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Enhanced Thermal Mechanical and Optical Behavior of PVA GO ZnO Hybrid Nanocomposite Films

Dr. Alak Das

State Aided College Teacher, Department of Physics,
Mahishadal Raj College, Mahishadal, Purba Medinipur, West Bengal.

Email: alakdas1981@gmail.com

ABSTRACT

A new kind of material with potential aspects on many uses is graphene-based polymer composites, which are attracting a lot of attention. This work demonstrated the effective synthesis of nanocomposite films based on polyvinyl alcohol (PVA) and reinforced with hybrid nanofillers of graphene oxide (GO) and zinc oxide (ZnO) utilizing a simple solution casting approach. The wet chemical approach was used to create the GO-ZnO hybrid nanofillers, which were then mixed with the PVA matrix at concentrations of 1, 3, and 5 weight percent. Incorporating and evenly dispersing GO-ZnO nanofillers into the PVA matrix was verified by XRD findings. Reduced weight loss and raised degradation temperatures suggested improved thermal stability with increasing filler content, according to thermal analysis. While keeping the stiffness at a sufficient level, mechanical tests showed a considerable increase in the tensile strength and the elongation at break, especially at larger filler loadings. The optical study revealed that the conductivity improved as the concentration of nanofiller rose, as the band gap energy decreased gradually.

Keywords: *Nanocomposite, Polymer, Graphene, Hybrid, Filler.*

I. INTRODUCTION

Polymer composites are eco-friendly materials that have many potential uses because to their adaptability, versatility, room-temperature properties, reusability, ease of production, and affordability, among other advantages. With the growing need for lighter and more powerful materials, particularly in the automotive, aerospace, and military industries, polymer nanocomposites have attracted a lot of attention. Because of their small size, unique form, and enormous surface area, nanostructured materials as reinforcements in a conventional polymer matrix display a broad array of extraordinary properties.

Graphene is a two-dimensional honeycomb carbon structure made of a planar sheet of carbon atoms that is one atom thick and is bound together in a sp2 bond. High thermal conductivity, exceptional electron transport properties, special mechanical capabilities, etc. are only a few of graphene's remarkable and distinctive properties. Graphene has several unusual and desirable characteristics, such as a high surface area, a big aspect ratio, tensile strength (TS), the ability to shield electromagnetic interference (EMI), transparency, and pliability. In comparison to more traditional nanofillers, graphene's intrinsic qualities make it a popular and desirable option.

The time and money needed to produce pure graphene in large quantities means it is not a good choice as a filler for polymer matrices. A more appropriate nanofiller for organic polymers composite would be graphene oxide, a graphene derivative that contains various functional groups (hydroxyl, epoxy, carbonyl, etc.), which can interact strongly with polymers and is easy, simple, and inexpensive to produce. Also, GO's variety of functional groups—including hydroxyl, epoxy, carbonyl, and others—make it possible for it to develop a strong contact with the polymer matrix. Because of the functional groups they contain, GO sheets are hydrophilic, meaning they expand and dissolve easily in water. Poly (vinyl alcohol) (PVA) and other hydrophilic polymers containing hydroxyl groups may have been the starting point for the synthesis of GO nanofillers in polymer nanocomposites. Because of its availability, dielectric strength, and potential optical characteristic, PVA finds significant usage in diverse applications. It is a hydroxyl-rich, water-soluble, biocompatible, and non-toxic polymer. Mechanical characteristics, thermal stability, and electrical conductivity are all enhanced when GO is molecularly uniformly dispersed in the PVA matrix. In addition, GO has a modest absorption in the visible range and an effective absorption in the ultraviolet (UV) zone, as shown by its optical band gap of around 1.5 eV. Therefore, the optical characteristics of the nanocomposites may undergo substantial alterations upon GO incorporation into the PVA matrix, including a significant decrease in the bandgap and an elevated absorbance value in the ultraviolet (UV) spectrum. The optical property tweaking and structural changes caused by the addition of GO directly impact the device's performance.

