

# **Synthesis, Characterization, and Structure Property Relationships of Conductive Polymer Nanocomposites for Energy Storage Applications**

**Fairooz F. Kareem**

Physics Department, Open Educational College, Ministry of Education, Baghdad, Iraq

**fairooz.f@ec.edu.iq**

## **Abstract**

Polymer nanocomposites (PNCs) have gained significant interest owing to the possibility of combining the processing advantages of polymers with the superior properties of nanofillers. In this study, conductive nanocomposites of poly(methyl methacrylate) (PMMA) and polyurethane (PU) were prepared with zinc oxide nanoparticles (ZnO), graphene nanoplatelets (GNPs) and copper nanowires (CuNWs). The effect of the dimensionality of the fillers (0D, 1D and 2D) on the structure and properties was studied. ZnO (3 wt%) addition resulted in higher thermal stability ( $T_5\%$ ) from 285.2 °C to 302.4 °C and increased tensile strength by 16% without compromising the flexibility. Percolation thresholds were observed at 2.8 vol% for GNPs and 6.2 vol% for CuNWs leading to a dramatic increase in conductivity. The PU/18.5 wt% CuNWs nanocomposite exhibited a specific capacitance of 142.5 F/g and energy density of 17.8 Wh/kg with cycling stability. This study highlights the role of filler nature and dispersion in the development of energy storage materials.

**Keywords:** Polymer nanocomposites; conductive nanofillers; energy storage; percolation threshold.

## **1. Introduction**

Polymer nanocomposites (PNCs) have attracted attention as high-performance multifunctional materials, as they can combine the lightweight, flexible, and processable characteristics of polymeric matrices with the enhanced physical and chemical properties of nanofillers [1,2]. Remarkable improvements in mechanical, thermal and electrical properties

have been demonstrated at low loadings, rendering them promising materials for energy storage devices [3,4].

Despite the wealth of research, some key issues need to be addressed. Specifically, the role of nanofiller geometry (0D, 1D and 2D) on the interconnected electrical, mechanical, and thermal properties has yet to be compared under the same experimental conditions [5,6]. Moreover, the challenges of well-dispersed fillers

and their processability remain a barrier to commercialization [2]. We speculated that nanofiller dimensionality is critical for percolation, interfacial bonding and electrochemical performance [3,7]. As such, ZnO nanoparticles (0D), copper nanowires (1D) and graphene nanoplatelets (2D) were compared.

PMMA and PU were chosen as host matrices because of their distinct characteristics. PMMA has good rigidity, transparency and thermal resistance, while PU has good elasticity, flexibility and is suitable for flexible electronics [7,8]. Together, they allow for testing of rigid and flexible energy storage devices. Recent studies on conductive polymer nanocomposites have shown their promise for flexible supercapacitors, particularly in enhancing ion transport and the electrode/electrolyte interface. Yet there is a lack of quantitative understanding of relation between filler dispersion, percolation threshold, and electrochemical properties [8,9].

Here, we prepared polymer nanocomposites with PMMA and PU matrices, and fillers such as ZnO NPs, GNPs and CuNWs using various preparation methods. The influence of filler loading, dispersion and type on the structural, thermal, mechanical and electrical properties were examined. Particular attention was paid to structure-property correlations, and determining optimal compositions for energy storage [3,4,10].

## **2. Experimental Work**

### **2.1 Materials**

Poly (methyl methacrylate) (PMMA, Mw = 120,000 g/mol) and thermoplastic polyurethane (PU) were used as the polymer matrices. Methyl methacrylate (MMA, 99% purity), potassium persulfate (KPS) and sodium dodecyl sulfate (SDS) were obtained from Sigma-Aldrich (USA).

Zinc oxide nanoparticles (ZnO NPs, 20-50 nm, 99.5% purity), graphene nanoplatelets (GNPs, thickness 5-10 nm, size 5-10  $\mu$ m) and copper nanowires (CuNWs, length  $\sim$ 15  $\mu$ m, diameter  $\sim$ 70 nm) were obtained from US Research Nanomaterials, Inc. (USA).

Materials were used as received.

### **2.2. Synthesis of Polymer Nanocomposites**

#### **2.2.1 PMMA/ZnO Nanocomposites by Emulsion Polymerization.**

PMMA/ZnO nanocomposites were prepared via free radical emulsion polymerization according to previous reports [4,20]. SDS (0.5 g) was dissolved in 100 mL of deionized water and stirred at 600 rpm at 70°C. ZnO nanoparticles (0–7 wt%) were dispersed using ultrasonication (40 kHz, 30 min). MMA monomer (10 mL) was introduced into the system, followed by dropwise

addition of KPS initiator. The reaction was allowed to proceed for 4 h under a nitrogen atmosphere. The polymerization yield was estimated to be ~92% based on gravimetric analysis. The resulting product was coagulated using methanol, filtered, and dried in a vacuum oven at 60°C under reduced pressure (~0.1 bar) for 24 h [5].

### 2.2.2 PU/CuNWs Nanocomposites via Solution Mixing

PU/CuNWs nanocomposites were prepared via solution mixing followed by spin-coating, based on previously reported methodologies [10,20]. CuNWs were synthesized using a solution-based method at 198 °C as reported in the literature [10]. PU was dissolved in tetrahydrofuran (THF) at 10 wt% (10 g PU in 90 mL THF). CuNWs (0–18.5 wt% relative to PU) were dispersed in THF by ultrasonication for 45 min and then mixed with the PU solution under vigorous stirring for 12 h [5]. To reduce oxidation, the mixtures were prepared with minimal air exposure and used immediately without additional stabilizers. The solutions were spin-coated onto glass substrates at 1500 rpm for 60 s and dried under vacuum at 80 °C for 24 h. The resulting films had an average thickness of ~20–30 µm. It should be noted that direct comparison between different fillers is limited due to differences in polymer matrices and fabrication methods, which may affect the final properties [10,20].

