO) nanopowders and less on binary phase ZnO–CuO nanopowders (BPMO-ZC) [1–4]. The combination of ZnO and CuO nanopowders in BPMO-ZC is envisaged to exhibit improved physicochemical properties compared to individual materials with interesting changes in structure, thermal and reflectance properties. ZnO is an important n-type semiconductor with a wide band gap of 3.37 eV and a high exciton binding energy of 60 meV at room temperature [3,5]. Due to the large band gap and high exciton binding energy, ZnO nanopowders exhibit high semiconducting properties used for high catalytic activity and biomedical field for wound healing and anti-inflammatory materials [4,6,7]. ZnO has attracted many research due to its unique properties. It has a hexagonal wurtzite structure [8–10]. Due to its specific properties, it has been used in applications, such as sensors, solar cells, photocatalysis, photodetectors, nanogenerators,

photodiodes, varistors, optical modulator optoelectronics, piezoelectric devices, medical and transparent thin film transistors [11–14]. ZnO is abundant, inexpensive, biocompatible, and non-toxic and can potentially be used in bio-imaging and medication delivery [15–17]. ZnO nanopowders at low concentrations destroy human cancer cells and might aid in the treatment of infectious diseases and in managing diabetes and cholesterol [15,18,19].

CuO is another important non-toxic p-type semiconductor, which has a narrow band gap of 1.2 eV with good electrical conductivity (76.5 W/mK) and is anti-ferromagnetic [20–22]. These properties enhance their applications in the preparation of optical, photovoltaic, sensing, electrical composites materials, for solar energy transformation and storage, electronics, gas sensors, magnetic storage media, semiconductors, varistors, catalysis, batteries, and for advanced environmental sciences [1, 20,23–25]. CuO has a monoclinic structure [20,22,26] with good structural, optical, and electrical properties with low-cost fabrication [13,26]. ZnO and CuO are excellent options for the development of new

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composite materials for advanced applications in the fields of nanocomposites, optoelectronics, solar energy cells, and photo catalysis [1, 23,27–29].

Biodegradable polymers such as poly (ϵ -caprolactone) (PCL) have gained attention because of the increasing environmental problems related to global warming and plastic pollution [28–30]. These polymers are readily available, non-toxic to the environment and degrade naturally [33,34]. The excellent biodegradability, biocompatibility and capacity to plasticize most polymers promoted the demand of PCL for possible applications in packaging, tissue engineering and drug delivery, advanced face mask filters and toy materials [32,34–37].

Polymer science has much attention to nanocomposites applications, which includes tyres, biomedical devices, electronic devices, and many more [34,38,39]. Metal oxide (MO) polymer nanocomposites combine features of the MO and the polymer, which are synthesized to achieve the desired mechanical, thermal, optical, and electrical properties [38, 40]. The aim of this study was to investigate the effect the BPMO-ZC brings on the structure, thermal and reflectance properties of PCL nanocomposites. There are not many reports on reflectance measurements of BPMO-ZC and PCL/BPMO-ZC, leaving scope to produce innovative nanocomposites for practical applications such as light emitting plastic toys and poly-diodes.

2. Experimental

2.1. Materials

All chemicals used to synthesize nanopowders were of analytical grade. These include: zinc acetate dihydrate [$\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$] (99 %), copper acetate monohydrate [$\text{Cu}(\text{CH}_3\text{COO}) \cdot \text{H}_2\text{O}$] (98 %), glacial acetic acid [CH_3COOH] (98 %), acetone [$\text{C}_3\text{H}_6\text{O}$] (0.78 g cm^{-3}), sodium hydroxide [NaOH] pellets ($M_r = 40.00$), supplied by Sigma-Aldrich (ordered from Merck) and deionized water [H_2O] (1.0 g cm^{-3}). All these reagents were used without further purification. PCL was of a commercial grade with the following specifications: It was supplied by Southern Chemicals in Johannesburg and had a density of 1.14 g cm^{-3} ; melting temperature of 60°C , glass transition temperature of -61°C

and its molecular weight (M_w) was $5.0 \times 10^4 \text{ g mol}^{-1}$. Chloroform was of a commercial grade and was used to dissolve PCL.

2.2. Synthesis of ZnO–CuO nanopowders

The nanopowders were prepared using a chemical bath deposition (CBD). The deionized water was used to prepare the solutions of copper acetate monohydrate (0.3 M), zinc acetate dihydrate (0.3 M) and sodium hydroxide (0.1 M) in 250 mL volumetric flasks. The NaOH aqueous solution was used as the precipitating agent. The temperature of water in the bath was kept at 80°C . Zinc, copper and NaOH solutions were held constant at ratio of 1:1:1 and one drop of glacial acetic acid was added in the mixture to keep the pH at 10 and was stirred for 2 h (h) to obtain the precipitate. The precipitate was vacuum filtered, and then washed several times with deionized water and acetone to remove impurities. The precipitate was left in a desiccator for 3 days to dry. Finally, the product was annealed at 700°C in air for 2 h using the Labcon furnace, 5014U (LC).

