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Evaluation of Synthesis and Characterization of Polystyrene, Polycarbazole and TTIP Nanofiber via Electrospinning Process

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***Abstract*— In the present study, Polystyrene/Polycarbazole/Titanium Tetra-Isopropoxide (PS/PCZ/TTIP) composite nanofibres were successfully fabricated using the electrospinning technique. The morphological features and material properties of the synthesized fibres were systematically characterized using scanning electron microscopy (SEM), energy-dispersive X-ray analysis (EDAX), X-ray diffraction (XRD), and UV–Visible absorption spectroscopy.. Polystyrene, a synthetic polymer available in both solid and foamed forms, present avenue for material innovation. Characterized by its transparency, rigidity, and ease of processing, PS offers unique properties for various applications. PCZ holds great promise as organic semiconductors for a multitude of vital applications, owing to their customizable physical and chemical properties, mechanical flexibility, lightweight nature, reversible doping capabilities, excellent biocompatibility, and ability to be produced on a large scale. Titanium tetra iso-propoxide (TTIP) is a precursor, with exceptional performance characteristics. The research work is carried out to study the effect of these hybrid polymers using morphological and optical properties. Further the IV analysis, Electrochemical Impedance (EIS), Photoelectrochemical analysis and Mott-Schottky plot analysis were carried out for nanofibers in the range of nm diameter for gas sensing, insulating applications.**

***Keywords*— insulating polymer, conductive polymer, electrospinning, nano fibres.**

I. INTRODUCTION

The fabrication of nanocomposites with precisely controlled morphology and tailored properties has become a significant area of research in recent years. Electrospinning is an effective and versatile technique widely employed for producing nanofibrous structures with uniform morphology and large surface area. In this process, a high electric potential in the range of 15–25 kV is applied to a polymer solution, causing the solution jet to undergo continuous stretching and splitting into finer streams. These elongated jets subsequently solidify into ultrafine polymer fibers and are deposited onto a collector substrate. The fiber diameter may range from several micrometers to a few nanometers, depending on factors such as polymer characteristics, applied voltage, and surrounding experimental conditions. Owing to their nanoscale dimensions, electro spun fibers exhibit a substantially higher surface-area-to-volume ratio compared to conventional continuous thin films. Tamil Selvan Ramadoss and coauthors [1] Researchers have utilized low-cost atactic polystyrene (aPS) as a base polymer for the fabrication of functional nanofibers through the electrospinning process.

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The morphology of the produced fibres was examined using field-emission scanning electron microscopy (FESEM), and a novel approach for pressure sensor fabrication was proposed. The developed sensor was tested under varying pressure conditions, and its electrical as well as mechanical responses were systematically evaluated.

Seema Agarwal and co-authors[2] reported that the electrospinning technique enables the production of nonwoven nanofibrous structures with fibre diameters in the nanometre range, high surface area, facile functionalization capability, and enhanced mechanical performance. Among its diverse application domains, biomedical engineering has emerged as a prominent field, while other applications include filtration systems, protective materials, electrical and optical devices, sensors, and nanofibre-reinforced composites.

Firas K Mohamad Alosfur et al [3] have reported on the TiO2 Titanium dioxide (TiO_2) is a widely studied semiconductor material owing to its distinctive electronic and optical characteristics. It has found extensive applications in pigments, food-related products, and photocatalytic systems. TiO_2 exists in three major crystalline forms, namely anatase, rutile, and brookite. Among these phases, anatase is considered metastable, whereas rutile exhibits superior chemical stability.

The electronic structure and charge transport behaviour of TiO_2 are significantly influenced by factors such as crystalline phase, surface condition, and atomic composition. In recent years, considerable attention has been directed toward the use of TiO_2 as a photocatalyst because of its appropriate band-gap energy, typically below 3.5 eV. Several studies have reported that the anatase phase of TiO_2 possesses an indirect band-gap structure, making it highly suitable for photocatalytic applications..