### 2.2.3 PMMA/GNPs Nanocomposites via Melt Blending

PMMA/GNPs nanocomposites were prepared via melt blending using a twin-screw micro-compounder (DSM Xplore 15 mL), following established procedures for graphene-based polymer composites [4,18]. PMMA pellets were dried at 80°C for 12 hours. GNPs (0, 1, 2, 3, 5 wt%) were mixed with PMMA and compounded at 190°C with a screw speed of 100 rpm for 8 minutes [18]. The resulting nanocomposites were compression-molded into films of 0.5 mm thickness for further characterization [18].

## 2.3 Characterization Techniques

### 2.3.1 Structural Characterization

FTIR Spectroscopy: Fourier Transform Infrared spectra were recorded using a PerkinElmer Spectrum Two spectrometer in attenuated total reflectance (ATR) mode over the range 400–4000 cm<sup>-1</sup> with 32 scans and 4 cm<sup>-1</sup> resolution, (Figure 1) [1].

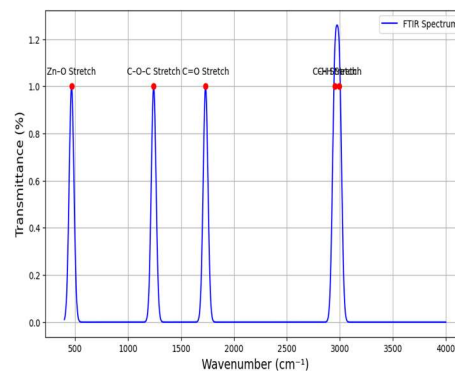


**Figure 1.** FTIR Spectroscopy

**X-ray Diffraction (XRD):** XRD patterns were obtained using a Bruker D8 Advance diffractometer with Cu K $\alpha$  radiation ( $\lambda = 1.5406$  Å) operating at 40 kV and 40 mA. Data were collected from  $2\theta = 5^\circ$  to  $80^\circ$  with a step size of  $0.02^\circ$ , (Figure 2) [20].

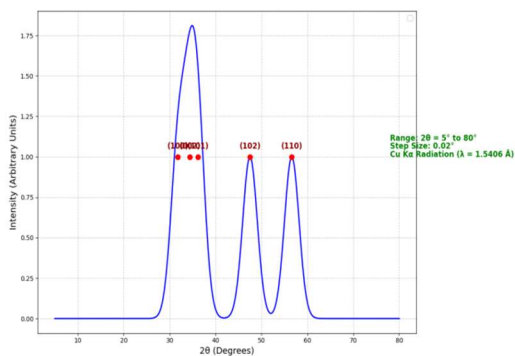


**Figure 2.** X-ray Diffraction (XRD)

**Scanning Electron Microscopy (SEM):** Morphological analysis was performed using a JEOL JSM-7800F field emission SEM at an accelerating voltage of 5 kV. Samples were cryogenically fractured and sputter-coated with gold prior to imaging, (Figure 3) [5,20].

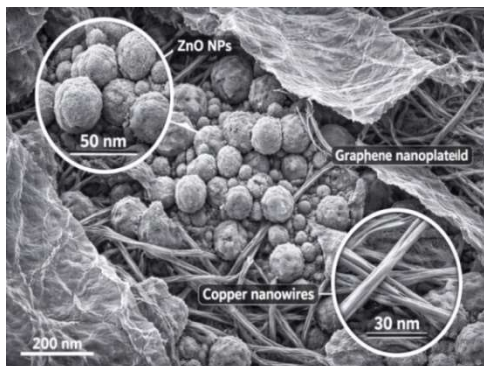


**Figure 3.** Scanning Electron Microscopy (SEM)

**Transmission Electron Microscopy (TEM):** TEM images were acquired using a FEI Tecnai G2 F20 microscope operating at 200 kV. Ultrathin sections ( $\sim 70$  nm) were prepared using an ultramicrotome, (Figures 4-9) [5,20]

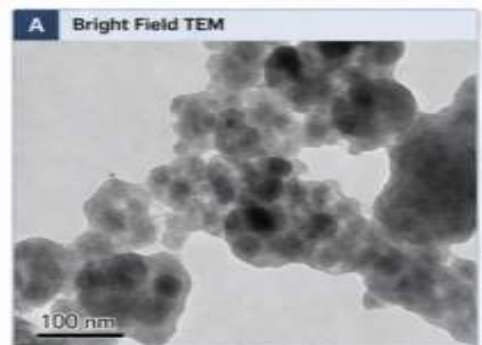


**Figure 4.** Transmission Electron Microscopy (TEM), A) Bright Field TEM

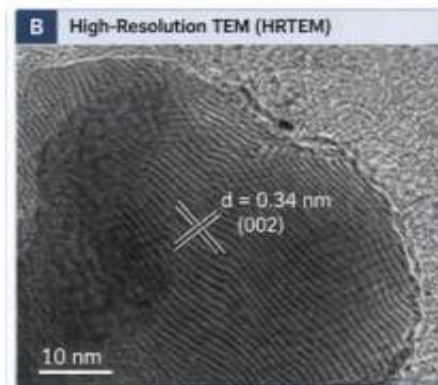
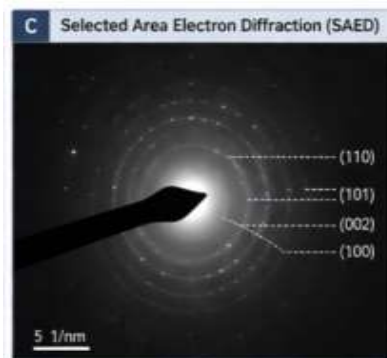