2.3. Preparation of nanocomposites

To prepare the nanocomposites, different ratios, by mass, were used to prepare all the PCL based nanocomposites. The mass of PCL range from 0.35 to 0.5 g while the mass of ZnO–CuO powder range from 0.025 to 0.15 g. Solution casting method was used to prepare all the samples using chloroform as a solvent. To prepare the films, different masses of PCL were measured and dissolved in 10 mL of chloroform which was placed in a 35°C water bath. Afterwards, different masses of the nanopowder (ZnO–CuO) were dispersed in each polymer (PCL) matrix in order to prepare the nanocomposites. A pure PCL solution was prepared as well. A pure PCL solution and PCL/ZnO–CuO mixtures were mechanically stirred for an hour then casted into different evaporating dishes and left to dry at ambient temperature and coalesce into films for seven days. Finally, the nanopowders and nanocomposites samples were characterized using various analysis techniques.

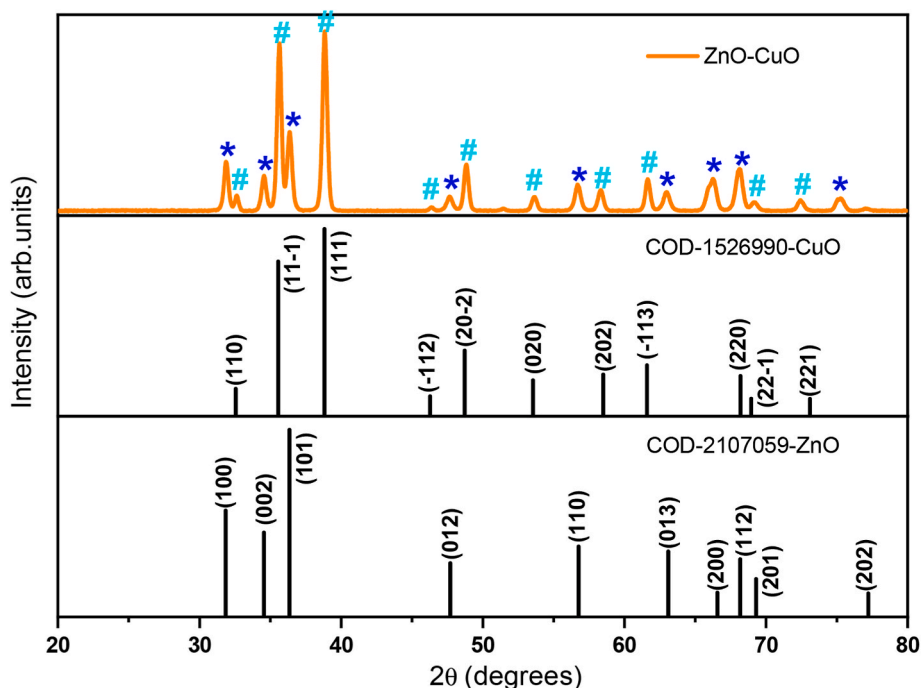


Fig. 1. X-ray diffraction pattern of the ZnO–CuO nanopowders with the corresponding COD peak also shown, (CuO peaks are marked with blue asterisks (*) and ZnO peaks with cyan hashtag (#)).

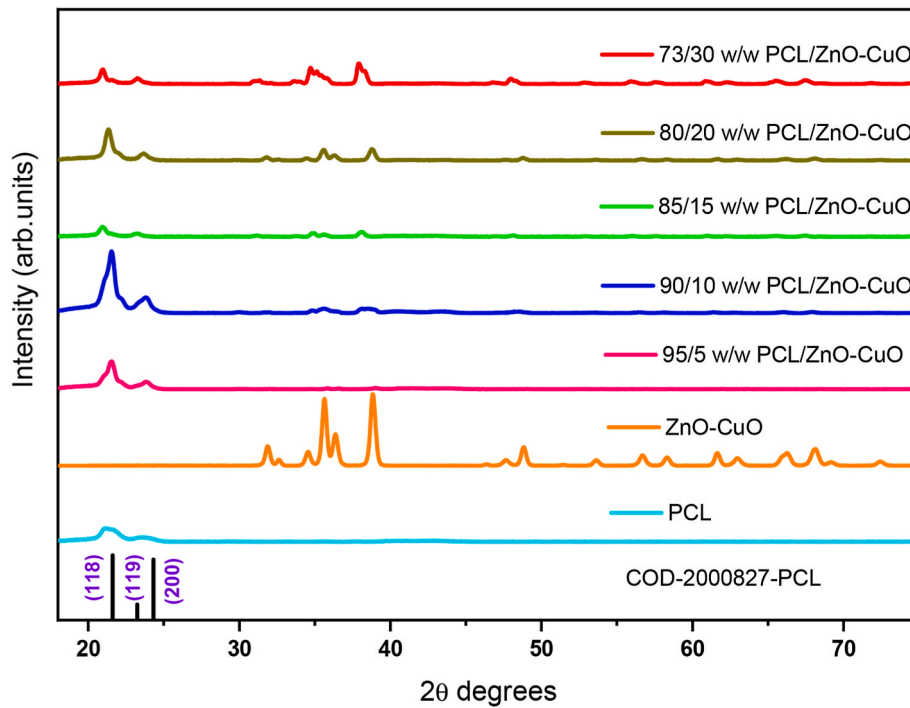


Fig. 2. X-ray diffraction patterns of the ZnO-CuO nanopowders, PCL and nanocomposites.