II. REVIEW OF LITERATURE

Padinhattayil, Sanoop & Rai, K. (2021) The goal of this study is to create and evaluate nanocomposites of polyvinyl alcohol (PVA) using a new hybrid nano filler consisting of graphene oxide and zinc oxide. A modified Hummer's technique was used to produce a GO-ZnO hybrid nanocomposite filler. Films made of polymer nanocomposite materials were created using the solution casting technique. The detailed technique for synthesizing GO-ZnO hybrids is described. The GO surface was evenly anchored with ZnO, which had an average size of 26.74 nm. Electrical, thermomechanical, and spectroscopic analyses were performed on the PVA film and PVA/Graphene Oxide/Zinc oxide composite film to determine their attributes. It was found that PVA composite films had improved mechanical characteristics and thermal stability when graphene oxide and zinc oxide were added to the PVA matrix. With the addition of 0.05% GO-ZnO to neat PVA, the tensile strength rises to 10.48 MPa, and the Young's modulus goes from 104.407 to 106.765 MPa. Adding a nano filler to a polymer improves its elongation behavior, which ranges from 15.94 MPa for a pure PVA polymer film to 239.52 MPa for a GO-ZnO hybrid filler with a 1% loading. The remarkable enhancement of mechanical capabilities at such low stacking levels of GO-ZnO is a result of a feature of the hybrid nano-Filler. DC conductivity tests were also performed on the materials, and with a 5% nanoparticle loading, the results showed a conductivity of 2.895×10^{-6} S·cm^{-1}, while for pure PVA, the value was 9.952×10^{-8}.

Hurayra, Abu et al., (2021) A new kind of material with potential aspects on many uses is graphene-based polymer composites, which are attracting a lot of attention. Nanocomposites of graphene oxide (GO) and polyvinyl alcohol (PVA) were synthesized in this study using an easy solution casting technique. We tested the effects of using low quantities of GO nanofiller (0.25%, 0.50%, 0.75%, and 1.0%) on the unique significant properties of the nanocomposites. Fourier transform infrared spectra (FTIR), ultraviolet-visible spectroscopy (UV-Vis), thermo-gravimetric analysis (TGA), and X-ray diffraction (XRD) were used to identify the optical, structural, chemical, and thermal characteristics of the as-synthesized nanocomposites, respectively. The structural study of the nanocomposite's crystallinity clearly shows that the amalgamation of the GO nanofiller produced a decrease in crystallinity. The GO nanofiller and PVA matrix interact better, according to the FTIR analysis. The optical band gap of the nanocomposite for both direct and indirect transitions was seen to be reduced with addition of GO. As the GO concentration rises in the nanocomposite, its Urbach energy rises as well, which may indicate the creation of localized states that lower the optical band gap. Potentially groundbreaking for polymer-based optoelectronic devices are PVA-GO nanocomposites that exhibit enhanced and modifiable physical characteristics and can be easily and affordably manufactured.

J., Selvi et al., (2020) In order to investigate how the nanofiller affected the characteristics of the composites, researchers created poly(vinyl alcohol) (PVA) nanocomposites and tested them. The FTIR and XRD analyses were performed on all of the produced samples. Indicating the interaction between ZnO and the PVA matrix, the samples showed an M-O stretching peak at 526 cm−1. It was established by the XRD patterns of the PVA nanocomposites that ZnO nanofiller was present. Using scanning electron microscopy, researchers were able to see the nanofiller's interaction with the PVA matrix and its uniform dispersion. According to the transmission electron microscopy, the ZnO nanoparticles (NPs) were smaller than 35 nm in size. We used UV-visible spectra to look at how the PVA nanocomposites absorbed and transmitted light. The produced PVA nanocomposite films showed a strong ability to absorb ultraviolet light. After adding the ZnO NPs, the band gap of the PVA was reduced. In order to evaluate the polymer nanocomposites' thermal property and non-isothermal degradation behaviour, a TGA instrument was used. Using the kinetic models, we were able to establish the activation energy linked to the thermal degradation behaviour of the polymer composites. When compared to pure PVA, nanocomposite films improved in DC electrical conductivity, mechanical characteristics, and thermal stability with the addition of ZnO NPs.