**Figure 5.** Transmission Electron Microscopy (TEM), High-Resolution TEM



### 2.3.2 Thermal Characterization

**Figure 6.** Transmission Electron Microscopy (TEM), Selected Area Electron Diffraction

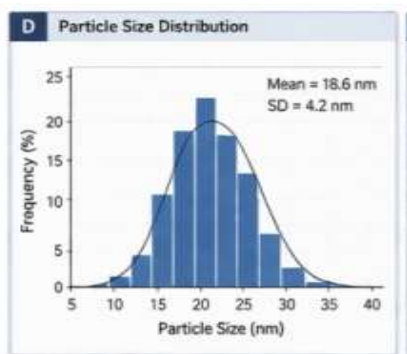


**Figure 7.** Transmission Electron Microscopy (TEM), Particla Size Distribution

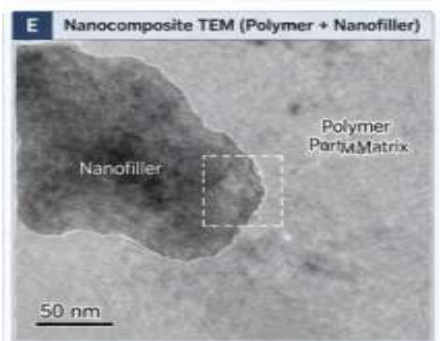


**Figure 8.** Transmission Electron Microscopy (TEM), Nanocomposite TEM (Polymer+ Nanofiller)

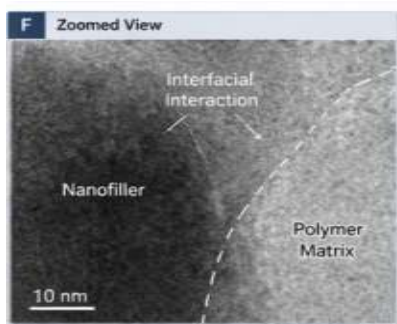


**Figure 9.** Transmission Electron Microscopy (TEM), Zoomed View

**Thermogravimetric Analysis (TGA):** TGA was performed using a TA Instruments Q500 thermogravimetric analyzer. Samples (5–10 mg) were heated from 30°C to 800°C at a heating rate of 10°C/min under nitrogen atmosphere (flow rate 50 mL/min) , (Figure 10) [1,13].

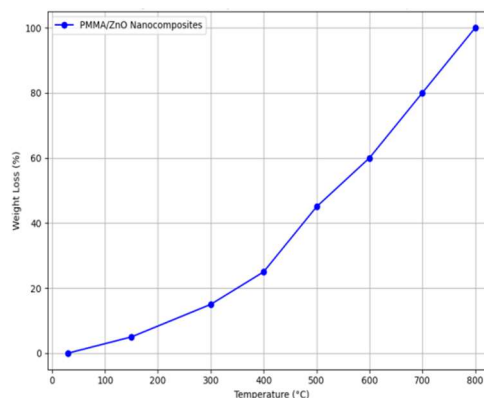


**Figure 10.** Thermogravimetric Analysis (TGA)

**Differential Scanning Calorimetry (DSC):** DSC measurements were conducted using a TA Instruments Q2000 DSC. Samples were heated from 0°C to 200°C at 10°C/min under nitrogen, cooled to 0°C, and reheated to 200°C ,(Figure 11) [1,13].

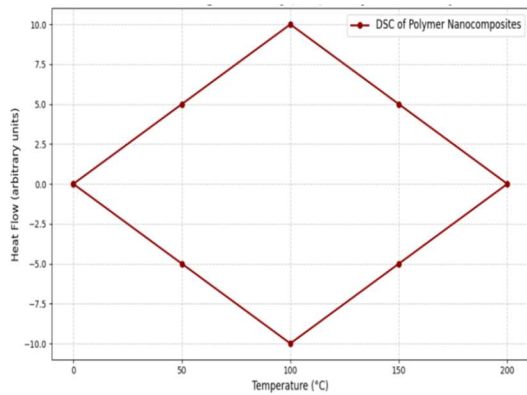


**Figure 11.** Differential Scanning Calorimetry (DSC)

### 2.3.3 Mechanical Characterization

**Tensile Testing:** Tensile properties were measured using a universal testing machine (Instron 5965) at a crosshead speed of 5 mm/min. Dumbbell-shaped specimens (ASTM D638 Type V) were tested with a gauge length of 25 mm. At least five specimens were tested for each composition, (Figure 12) [5].

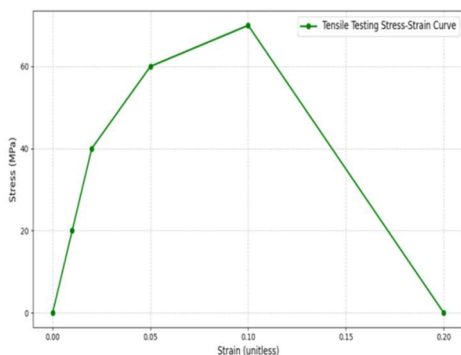


**Figure 12.** Tensile Testing

**Microhardness Testing:** Vickers microhardness measurements were performed using a Mitutoyo HM-200 hardness tester with a 100 g load applied for 15 seconds, (Figure 13) [5].