2.4. Characterization

The structural analysis of the samples was performed with a Bruker D8 AXS Discover x-ray diffractometer with Cu K α (1.54 Å) radiation with rotation stage. Continuous scans were carried out at 40 mA and 40 kV using a locked coupled at a count interval of 1 s over a wide range of Bragg's angle ($20^\circ \leq 2\theta \leq 80^\circ$). The D values were estimated using a well-known Scherrer equation [8,52] as shown in equation (1).

$$D = \frac{0.9\lambda}{\beta \cos \theta} \quad (1)$$

where D , λ , β , and θ represents the crystallite size, the X-ray wavelength, full width at maximum height of the XRD diffraction peak and the Bragg diffraction angle, respectively. Morphology and elemental composition of the prepared samples (nanopowders and nanocomposites) were analysed using a Zeiss Supra 55 scanning electron microscope (SEM) equipped with an energy dispersive X-ray spectrometer (EDS), on a high-resolution scan mode for surface and backscattered electron mode (AsB) for the cross-section of PCL and nanocomposites. The AsB mode showed particles of higher atomic mass such as (Zn and Cu) relatively brighter than lower Z elements (like the carbon-based background). Samples

were coated with carbon thickness 40.0 nm, and density 2.25 g cm^{-3} . The element used for optimization was copper. Differential scanning calorimetry (DSC) was performed on a PerkinElmer DSC 6000. The PCL and nanocomposites sealed in aluminium pans with weight around 5–10 mg were heated from -25 to 120°C with a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ (first run). The samples were cooled to 25°C at a cooling rate of $10^\circ\text{C} \cdot \text{min}^{-1}$ (second run) and reheated to 120°C at the same rate. The degree of crystallinity (X_c) of PCL and the nanocomposites was determined using equation (2) [41,42]:

$$X_c(\%) = \frac{\Delta H_m}{w_{\text{PCL}} \times \Delta H_m^\circ} \times 100 \quad (2)$$

where ΔH_m is the experimental melting enthalpy, ΔH_m° is the melting enthalpy of 100 % crystalline PCL taken as 139.50 J g^{-1} and w_{PCL} is the weight fraction in the PCL nanocomposites [43,44]. The thermo-gravimetric analysis (TGA) was done on a PerkinElmer TGA. The samples of around 25 mg were heated from 30 to 600°C with a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$, under constant nitrogen flow ($50 \text{ cm}^3 \text{ min}^{-1}$). The ultraviolet-visible near infrared (UV-Vis NIR) reflectance measurements were carried out on a PerkinElmer Lambda 750s spectrometer. The reflectance spectra of the samples were obtained in the range of

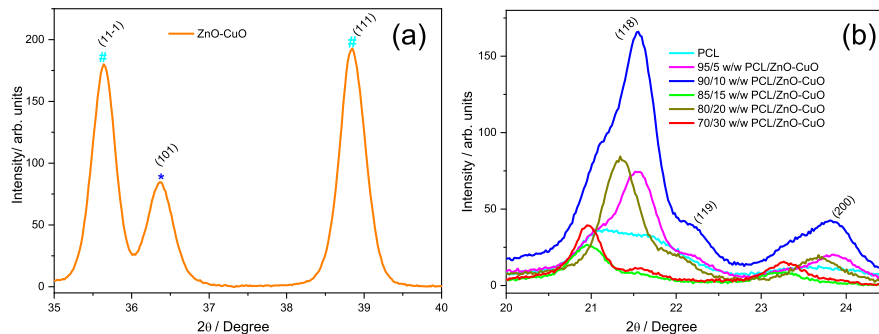


Fig. 3. Diffraction peaks of (a) nanopowders for (11-1), (101) and (111); and (b) PCL and the nanocomposites for (118), (119) and (200).

Table 1

The Crystallite sizes of ZnO–CuO nanopowder, PCL and nanocomposites.

Sample ID	2 θ (°)	β (Rad)	D (nm)
ZnO–CuO	35.6–38.8	0.004	43.26 $\pm$ 0.004
PCL	21.4–23.6	0.016	10.62 $\pm$ 0.016
95/5 w/w PCL/ZnO–CuO	20.5–24.5	0.007	24.01 $\pm$ 0.007
90/10 w/w PCL/ZnO–CuO	21.5–23.7	0.006	22.96 $\pm$ 0.006
85/15 w/w PCL/ZnO–CuO	21.0–23.2	0.004	32.20 $\pm$ 0.004
80/20 w/w PCL/ZnO–CuO	21.3–23.7	0.005	26.98 $\pm$ 0.005
70/30 w/w PCL/ZnO–CuO	21.0–23.3	0.004	36.61 $\pm$ 0.004

300–1200 nm. A 1 nm interval was used between each scan. The optical energy band gap (E_g) of the BPMO-ZC and PCL based nanocomposite films were calculated using Kubelka-Munk function [45–47] as shown in equation (3):

$$(K\hbar\nu)^2 = (\hbar\nu - E_g) \quad (3)$$

where K is the proportionality constant $= (1-R)^2/2R$, and $\hbar\nu$ is the photon energy.