Namsheer K and Chandra Sekhar Rout [4] have reviewed different Conducting polymers, along with the transport models describing their conduction mechanisms, have been extensively investigated to understand their charge transport behaviour and functional performance. Various synthesis methods and the associated physical characteristics, including electrical, optical, and mechanical properties, have also been widely reported. In recent years, significant advancements have been achieved in their applications such as energy storage devices, photocatalytic systems, anti-corrosion coatings, biomedical technologies, and sensing platforms. Furthermore, the structural characteristics of the composites strongly influence their overall performance and functional efficiency.

Tadeusz Dziubak and Sebastian Dominik Dziubak [5] Researchers have reported that thin nanofibrous layers, typically with thicknesses ranging from 1 to 5 μm, possess comparatively lower mechanical strength and durability. Therefore, these nanofibre layers are generally deposited onto conventional filter substrates with greater thickness and structural stability. The nanofibres may be coated on either one or both surfaces of the supporting filter medium, such as cellulose, nylon, or polyester. Incorporation of nanofibrous layers into air filtration systems used in motor vehicles has been shown to considerably enhance particle separation efficiency and overall filtration performance.

Thermal properties of electrospun polyvinylpyrrolidone/titanium tetraisopropoxide composite nanofibers are reported by Orsolya Ke´ri[6] . The morphology and the properties of the fibers were investigated by SEM, Raman spectroscopy, and XRD.

Carbazole as Conductive polymer, polystyrene as insulating polymer and filler TTIP with different ratios were used for electrospinning process. The SEM, XRD, FTIR and optical properties were obtained for different ratio of the filler with base solution.

From the literature survey carried out a nano fibre from Polystyrene, Polycarbazole and TTIP can be produced which have the properties suitable for sensing applications.

II. EXPERIMENT

A. Materials

Polystyrene and carbazole from Aldrich were purchased from Padmashree Chemicals Pvt. Ltd, Mysuru. Polystyrene and TTIP is used as received. Polycarbazole was synthesised from carbazole using precipitate method. Distilled water is used for all the process carried out.

B. Polycarbazole synthesis

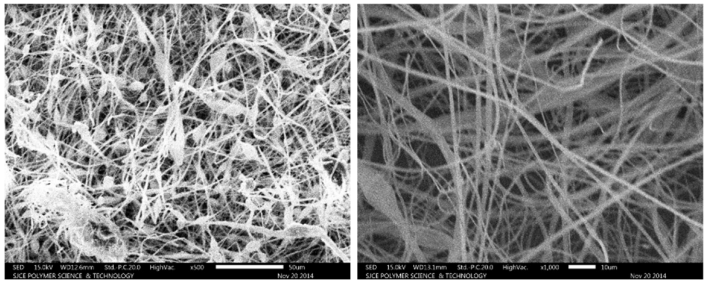
In the first method, Carbazole was used as purchased. In this approach, a precursor solution was prepared by dissolving 4 g of carbazole in 96 mL of dichloromethane (DCM). Separately, 15 g of polystyrene was dissolved in 85 mL of dimethylformamide (DMF). Both solutions were subsequently combined to obtain a homogeneous base solution, which is illustrated in Figure 1.

Figure1: Base solution prepared using direct method.

In the second method, A 60 mM carbazole solution was prepared in 250 mL of dichloromethane (DCM), while 1.2 M ammonium persulfate (APS) was dissolved in 0.5 M HCl solution. The carbazole solution was gradually introduced into the acidic APS solution under continuous stirring. The resulting mixture was maintained at room temperature for 24 h to facilitate polymerization. Subsequently, the obtained product was separated through filtration, and the precipitate formed was dried under ambient atmospheric conditions. The synthesized polycarbazole (PCZ) precipitate was then incorporated into a polystyrene solution prepared using dimethylformamide (DMF) as the solvent. The mixture was stirred continuously for 2 h to achieve uniform dispersion. The prepared solution was further utilized for the electrospinning process, carried out at an applied voltage ranging from 20 to 25 kV and a solution flow rate of 5 mL/h. The prepared precursor solution containing the synthesized precipitate is presented in Figure 2.