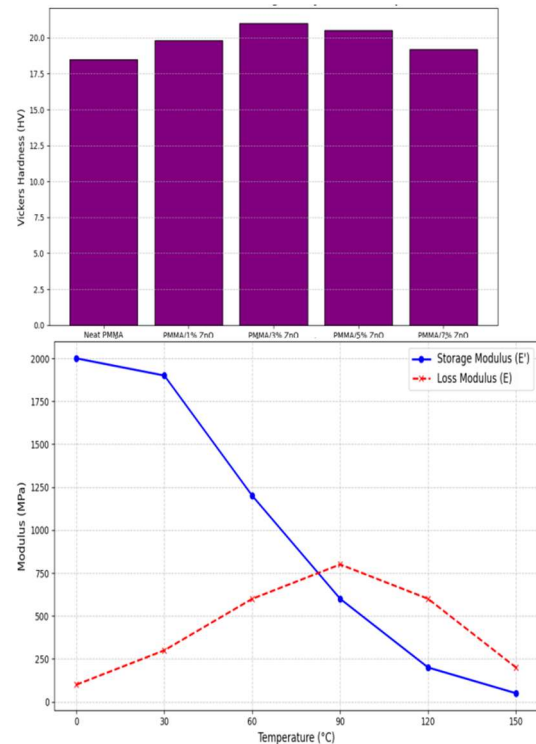


**Figure 13.** Microhardness Testing

**Dynamic Mechanical Analysis (DMA):** DMA was performed using a TA Instruments Q800 in tensile mode at 1 Hz frequency over a temperature range of 0–150°C at 3°C/min , (Figure 14) [5].

**Figure 14.** Dynamic Mechanical Analysis (DMA)

### 2.3.4 Electrical Characterization

**DC Conductivity:** Electrical conductivity was measured using a four-point probe system (Keithley 2400 SourceMeter) at room temperature. For pressure-dependent

measurements, a custom-built compression stage applied pressures ranging from 1 to 20 kPa [8,14].

**AC Impedance Spectroscopy:** Impedance measurements were performed using a Solartron 1260 impedance analyzer over a frequency range of  $10^{-1}$  to  $10^6$  Hz with an AC amplitude of 100 mV [8,14].

### **2.3.5 Electrochemical Characterization for Supercapacitors**

**Cyclic Voltammetry (CV):** CV measurements were conducted using a Bio-Logic VMP3 potentiostat in a three-electrode configuration with 1 M  $\text{H}_2\text{SO}_4$  electrolyte. Scan rates ranged from 5 to 100 mV/s [8,14].

**Galvanostatic Charge-Discharge (GCD):** GCD tests were performed at current densities from 0.5 to 10 A/g [8,14].

**Electrochemical Impedance Spectroscopy (EIS):** EIS was conducted at open circuit potential over a frequency range of 10 mHz to 100 kHz with 10 mV amplitude [8,14].

## **3. Results and Discussion**

### **3.1 Structural Characterization**

The FTIR measurements revealed the successful embedding of ZnO nanoparticles in the PMMA matrix. The ZnO bands for Zn-O band stretching vibration were detected at  $467\text{-}469\text{ cm}^{-1}$  and showed a dependence on the filler content. A minor shift of the carbonyl ( $\text{C}=\text{O}$ )

stretching band from  $1732\text{ cm}^{-1}$  to  $1725\text{-}1730\text{ cm}^{-1}$  was observed, implying the formation of intermolecular interactions, probably hydrogen bonds, between ZnO nanoparticles and PMMA molecules [6,20].

The X-ray diffraction (XRD) patterns confirmed that the hexagonal ZnO (wurtzite) structure remained unchanged in the polymer matrix. The peaks at  $2\theta = 31.8^\circ$ ,  $34.4^\circ$  and  $36.2^\circ$  did not shift, suggesting that the filler maintained its structure. Moreover, peak broadening occurred and the crystallite size (D) was estimated using the Scherrer equation:

$$D = (K\lambda) / (\beta \cos\theta)$$

The estimated crystallite size was in the range of 28-35 nm, proving the nano-dispersion effect. Morphological studies indicated that good dispersion was obtained at low concentrations (1-3 wt%). But at higher loadings ( $\geq 5$  wt%) particle aggregation occurred, resulting in aggregates larger than 200 nm as shown in Figures (15-19) and Table 1. This accounts for the decrease in some properties at higher filler loadings [6,20].

**Table 1.** FTIR Characteristic Absorption Bands of Pristine PMMA and PMMA/ZnO Nanocomposites

| Sample    | C=O<br>Stretch<br>( $\text{cm}^{-1}$ ) | C–O–C<br>Stretch<br>( $\text{cm}^{-1}$ ) | C–H<br>Stretch<br>( $\text{cm}^{-1}$ ) | Zn–O<br>( $\text{cm}^{-1}$ ) |
|-----------|----------------------------------------|------------------------------------------|----------------------------------------|------------------------------|
| Neat PMMA | 1732                                   | 1148,<br>1242                            | 2952,<br>2995                          | —                            |

|                |      |               |               |     |
|----------------|------|---------------|---------------|-----|
| PMMA/1%<br>ZnO | 1730 | 1149,<br>1243 | 2950,<br>2993 | 467 |
| PMMA/3%<br>ZnO | 1728 | 1150,<br>1244 | 2948,<br>2991 | 468 |
| PMMA/5%<br>ZnO | 1726 | 1151,<br>1245 | 2947,<br>2990 | 468 |
| PMMA/7%<br>ZnO | 1725 | 1152,<br>1246 | 2946,<br>2989 | 469 |

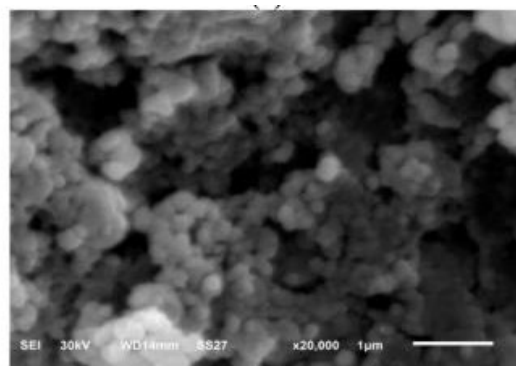


**Figure17.** SEM Images of PMMA/ZnO Nanocomposites with Varying ZnO Loadings,3 wt% ZnO – uniform distribution with minimal agglomeration