J., Selvi et al., (2019) This study delves further into the investigation of the impact of SrO nanofillers on the physical and chemical characteristics of freshly synthesized PVA nanocomposites. We used Fourier transform infrared spectroscopy (FTIR) for surface chemistry and XRD for crystallographic nature to examine the structure of SrO nano powder and PVA nanocomposites. The TEM micrographs revealed the size and distribution of the SrO nano powders. The SrO nano powder had an average particle size of 57 nm. Through transmission electron microscopy, the SrO nanofillers were shown to be evenly distributed throughout the PVA host matrix. The PVA nanocomposites that were made showed a lot of UV absorption. Adding SrO nanofillers to PVA nanocomposites improved their thermal stability. The produced PVA nanocomposites were subjected to a nonisothermal degradation analysis using several kinetic models. In comparison to pure PVA, the nanocomposites exhibited greater Young's modulus (Y) and tensile strength. Incorporating SrO nanoparticles into PVA also improved its DC conductivity. Features The innovative PVA nanocomposites including SrO nanofillers were manufactured using the solution casting technique. A reduction in the band gap of PVA was seen with an increase in the concentration of SrO nanofillers. Under nonisothermal heating, several kinetic models were used to study the thermal deterioration of polymer composites. Adding SrO nanofillers to PVA improved its thermal stability. Nanocomposites made of PVA also showed improvements in their mechanical and electrical properties.

III. MATERIALS AND METHODS

Materials

In this lab, we employ distilled water for all of our investigations, GO-ZnO hybrid nanofillers that we manufacture, polyvinyl alcohol (PVA) with a molecular weight of 1,25,000, and AR grade from Merck India Ltd. in India.

Synthesis of GO/ZnO Hybrid

Using a straightforward wet chemical process, the GO/ZnO hybrid nanocomposite was created. For this procedure, a solution of graphene oxide and ethanol was sonicated for one hour at room temperature after being mixed in a 2:1 weight-to-volume ratio. Then, 0.880g of ZnC4H6O4.2H2O was added to the mixing bowl. After 30 minutes of stirring, the pH was brought down to 10 by adding 1M NaOH solution. The mixture was refluxed for 24 hours at 140◦c in an inert environment. After being created, the hybrid nanocomposites underwent several washes with distilled water and ethanol before being centrifuged. To get a fine powder of GO/ZnO hybrid nanocomposites, the product was dried in a vacuum oven for six hours.

Preparation of Composite Films

The PVA/GO-ZnO polymer nanocomposite films were made using the solution casting method. A 4% PVA solution was made by dissolving PVA in 4 weight percent distilled water at 70-80◦ C. Thereafter, GO-ZnO nanoparticles were introduced to the PVA homogenous solution in varying quantities of 1, 3, and 5 weight percent. The ingredients were left to mingle for around 24 hours. To make sure the mixture was evenly distributed, an ultrasonicator set to 10 Hz was used for 15 to 30 minutes. For the production of a thin layer, the homogenous solution was poured into polypropylene plates and placed in a hot air oven set at 65-70◘C for 24 hours. The result was a thin sheet of a nanocomposite polymer. Desiccators were used to preserve the film for future research.

Structural Characterization

It was conducted using a Bruker diffractometer (model 8600 USA) with Cu Ka radiation (k = 0.15406 nm) to examine the PVA and composite film structure of the PVA/GO-ZnO nanocomposite using X-Ray Diffractometer (XRD). The scanning rate was 2 degrees per minute from 10 to 80 degrees (2θ), with the voltage set at 40 kilovolts.

Thermal and Mechanical characterization

The Perkin Elmer DSC/TGA equipment was used to draw the thermal characteristics of the PVA/GO-ZnO nanocomposite films. The nanocomposites films were heated in a nitrogen atmosphere at a rate of 30˚C per minute.

Optical Characterization

All of the samples were optically analyzed using a UV-1800 spectrophotometer. Band gap energy (Eg) of PVA and PVA/GO-ZnO nanocomposite films was computed using the Tauc mathematical connection.

IV. RESULTS AND DISCUSSION

XRD Characterization

When it comes to nanocomposites containing GO-ZnO hybrid fillers, XRD is a crucial tool for characterizing delamination and scattering. Both the clean PVA and the PVA/GO-ZnO nanocomposite films are shown in Figure 1 by means of the XRD pattern. The XRD patterns of the PVA/GO-ZnO nanocomposite show distinguishing peaks at 2 = 31.76◦, 34.36◦, 36.24◦, and 47.54◦, which are the reflection planes of the hexagonal wurtzite crystal structure of the ZnO nanoparticles, in contrast to the pure PVA patterns. The extra peaks seen here are identical to those in ZnO nanoparticles.