3. Results and discussions

3.1. Structural and compositional analyses

Fig. 1 shows the X-ray diffraction (XRD) pattern of the ZnO–CuO nanopowders. The diffraction peaks of the nanopowders correspond with the monoclinic phase of CuO and the hexagonal wurtzite phase of ZnO. The diffraction data of the annealed ZnO–CuO nanopowders are well consistent with the following COD card no: 1526990 (CuO) and 2107059 (ZnO). No additional peaks were observed indicating pure crystalline formation of ZnO–CuO nanopowders. The sharp and high intensity of diffraction peaks demonstrate the high purity and crystalline nature of nanopowders.

Fig. 2 illustrates the XRD pattern of the PCL and nanocomposites. The clear and sharp diffraction peaks at 2θ of 22°, 23.5° and 24°, which correspond to the (118), (119) and (200) planes in the semi-crystalline, orthorhombic PCL as confirmed by the COD 2000827 [48–51]. It could be observed that the nanocomposites have a mixture of both the PCL and ZnO–CuO structures since some of the peaks correspond to the Miller indexed of PCL and others are due to the nanopowders. The XRD pattern showed that the BPMO-ZC increases the crystalline quality of PCL in the nanocomposites.

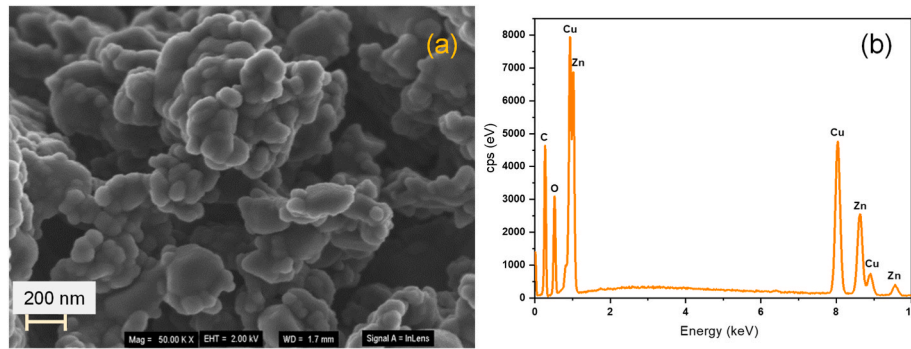


Fig. 4. (a) SEM image and (b) EDS of ZnO–CuO nanopowder.

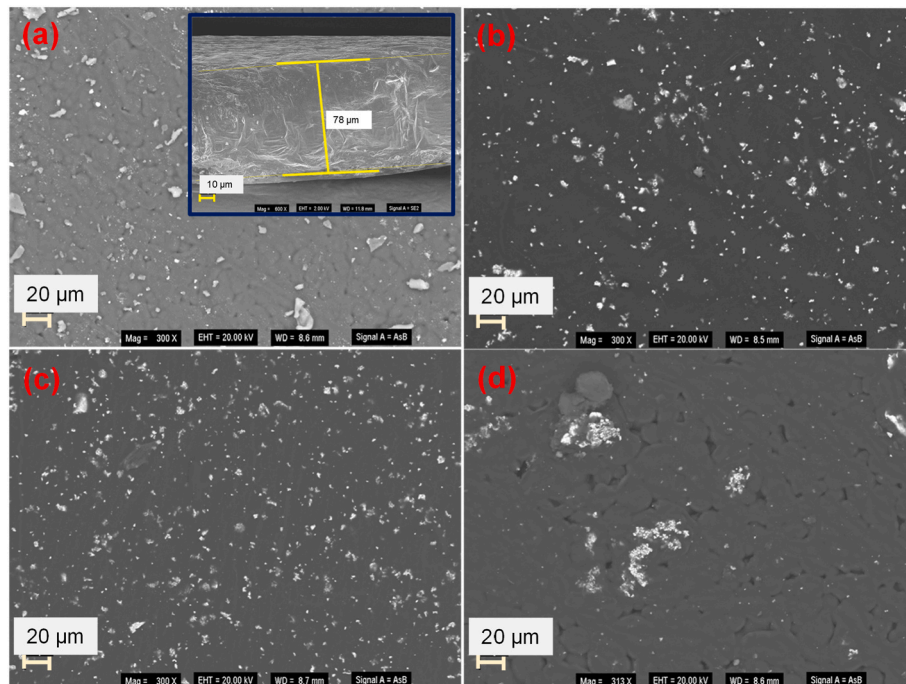


Fig. 5. Surface (a)–(d) SEM images of PCL and 90/10, 80/20, 70/30 w/w PCL/ZnO–CuO nanocomposites and insert is the cross-sectional SEM image of PCL.