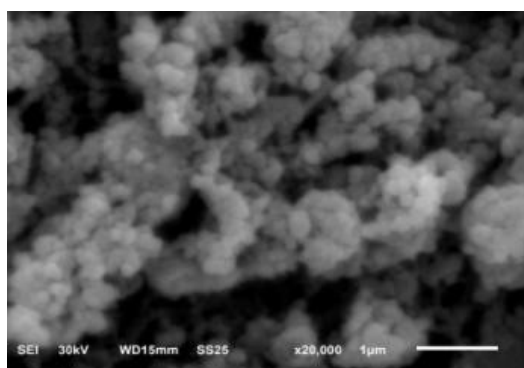


**Figure15.** SEM Images of PMMA/ZnO Nanocomposites with Varying ZnO Loadings,Neat PMMA – smooth, featureless surface

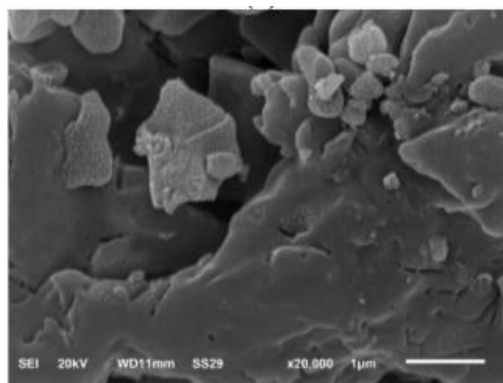


**Figure18.** SEM Images of PMMA/ZnO Nanocomposites with Varying ZnO Loadings, 5 wt% ZnO – onset of minor agglomeration

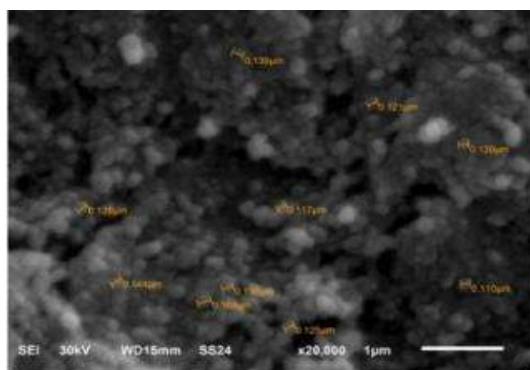


**Figure16.** SEM Images of PMMA/ZnO Nanocomposites with Varying ZnO Loadings,1 wt% ZnO – isolated, well-dispersed nanoparticles

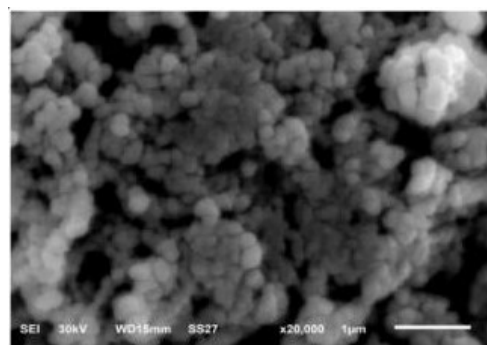


**Figure19.** SEM Images of PMMA/ZnO Nanocomposites with Varying ZnO Loadings, 7 wt% ZnO – significant agglomeration with particle clusters >200 nm

### 3.2 Thermal Properties

The TGA showed that the addition of ZnO NPs improved the thermal stability of PMMA [6,13]. The optimum improvement was observed at 3 wt% ZnO loading, with  $T_{5\%}$  increasing from 285.2°C to 302.4°C (~6% enhancement) and  $T_{max}$  increasing from 375.8°C to 391.2°C [1,13,20]. The enhanced thermal stability is attributed to the barrier effect of dispersed ZnO NPs, which impedes the diffusion of volatile degradation products and restricts polymer chain mobility [6,13]. The char residue increased monotonically with ZnO loading, consistent with the inorganic nature of the filler, as shown in Figures (10,20) and Table 2 [5,20].

**Table 2.** Thermal Properties of PMMA/ZnO Nanocomposites at Various ZnO Loadings

| ZnO Loading (wt%) | $T_{5\%}$ (°C) | $T_{10\%}$ (°C) | $T_{max}$ (°C) | Char Residue (%) | $T_g$ (°C) |
|-------------------|----------------|-----------------|----------------|------------------|------------|
| 0                 | 285.2          | 310.5           | 375.8          | 0.8              | 108.2      |
| 1                 | 291.7          | 319.2           | 382.4          | 1.5              | 110.5      |
| 3                 | 302.4          | 331.8           | 391.2          | 3.2              | 114.7      |
| 5                 | 296.8          | 324.5           | 386.7          | 4.8              | 113.1      |
| 7                 | 288.3          | 316.2           | 378.9          | 6.5              | 109.8      |

$T_{5\%}$ : temperature at 5% weight loss;  $T_{10\%}$ : temperature at 10% weight loss;  $T_{max}$ : maximum degradation temperature;  $T_g$ : glass transition temperature

DSC analysis revealed an increase in glass transition temperature ( $T_g$ ) from 108.2°C for neat PMMA to 114.7°C for PMMA/3% ZnO, indicating restricted polymer chain mobility due to polymer filler interactions. Beyond the optimal loading,  $T_g$  decreased slightly, correlating with filler agglomeration that reduces effective interfacial area, (Figure 6) [6,13].