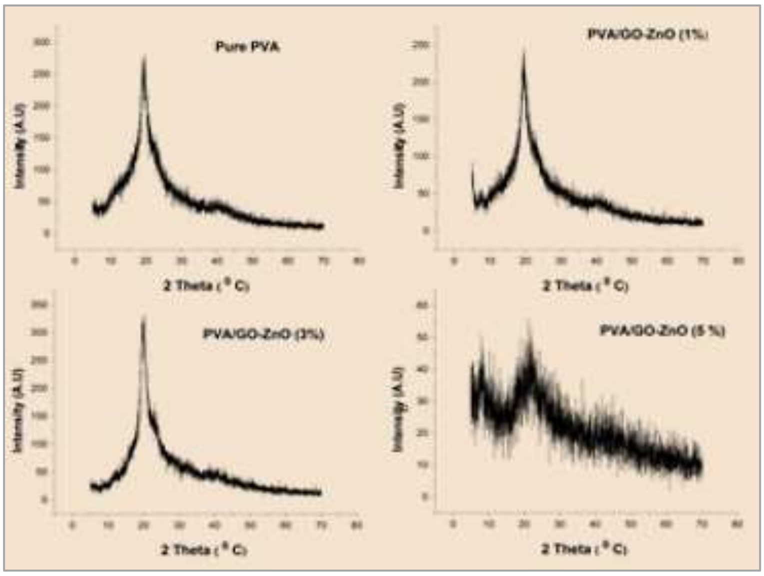

Figure 1: XRD Chromatogram Spectra of PVA Nanocomposite Films with Different Weight Percentage of GO-ZnO Filler

Adding ZnO NPs and GO to the composites causes a very strong peak at $2\theta = 19.48$◦ in the (1 0 1) diffraction peak of the PVA crystals. Nevertheless, its position decreases to 19.2◦, its intensity decreases, and the crystallization peak widens, suggesting that the three compounds are in touch to some extent. Every one of the newly observed diffraction peaks is associated with the peaks seen in GO-ZnO hybrid nanoparticles. This finding provides further evidence that PVA and GO-ZnO hybrid nanoparticles are miscible.

Thermal Characterization

To analyze the thermal dependability of PVA/GO-ZnO nanocomposites, TGA-DSC techniques are used. Figure 2 displays the TGA thermograms of the PVA/GO-ZnO composite films that have been prepared. The first stage of debasement, which occurs at around 100◦C, involves the removal of moisture and the evaporation of any retained solvent. During the first phase of nanocomposite film deterioration, the second step manifests itself in the temperature range of 100◦C to 200◦C, indicating a shift in thermal stage. Composite films recognized by side chain or functional group disentanglement disintegrate during the third degradation, which occurs between 200◦C and 300◦C. Step four, which occurs at temperatures over 400◦C, is associated with the polymer's full deterioration curve.

At different temperatures, the weight loss % of PVA/GO-ZnO hybrid nanocomposite films is shown in Table 1. Increasing the ratio of the GO-ZnO filler to the PVA matrix increases the thermal stability of the polymer, as seen in the TGA thermograms of PVA and PVA/GO-ZnO polymer nanocomposite films (Figure 2). Adding 5% GO-ZnO reduces the weight decrease of PVA pure film from 25.47% at 300◦C to 16.77%. Adding GO-ZnO to PVA film increases its thermal stability, and this further solidifies that improvement.

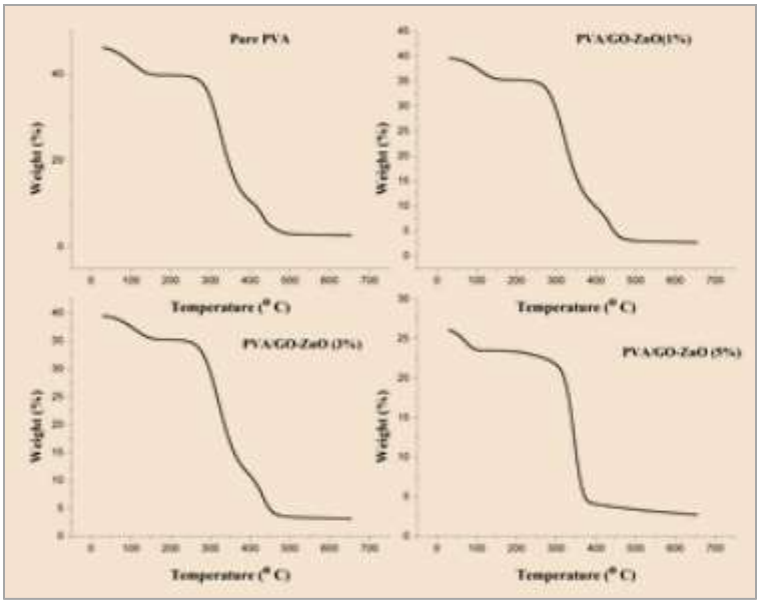

Figure 2: TGA Thermograms of PVA/GO–ZnO Nanocomposite Films at Different Filler Loadings (wt%)