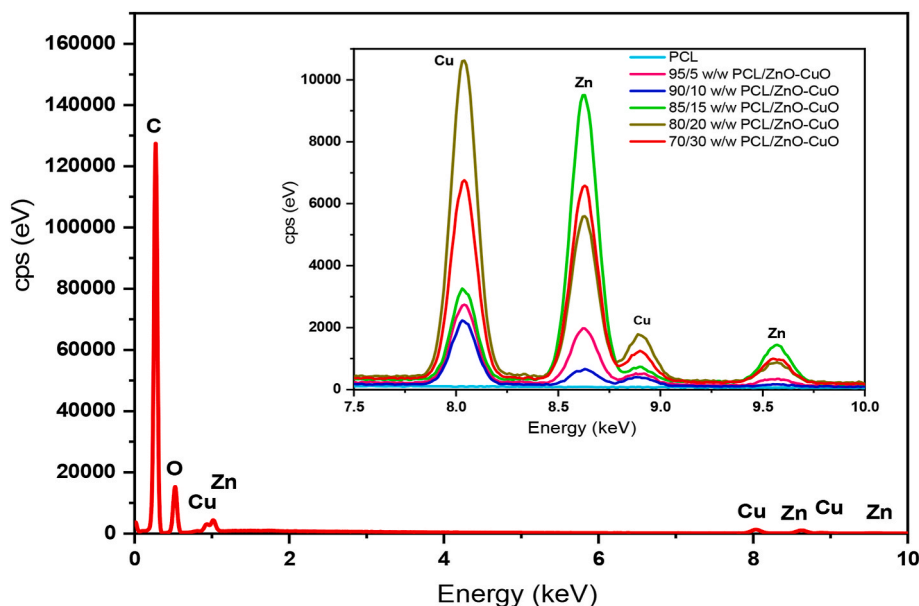


Fig. 6. The energy dispersive X-ray spectrometer spectra of the 70/30 w/w PCL/ZnO-CuO nanocomposite. The insert is the enlarged part from 7.5 to 10 keV of the PCL and nanocomposites.

Fig. 3 shows the zoomed diffraction patterns of (a) at diffraction peaks (11-1), (101), (111) for ZnO-CuO nanopowders, and (b) (118), (119), (200) for PCL and nanocomposites, respectively. The peaks used to estimate the average crystallite size (D) are shown in Table 1. The D of the nanopowders and PCL is respectively 43.26 nm and 10.62 nm while the nanocomposites have the intermediate D ranging from 22.96 to 36.61 nm. Note that the diffraction peaks at 35.6 and 38.8°, which are characteristic of CuO, have higher intensity than that of ZnO (101) at 36.5°. The high intensity of the diffraction peaks suggests that CuO content precedes that of ZnO due to the partial substitution of smaller radius Cu^{2+} (0.071 nm) ion into the sites of Zn^{2+} (0.074 nm) [14,28,53]. The D of the nanocomposites increases with slight fluctuation as the concentration of nanopowders increase in reference to PCL. This could mean that, the nanopowders tend to attract each other as they are dispersed within the polymer matrix and form larger particles [54]. The increase may also be due to the decrease in estimated β values of PCL/ZnO-CuO compared to PCL [50,55,56].

Fig. 4 (a) shows the SEM image of the ZnO-CuO nanopowders taken at the magnification of 200 nm. The morphology of the binary phase ZnO-CuO nanopowder system reveals an aggregation of hetero-structures. The aggregation gives a cauliflower like morphology probably from the combination of ZnO and CuO hetero morphologies. The surface morphology of a single phase ZnO was studied by Malimabe et al. [14] they found that ZnO particles have a flower-like morphology. Mahmoud et al. [22] reported that the surface single phase CuO had

tubular morphology.

Fig. 4 (b) shows the EDS of the binary phase ZnO-CuO nanopowder system. The spectrum confirmed the presence of zinc (Zn), copper (Cu), oxygen (O) and carbon (C) atoms as expected. The carbon (C) peak, which appeared in the spectrum was due the conductive carbon tape of the sample holder and the C-coating on the sample during the measurements [57–59]. Except for C, no other peaks related to impurities were observed in the EDS spectrum as confirmed in the XRD results in Fig. 1.

The SEM micrograph in Fig. 5 (a) shows that PCL has a porous surface morphology and the cross-sectional SEM image in the insert shows the estimated thickness of the PCL film at $78 \mu\text{m} = (0.078 \text{ mm})$. Fig. 5 (b), (c) and (d) demonstrates the presence of inhomogeneous ZnO-CuO nanopowder aggregates dispersed randomly in the PCL matrix. The aggregates occurred when the particles coalesce as the solvent evaporates during the nanocomposites film formation [60]. The ZnO-CuO nanopowders form the aggregates because they have high surface energy and they have strong particle-particle interactions, which then prevents their dispersion in the polymer matrix to be homogeneous [7, 60]. The distribution in Fig. 5 (b) and (c) of the 90/10 and 80/20 w/w PCL/ZnO-CuO nanocomposites is finer and closer to homogeneity than the 70/30 w/w PCL/ZnO-CuO nanocomposite, which had lower intensity peak in the XRD results. The increase in the ZnO-CuO nanopowder concentration increases aggregation in PCL matrix. The increasing aggregation of in the polymer matrix restricts the movement