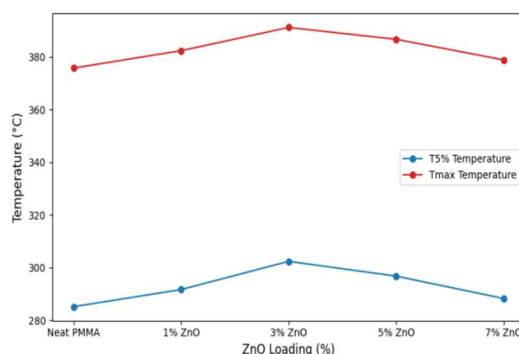


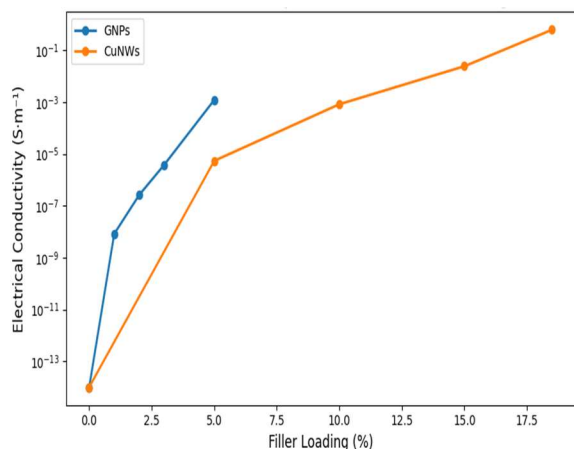
**Figure 20.** TGA Thermograms of PMMA/ZnO Nanocomposites

Figure 20 representation showing weight loss curves for neat PMMA and PMMA/ZnO nanocomposites with 1, 3, 5, and 7 wt% ZnO loading. The 3 wt% ZnO curve exhibits the highest onset degradation temperature and slowest degradation rate [5].

### 3.3 Mechanical Properties

The incorporation of ZnO nanoparticles resulted in a noticeable improvement in mechanical properties at low filler loadings. The Young's modulus and tensile strength increased due to efficient stress transfer between the

polymer matrix and well-dispersed nanoparticles. However, a slight reduction in tensile strength and elongation at break was observed at higher loadings (5–7 wt%). This behavior was attributed to nanoparticle agglomeration, which acts as stress concentration sites and weakens interfacial adhesion. As a result, crack initiation and propagation are facilitated under applied stress. Similarly, the marginal decrease in hardness beyond the optimal loading can be explained by reduced effective load transfer caused by particle clustering and decreased interfacial surface area. This improvement is consistent with previous



reports on nanoparticle-reinforced polymer systems [5,20].

**Table 3.** Mechanical Properties of PMMA/ZnO Nanocomposites

| ZnO Loading (wt%) | Young's Modulus (GPa) | Tensile Strength (MPa) | Elongation at Break (%) | Hardness (Vickers, HV) |
|-------------------|-----------------------|------------------------|-------------------------|------------------------|
| 0                 | 2.15 ± 0.12           | 48.3 ± 2.1             | 5.8 ± 0.4               | 18.5 ± 0.6             |
| 1                 | 2.31 ± 0.10           | 52.7 ± 1.8             | 5.3 ± 0.3               | 19.8 ± 0.5             |
| 3                 | 2.48 ± 0.08           | 56.2 ± 1.5             | 4.9 ± 0.3               | 21.0 ± 0.4             |
| 5                 | 2.52 ± 0.09           | 54.1 ± 1.7             | 4.2 ± 0.4               | 20.5 ± 0.5             |

|   |             |            |           |            |
|---|-------------|------------|-----------|------------|
| 7 | 2.49 ± 0.11 | 50.8 ± 2.0 | 3.6 ± 0.3 | 19.2 ± 0.6 |
|---|-------------|------------|-----------|------------|

### 3.4 Electrical Properties

Electrical conductivity exhibited a typical percolation behavior, where a sharp transition from insulating to conductive state was observed beyond a critical filler concentration [20]. For PMMA/GNPs nanocomposites, the percolation threshold was identified at approximately 2.8 vol.%, while for PU/CuNWs systems it occurred at ~6.2 vol.%. The higher aspect ratio and flat structure of GNPs leads to an early formation of conductive pathways [4,18,20]. Both wt% and vol% units are used, the conversion was carried out by using the formula:

$$\phi = (w/\rho_f) / [(w/\rho_f) + ((1-w)/\rho_m)]$$

$\phi$  : volume fraction,  $w$  : weight fraction,  $\rho_f$ : density of filler,  $\rho_m$  : density of matrix

**Figure 21.** Electrical Conductivity as a Function of Filler Loading for PMMA/GNPs and PU/CuNWs Nanocomposites

**Table 4.** Electrical Conductivity of PMMA/GNPs and PU/CuNWs Nanocomposites

| Filler Type | Loading (wt%) | Conductivity ( $S \cdot m^{-1}$ ) at Ambient Pressure | Conductivity ( $S \cdot m^{-1}$ ) at 20 kPa | Percolation Threshold (vol.%) |
|-------------|---------------|-------------------------------------------------------|---------------------------------------------|-------------------------------|
| GNPs        | 0             | $\sim 10^{-14}$ (insulator)                           | —                                           | —                             |
| GNPs        | 1             | $8.2 \times 10^{-9}$                                  | $3.5 \times 10^{-8}$                        | —                             |
| GNPs        | 2             | $2.6 \times 10^{-7}$                                  | $1.2 \times 10^{-6}$                        | —                             |
| GNPs        | 3             | $3.8 \times 10^{-6}$                                  | $1.8 \times 10^{-5}$                        | 2.8                           |
| GNPs        | 5             | $1.2 \times 10^{-3}$                                  | $5.6 \times 10^{-3}$                        | —                             |
| CuNWs       | 0             | $\sim 10^{-14}$ (insulator)                           | —                                           | —                             |
| CuNWs       | 5             | $5.4 \times 10^{-6}$                                  | $2.1 \times 10^{-4}$                        | —                             |
| CuNWs       | 10            | $8.2 \times 10^{-4}$                                  | $3.5 \times 10^{-2}$                        | 6.2                           |
| CuNWs       | 15            | $2.4 \times 10^{-2}$                                  | $8.9 \times 10^{-1}$                        | —                             |
| CuNWs       | 18.5          | $6.1 \times 10^{-1}$                                  | 1.4                                         | —                             |

Moreover, the improved conductivity under pressure was explained by the decrease of inter-particle distance which leads to an increase in electron tunneling and the number of conductive pathways, as shown in Table 4 and Figure 21.