Table 1: Percentage Weight Loss of PVA/GO–ZnO Hybrid Nanocomposites at Various Temperatures

Sample Code	Percentage of Weight Loss at Various Temperature						Residue
	100◦ C	200◦ C	300◦ C	400◦ C	500◦ C	600◦ C	
Pure PVA	7.5	13.94	25.47	77.01	93.52	94.10	5.9
PVA/ GO-ZnO (1%)	5.13	11.03	27.50	75.60	92.41	92.9	7.1
PVA/ GO-ZnO (3%)	4.76	10.77	26.26	72.44	91.9	91.79	8.21
PVA/ GO-ZnO (5%)	9.58	12.32	16.77	84.42	87.07	90.75	9.25

Figure 3 displays the diffractometer readings for the PVA and PVA/GO-ZnO hybrid nanocomposite films. Pure PVA film has a glass transition temperature (Tg) of 103.79◦C. The Tg of the film grows in direct proportion to the amount of Hybrid nano filler. The glass transition temperatures are 105.1◦C and 104.91◦C for a 2% (w/v) loading of hybrid nano filler, however there is no significant increase seen with a 5% (w/v) filler charge. As the amount of hybrid filler added to the PVA matrix grew, the glass transition temperature (Tg) and melting point (Tm) of the PVA/GO-ZnO polymer nanocomposite films also rose. Adding a hybrid nano filler raises the melting point of pure PVA from 186.46◦C to 187.39◦C and 188.29◦C, respectively. The enhanced thermal characteristics of the polymer may be attributed in large part to the GO-ZnO hybrid nano filler.

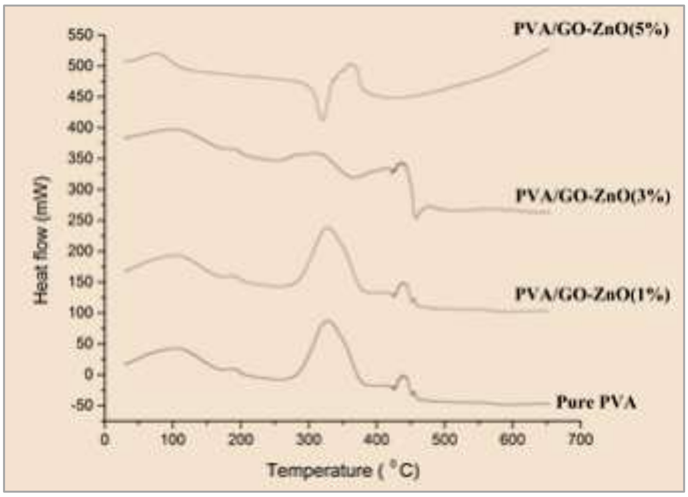

Figure 3: DSC Thermograms of PVA/GO–ZnO Nanocomposite Films at Different Filler Loadings (wt%).

Mechanical Characterization

The mechanical characteristics are expected to be greatly affected by the composites' homogeneity and the solid interfacial connection between the hybrid nano film and the polymer network.

As shown in Table 2, there are some minor variations in the mechanical characteristics. It is clear that when the GO-ZnO concentration increased, there was a rising trend in both the tensile strength and Young's modulus. The Young's modulus of pure PVA is 104.409 MPa, which indicates substantial stiffness. However, the elongation at break is only 15.91% and the tensile strength is just 3.85 MPa. Adding 1% GO-ZnO makes the material very ductile; the rigidity goes down to 61.309 MPa, but the elongation at break goes up to 239.55%, which is a huge improvement. The tensile strength also increases, reaching 5.80 MPa. As the percentage of GO-ZnO in the nanocomposite increases to 3%, it finds its sweet spot, with a Young's modulus (104.842 MPa) that is almost identical to pure PVA and a very high elongation at break (239.39%). The ultimate tensile strength also rises significantly to 9.74 MPa. The composite demonstrates maximum tensile strength (10.50 MPa), continuously high elongation (239.79%), and slightly greater stiffness (106.763 MPa) with a 5% GO-ZnO loading, making it the best mechanically overall.