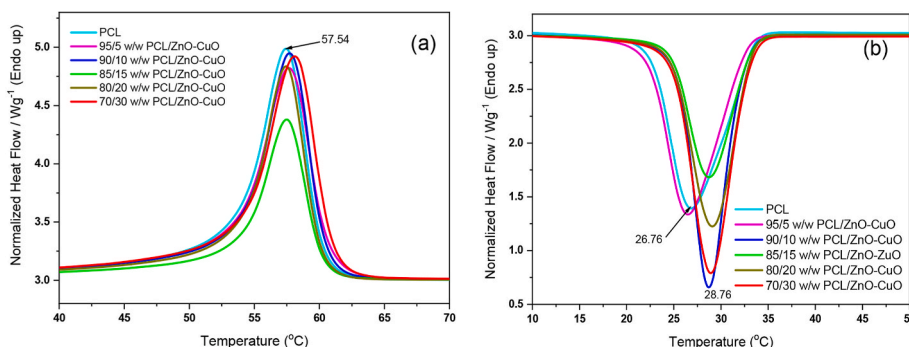


Fig. 7. Differential scanning calorimetry (a) second heating and (b) cooling curves of the PCL and nanocomposites.

Table 2

Differential scanning calorimetry heating and cooling results for PCL and nanocomposites.

Sample ID	T_m (°C)	ΔH_m (J/g)	T_c (°C)	ΔH_c (J/g)	X_c (%)
PCL	57.54 ± 1.32	46.61 ± 1.05	26.76 ± 0.41	−55.46 ± 0.67	33.42
95/5 w/w PCL/ ZnO–CuO	57.88 ± 0.08	44.45 ± 0.13	26.47 ± 0.25	−48.35 ± 3.76	33.54
90/10 w/w PCL/ ZnO–CuO	57.89 ± 0.22	45.94 ± 7.50	28.70 ± 0.36	−50.50 ± 7.67	36.59
85/15 w/w PCL/ ZnO–CuO	57.81 ± 0.03	41.43 ± 5.59	28.72 ± 0.13	−48.08 ± 6.74	34.94
80/20 w/w PCL/ ZnO–CuO	57.57 ± 0.01	44.18 ± 0.60	29.11 ± 0.01	−46.28 ± 0.61	36.89
70/30 w/w PCL/ ZnO–CuO	58.39 ± 0.69	48.21 ± 13.42	29.02 ± 0.57	−50.43 ± 13.60	49.38

T_m and T_c = melting and crystallization temperature, ΔH_m and ΔH_c = enthalpy of melt and crystallizing, X_c = degree of crystallization.

of polymer chains, which may bring about a slight increase in the melting temperatures of the nanocomposites [12,30,61].

Fig. 6 shows the EDS spectra of the PCL and nanocomposites. The insert is the enlarged EDS part of the nanocomposites from 7.5 to 10 keV. The EDS spectra of the PCL based nanocomposites confirmed the presence of carbon (C) at $K\alpha \approx 0.27$ keV, oxygen (O) at $K\alpha \approx 0.53$ keV as expected from the PCL structure $(C_6H_{10}O_2)_n$ [7,60,62]. The enlarged part in Fig. 6 clearly shows the presence of Zn and Cu in the nanocomposites.

3.2. Thermal analysis

Fig. 7 shows the DSC (a) second heating and (b) cooling curves of PCL and PCL/ZnO–CuO nanocomposites. The thermal data are illustrated in Table 2. The endothermic and exothermic peaks at 57.54 °C and 26.76 °C indicate the melting (T_m) and crystallization (T_c) peaks of the semi-crystalline PCL crystals [31,34,50]. These peaks, T_m and T_c , are slightly lower than the as-received PCL pellets due to the plasticizing effect by the solvent (chloroform) that was used to prepare the films [31, 63]. The T_m and T_c of PCL increased slightly to higher temperature with the addition of ZnO–CuO nanopowders due to the stiffening effect brought about by the nanopowders [31–34]. This observation agrees with the SEM results since it showed the formation of aggregates with addition of nanopowders. Nevertheless, the addition of high content of ZnO–CuO nanopowders produces agglomerates as observe from SEM, which hinder the movement of chains thus producing crystals with a thinner lamellar [57,59]. There is a slight decrease in the enthalpies of melt (ΔH_m) and crystallization (ΔH_c) of the nanocomposites than the PCL as shown in Table 2. The slight decrease in the $\Delta H_m/\Delta H_c$ suggests an increase in the degree of crystallization (X_c), which is observed as BPMP-ZC nanopowders were added into PCL polymer matrix [34,50, 64–66]. The increase in X_c agrees with the observed increase in the XRD

values of D and smaller β values of the nanocomposites showing improved crystalline quality.