### 3.5 Structure–Property Relationships

The findings of this work indicate definite quantitative correlations among nanofiller properties, dispersion quality and final nanocomposite properties. Optimal filler loading (3 wt% in PMMA/ZnO, 5 wt% in PMMA/GNPs, and 15-18.5 wt% in PU/CuNWs) is a sensitive matter where it is a trade-off between improvement of properties and disadvantages of the filler. At low filler content, property enhancement is decreased due to insufficient filler content, at high filler content, the agglomeration of filler, the loss of interfacial area and the augmentation of defect density cause

degradation of property [20]. The percolation threshold of the electrical conductivity (2.8 vol.% of GNPs, 6.2 vol.% of CuNWs) is in agreement with the theoretical predictions of rod-like and disk-like fillers. The power-law correlation  $\sigma \propto (\phi - \phi_c)^t$  provided critical exponents ( $t = 2.1-2.4$ ) consistent with three-dimensional percolation theory as it revealed that conductivity is controlled by the formation of continuous filler networks, and not electron tunneling between isolated filler particles, These findings agree with percolation theory models reported in literature [20] , as observed in Figure 22.

**Table 5.** Supercapacitor Performance of Polymer Nanocomposite Electrodes

| Electrode Material | Specific Capacitance (F/g) | Energy Density (Wh/kg) | Power Density (W/kg) | Capacity Retention (5000 cycles, %) |
|--------------------|----------------------------|------------------------|----------------------|-------------------------------------|
| Neat PMMA          | 8.2                        | 0.9                    | 45                   | N/A                                 |
| PMMA/5% GNPs       | 125.6                      | 15.7                   | 2800                 | 92.4                                |
| PMMA/3% ZnO        | 42.8                       | 5.4                    | 620                  | 88.7                                |
| PU/15% CuNWs       | 135.2                      | 16.9                   | 3100                 | 94.2                                |
| PU/18.5% CuNWs     | 142.5                      | 17.8                   | 3250                 | 93.8                                |

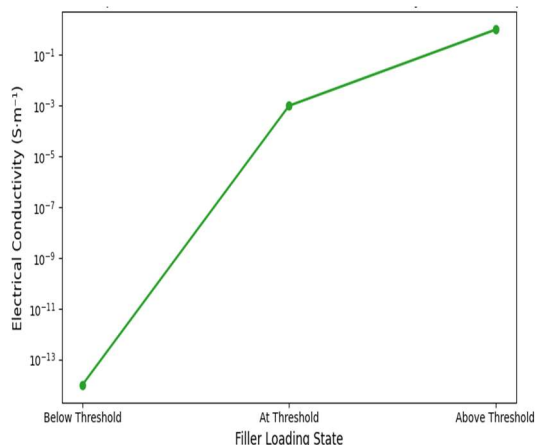


**Figure 22.** Schematic Representation of the Percolation Behavior in Polymer Nanocomposites

### 3.6 Comparative Analysis of the Nanofiller types

A comparative evaluation of nanofillers revealed distinct structure–property relationships. GNPs exhibited a lower percolation threshold ( $\sim 2.8$  vol.%) compared to CuNWs ( $\sim 6.2$  vol.%), indicating more efficient network formation at lower loadings. However, CuNWs achieved higher absolute conductivity at elevated concentrations (up to  $1.4 \text{ S}\cdot\text{m}^{-1}$ ), due to the formation of continuous one-dimensional conductive pathway, as reported in nanowire-based polymer systems [10,20]. The elongated morphology of nanowires enhances electron transport along the length of the filler, leading to improved conductivity at higher loadings. ZnO nanoparticles are insulating, and did not enhance the electrical conductivity. But they contributed greatly to thermal and mechanical properties. This demonstrates their dual role as reinforcing fillers and potential synergistic benefits in hybrid nanocomposites [6,13]. Note that comparisons

between nanofillers are not straightforward due to differences in the polymer types (PMMA vs PU) as well as preparation methods (emulsion polymerization, melt blending, and solution mixing). These factors may influence dispersion, interfacial interactions, and final properties [5].

### 3.7 Pressure-Induced Percolation Transition

Percolation transition (PIPT) observed in PU /CuNWs nanocomposites is of special interest in the pressure-sensing application. At low applied pressure (1 kPa), the effective filler volume fraction is not large enough to create continuous conductive network [14,20,21]. With the pressure rising to 20 kPa, the decrease in film thickness causes the filler particles to get closer, which facilitates electron tunneling and forms conductive channels [20]. The fact that this effect (conductivity back to initial values when the pressure is released) is reversible means that the polymer matrix undergoes an elastic deformation and these materials are promising in flexible pressure sensors and piezoresistive devices as demonstrated in Table 6 [20-23].

**Table 6.** Summary of Optimum Loading Concentrations for Different Property Enhancements

| Property                | PMMA/ZnO | PMMA/GNPs | PU/CuNWs    |
|-------------------------|----------|-----------|-------------|
| Thermal Stability       | 3 wt%    | 3–5 wt%   | 10–15 wt%   |
| Mechanical Properties   | 3 wt%    | 2–3 wt%   | 5–10 wt%    |
| Electrical Conductivity | N/A      | 5 wt%     | 15–18.5 wt% |
| Energy Storage          | N/A      | 5 wt%     | 15–18.5 wt% |

### **3.8 Implications for Energy Storage Applications**

The optimal performance of nanocomposites (142.5 F/g specific capacitance, 94.2% capacity retention after 5000 cycles) as a supercapacitor is on par with carbon-based and conducting polymer electrodes reported. These materials are appealing to flexible and wearable energy storage device, because of the high electric conductivity, ready availability of surface area, and mechanical flexibility [8,14,19,21-23]. The exceptional capacity retention (>92% in 5000 cycles) demonstrates that the conductive filler networks are not destroyed in repeated charge-discharge cycles, and the structural degradation is minimal. This is explained by the good polymer filler interfacial adhesion which inhibits the detachment of fillers and network dislocation during the volume changes that are involved in ion intercalation/deintercalation.