Table 2: Mechanical Properties of Pure PVA and PVA/GO-ZnO Nanocomposites

Sample Code	Young's Modulus (MPa)	Elongation at Break (%)	Tensile Strength (MPa)
Pure PVA	104.409	15.91	3.85
PVA/ GO-ZnO (1%)	61.309	239.55	5.80
PVA/ GO-ZnO (3%)	104.842	239.39	9.74
PVA/ GO-ZnO (5%)	106.763	239.79	10.50

Optical Characterization

The optical band gap shifts in response to a change in the polymer's molecular structure. Figure 4 shows that the UV-visible spectra absorption edge of the PVA/GO-ZnO NP nanocomposite films provides information on the optical band gap. To find the optical band gap, we extrapolated straight sections to the (hν) axis from the (αhν) 2 against (hν) plots, where α is the absorption coefficient and hν is the incoming energy of the light photon.

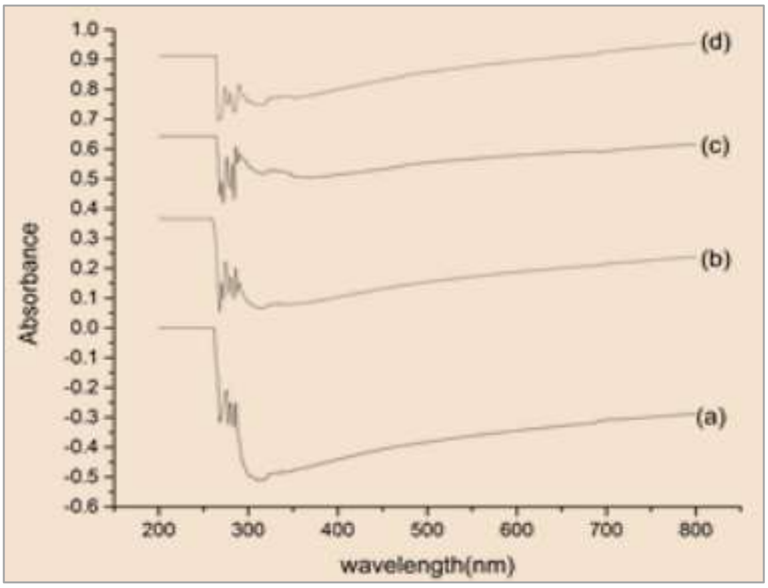

Figure 4: UV–Vis Absorption Spectra of (a) Pure PVA and PVA/GO–ZnO Nanocomposite Films with (b) 1 wt%, (c) 3 wt%, and (d) 5 wt% Filler Loadings

All of the nanocomposite films measured optical band gap energies are in Table 3. After incorporating 1% GO-ZnO, the optical band gap of pure PVA was found to be 4.52 eV. It is clear from Table 3 that band gap energies fall as the inclusion of nanoparticles increases, and it is displaced by 4.28 eV. A change in the crystal structure of the polymer network would be caused by the cross linking that occurred as a consequence of adding GO-ZnO nanoparticles to the amorphous section of the polymer matrix. The band gap energy is decreasing, which means that the polymer is becoming more conductive as the dose of nanoparticles rises.

Table 3: Optical Band Gap Energies of Pure PVA and PVA/GO-ZnO Nanocomposites

Sample Code	Band gap (eV)
Pure PVA	4.52
PVA/ GO-ZnO (1%)	4.28
PVA/ GO-ZnO (3%)	4.23
PVA/ GO-ZnO (5%)	4.21

V. CONCLUSION

There was a noticeable change in the mechanical, optical, structural, and thermal properties of the polymer matrix after adding GO-ZnO nanofillers. XRD testing verified that the nanofillers were evenly distributed and interacted with the PVA matrix. Investigations into thermal stability revealed that increasing the filler content resulted in better stability, less deterioration, and more resistance to heat breakdown. Mechanical testing showed that tensile strength and flexibility were significantly improved, particularly at loadings of 3 wt% and 5 wt%, suggesting that there were effective stress transmission and strong interfacial bonding. In addition, optical measurements revealed that the band gap energy decreased as the nanofiller concentration increased, indicating that the electrical conductivity of the nanocomposites improved. Overall, the 5 wt% GO-ZnO nanocomposites performed the best out of all the compositions.

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