The TGA and derivative thermogravimetric (DTGA) curves of PCL and PCL/ZnO nanocomposite films are shown in Fig. 8 (a) and (b) respectively. The weight loss temperatures at 10 wt% ($T_{10\%}$), 50 wt% ($T_{50\%}$) and residue for the films are summarized in Table 3. Fig. 8 (a) shows a single step degradation of PCL at T_{10} (370.56 °C) up to T_{50} (404.36 °C), leaving no residue at 500 °C. The maximum degradation temperature (T_{max}) is at 411.68 °C as shown on the DTGA curve in Fig. 8 (b). The nanocomposite exhibited the same thermal degradation profile, showing a mass loss step in the range of 347.24–411.68 °C. This degradation is attributed to the chain scission and the unzipping from hydroxyl end leading to the formation of ϵ -caprolactone [61,67,68]. It is generally believed that the introduction of inorganic fillers into the polymer matrix can enhance the thermal stability of nanocomposites [33,58], but in this case the addition of ZnO–CuO nanopowders decreased the thermal stability of PCL. An increase in the content of ZnO–CuO nanopowder decreased the $T_{10\%}$ and $T_{50\%}$ of the nanocomposites even more. This is because increasing the amount of ZnO–CuO nanopowders could reduce the crystal perfection of PCL as the interaction at the interface of the nanopowders and PCL tends to reduce [33,67]. In addition, the ZnO–CuO nanopowders might have promoted an oxidative decomposition of the surrounding carbon, thus shifting the thermal degradation of PCL to lower temperatures [28,31,33,34]. The residue in the nanocomposites increases ranging from 0.70 to 30.06 %, as the concentration of the ZnO–CuO nanopowders increased in the polymer matrix. The inorganic part (BPMP-ZC) contributes towards the increase in the total mass residue since they are not expected to degrade at lower temperatures [1,20,29].

3.3. Optical reflectance properties

The UV–Vis NIR reflectance spectra of ZnO–CuO nanopowders and

Table 3

Thermogravimetric analysis and derivative thermogravimetric results for PCL and nanocomposites.

Sample ID	$T_{10\%}$ onset (°C)	$T_{50\%}$ onset (°C)	T_{max} (°C)	Residue (wt %) @ 500 °C
PCL	370.56	404.36	411.68	0.70
95/5 w/w PCL/ ZnO–CuO	358.53	375.08	377.56	5.52
90/10 w/w PCL/ ZnO–CuO	351.76	369.06	370.99	6.83
85/15 w/w PCL/ ZnO–CuO	355.52	372.07	375.11	10.34
80/20 w/w PCL/ ZnO–CuO	349.50	358.53	356.33	20.42
70/30 w/w PCL/ ZnO–CuO	347.24	356.27	354.67	30.06

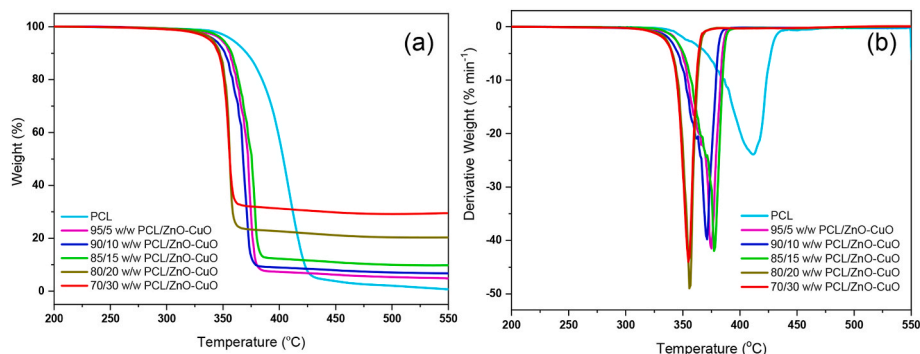


Fig. 8. (a) Thermogravimetric analysis and (b) derivative thermogravimetric curves of the PCL and nanocomposites.

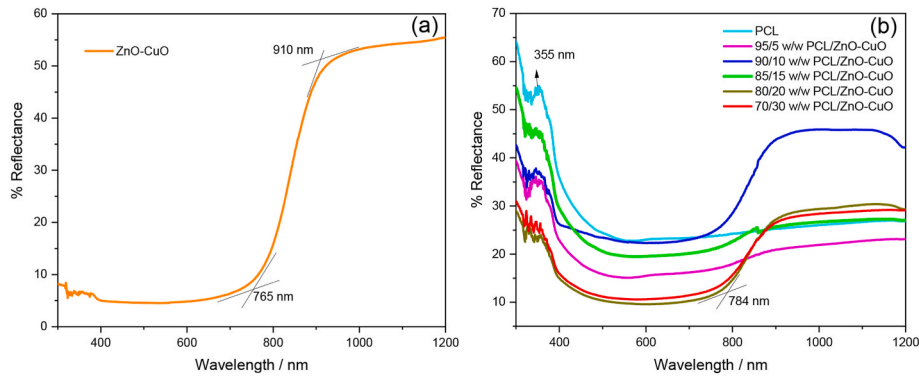


Fig. 9. The UV-Vis NIR reflectance spectrum of the (a) ZnO-CuO nanopowders and (b) PCL and nanocomposites.

Table 4

The UV-Vis NIR absorption edges and the energy band gap of the ZnO-CuO nanopowders, PCL and nanocomposites.