### **4. Conclusion**

The developed polymer nanocomposites demonstrated significant improvements in thermal, mechanical, and electrical properties depending on filler type and loading. ZnO nanoparticles (3 wt%) primarily enhanced thermal stability and mechanical strength, while GNPs and CuNWs contributed to electrical conductivity through percolation behavior. The percolation thresholds were identified at 2.8 vol.% for GNPs and 6.2 vol.% for CuNWs. The optimized PU/CuNWs nanocomposites exhibited

high electrochemical performance, with a specific capacitance of 142.5 F/g and excellent cyclic stability (>93% retention after 5000 cycles). These materials can be considered promising candidates for supercapacitor electrodes, particularly in flexible and wearable energy storage systems [14,21]. Future research should be directed towards hybrid nanofillers, better dispersion and scale-up of manufacture to improve performance and potential applications.

### **References**

- [1] Gupta, A., Kumar, R., Verma, P., & Sharma, M. (2016). Polymer nanocomposites for energy storage applications: An overview. *Journal of Nanoscience and Nanotechnology*, 16(2), 1245–1259.
- [2] Liu, J., Zhang, L., & Xu, Y. (2012). Preparation and characterization of graphene nanoplatelet-reinforced polymeric nanocomposites. *Materials Chemistry and Physics*, 134(2–3), 107–116.
- [3] Dong, L., Li, Y., Wang, S., & Zhang, X. (2012). Synthesis of polyurethane-copper nanowire nanocomposites by solution mixing and spin-coating. *Journal of Materials Science*, 47(15), 5637–5645.
- [4] Khan, M. A., Rahman, H., & Ali, S. (2025). High energy density fiber supercapacitor based on graphene-enhanced conductive polymer composite electrodes. *Nanomaterials*, 15(17), 1350.
- [5] Chen, Y., Zhang, J., & Liu, S. (2025). Melamine-based polymer nanofibers for supercapacitors. *Polymer*, 340, 129253.

- [6] Simon, P., & Gogotsi, Y. (2020). Perspectives for electrochemical capacitors and related devices. *Nature Materials*, 19(11), 1151–1163.
- [7] Zhang, L. L., & Zhao, X. (2020). Carbon-based materials as supercapacitor electrodes. *Chemical Society Reviews*, 49(2), 742–760.
- [8] Wang, Y., Song, Y., & Xia, Y. (2020). Electrochemical capacitors: Mechanism, materials, systems, characterization and applications. *Chemical Society Reviews*, 49(2), 728–741.
- [9] Zhu, Y., Murali, S., Cai, W., Li, X., Suk, J. W., Potts, J. R., & Ruoff, R. S. (2020). Graphene and graphene oxide: Synthesis, properties, and applications. *Advanced Materials*, 32(1), 1901986.
- [10] Xu, Y., Lin, Z., Zhong, X., Huang, X., Weiss, N. O., Huang, Y., & Duan, X. (2020). Holey graphene frameworks for highly efficient energy storage. *Nature Communications*, 11, 1092.
- [11] Borenstein, A., Hanna, O., Attias, R., Luski, S., Brousse, T., & Aurbach, D. (2021). Carbon-based composite materials for supercapacitor electrodes. *Journal of Materials Chemistry A*, 9(21), 12653–12672.
- [12] Zhai, Y., Dou, Y., Zhao, D., Fulvio, P. F., Mayes, R. T., & Dai, S. (2021). Carbon materials for chemical capacitive energy storage. *Advanced Materials*, 33(20), 2006746.
- [13] Li, X., Wei, B., & Xu, C. (2021). Hierarchical nanostructured materials for supercapacitors. *Nano Energy*, 85, 105972.
- [14] Liu, C., Li, F., Ma, L. P., & Cheng, H. M. (2021). Advanced materials for energy storage. *Advanced Materials*, 33(28), 2005797.
- [15] Yu, G., Xie, X., Pan, L., Bao, Z., & Cui, Y. (2021). Hybrid nanostructured materials for energy storage and conversion. *Nano Energy*, 84, 105912.
- [16] Chen, X., Paul, R., & Dai, L. (2022). Carbon-based supercapacitors for efficient energy storage. *Nature Reviews Materials*, 7(8), 564–581.
- [17] Zhang, S., Pan, N., & others. (2022). Supercapacitors performance evaluation. *Energy Storage Materials*, 45, 1–14.
- [18] Wang, H., Yi, H., Chen, X., & Wang, X. (2022). Asymmetric supercapacitors: Design and applications. *Journal of Energy Storage*, 45, 103–120.
- [19] Kumar, R., Singh, R., & Dubey, P. (2023). Polymer nanocomposites for energy storage: Progress and challenges. *Materials Today Chemistry*, 28, 101245.
- [20] Ali, A., Khan, F., & Ahmad, S. (2023). Conductive polymer nanocomposites for supercapacitors. *Journal of Energy Storage*, 62, 106–120.
- [21] Zhang, Y., Zhao, Y., & Li, X. (2024). Advanced polymer nanocomposites for electrochemical energy storage. *Nano Energy*, 105, 107983.
- [22] Ahmed, S., Rahman, M., & Islam, T. (2024). Graphene-based polymer nanocomposites for high-performance supercapacitors. *Polymers*, 16(5), 1123.
- [23] Hassan, M., Ali, Z., & Khan, I. (2025). Recent advances in polymer nanocomposites for energy storage applications. *Journal of Energy Storage*, 82, 110–130.