Sample ID	λ (nm)	E_g (eV)
ZnO-CuO	765	1.62
PCL	355	3.58
95/5 w/w PCL/ZnO-CuO	758	1.54
90/10 w/w PCL/ZnO-CuO	760	1.56
85/15 w/w PCL/ZnO-CuO	758	1.43
80/20 w/w PCL/ZnO-CuO	784	1.47
70/30 w/w PCL/ZnO-CuO	781	1.48

PCL and nanocomposites are presented in Fig. 9 (a) and (b) respectively. The estimated reflectance peak of ZnO-CuO nanopowders is around 910 nm. The reflectance peak may be due to the defect within CuO. There is also a reflectance edge at around 765 nm, which is due to the free exciton of CuO [69–72]. The PCL showed a reflectance peak at 355 nm, which is an attribute to the presence of the π - π^* carbonyl group transitions [31,32,34,50]. It is clear from Fig. 9 (b) that with the incorporation of ZnO-CuO nanopowders in PCL, the reflectance peak emerges at around 879 nm coupled with a reflectance edge at around 758 nm. The reflectance edges for the nanocomposites shifted slightly to higher wavelengths than 758 nm with the variation in the BPZO-ZC content. The shift of the nanocomposites towards higher wavelengths compared to PCL is an indication of good interaction of PCL with the nanopowders [32,34,50,69]. The increase in the BPZO-ZC content and a consequence increase in estimated crystallite sizes as confirmed by the XRD analysis and Table 1 attest to the shift to higher wavelengths [73,74].

The UV-Vis NIR absorption edges and the optical energy band gap (E_g) of the ZnO-CuO nanopowders, PCL and nanocomposites are given in Table 4. Fig. 10 shows the optical energy band gap (E_g) of the (a) ZnO-CuO nanopowders and (b) PCL and nanocomposites as determined from the Kubelka Munk theory [75–77]. The E_g of the prepared

ZnO-CuO is estimated at about 1.62 eV and is due to the CuO [20,21]. This low E_g value suggests that electrons are readily promoted from the valence band to the acceptor level, and that ZnO-CuO nanopowders are in general a p-type semiconductor [20,27,70]. The 3d orbital of the Cu atom is much shallower than that of Zn. Thus, a strong coupling occurs between the d orbital of the Cu atom and the p-orbital of the O atom, which narrows the E_g . The 3d-orbital of the Cu atom also creates impurity bands, which further contributes to a decreased E_g Refs. [27,28]. Clearly, the E_g for the nanocomposites decrease to that of PCL due to the improvement in crystallinity as shown in Fig. 3 and Table 1 [50,78]. The reduction in the E_g of the nanocomposite films to PCL ensures potential to use the PCL/BPZO-ZC system in light emitting plastic toys.

4. Conclusions

The ZnO-CuO nanopowders were successfully synthesized by chemical bath deposition and distributed in the PCL polymer matrix through solution casting to form nanocomposites. The XRD confirmed formation of ZnO-CuO nanopowders comprising ZnO (hexagonal) and CuO (monoclinic) structures. The average crystallite size obtained gradually increased with fluctuations in reference to PCL. The SEM images revealed a heterogeneous distribution and an increased aggregation as concentration of the BPZO-ZC nanopowders varied within the PCL polymer matrix. The EDS confirmed the presence of expected elements. Incorporation of the nanopowders into PCL increased the degree of crystallinity and led to a decrease in thermal stability of the nanocomposites. The UV-Vis NIR revealed a shift to higher wavelengths of the nanocomposites compared to PCL. Due to the changes, PCL/ZnO-CuO nanocomposites can be used in advanced fields as polydiodes, and plastic toy devices.

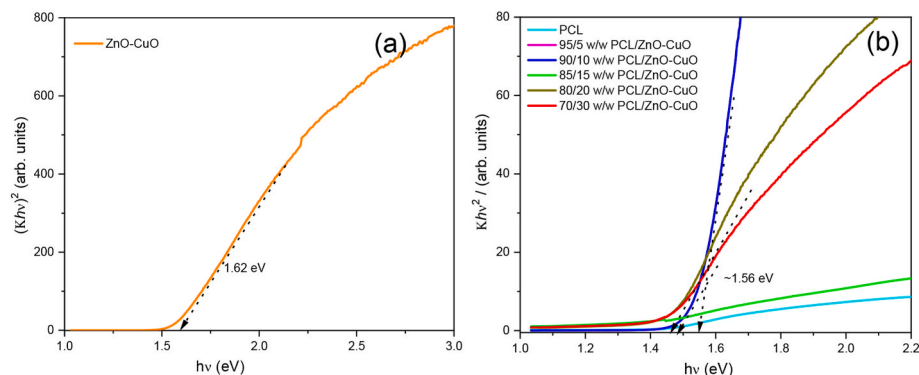


Fig. 10. The plot to determine the energy band gap of the (a) ZnO-CuO nanopowders, (b) PCL and nanocomposites.

Credit author statement

Authors declare consolidative effort towards restructuring and responding to the reviewer's comments.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data will be made available on request.

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