Figure2: Base solution prepared using precipitate method.

The base solution (combination of PS and PCZ) using precipitate method was considered for electrospinning process as SEM analysis showed a bead free structure compared to direct method of preparation. The comparison of both SEM images is shown in figure 3.



(a) direct method (b) Precipitate method

Figure 3: SEM images of Base solution (PCZ+PS) Nanofibers by

IV. Results and Discussion

The base solution (PS+PCZ) solution with precursor Titanium isopropoxide is considered for Electrospinning the nanofiber. Fibers are spun for the different ratios of polymer with filler as 10wt%, 20wt% and 30wt%. Electrospinning process was carried out for the prepared polymer solutions at 20KV-25KV with flow rate of

5ml/hr. The produced Electrospun nanofibers samples with different ratios were analysed by taking SEM images, EDAX, XRD, FTIR, UV-Vis absorption analysis. The below table shows the different concentration of the filler added to the base solution.

TABLE I: SAMPLES WITH FILLER CONCENTRATION

Sl. No	Samples	Concentration
1	T0	PS+PCZ (0 Wt%)
2	T1	PS+PCZ+TTIP (10 Wt%)
3	T2	PS+PCZ+TTIP (20 Wt%)
4	T3	PS+PCZ+TTIP (30 Wt%)

A. SEM analysis

Scanning Electron Microscopy (SEM) is an efficient and highly accurate characterization technique used to investigate the surface morphology and microstructural features of materials. The method generates high-resolution images by scanning a focused electron beam over the specimen surface and detecting the emitted secondary or backscattered electrons. SEM enables detailed examination of characteristics such as surface uniformity, fibre distribution, and thickness. In the present study, SEM analysis was performed for different compositions of the base polymer incorporated with filler materials.

Figure 4 shows the SEM analysis of the samples with different weight ratios of the filler. It is observed that the nanofibers electrospun through spinning process produces nanofibers in the diameter of few nm. As the filler concentration increased fibers diameters reduced. The diameter range is from 1.32micrometer to 140 nanometers.

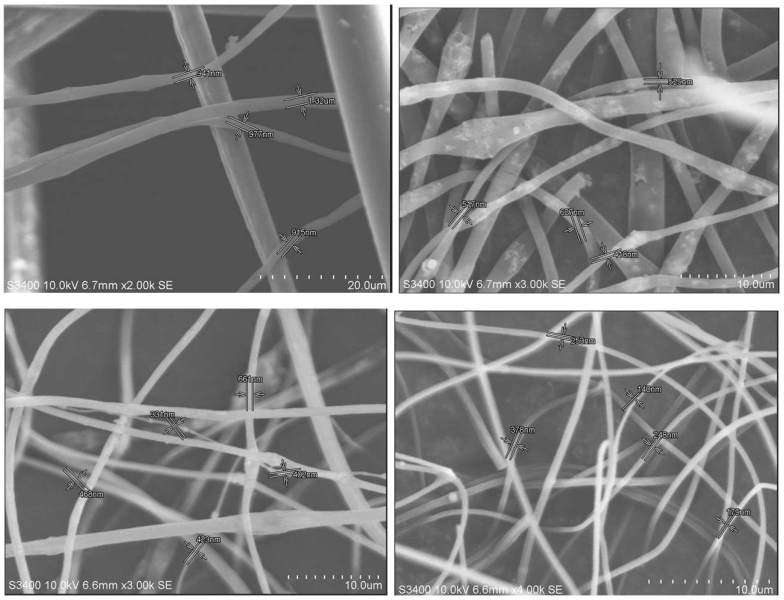


Fig 4: SEM images of the samples with a) 0wt%b)10 wt% c)20wt% and d) 30wt%

B. EDAX Analysis

Energy Dispersive X-ray Spectroscopy (EDS/EDAX) integrated with scanning electron microscopy enables the identification and quantification of elemental composition on the sample surface through the detection of characteristic X-ray emissions. In this technique, a focused electron beam generated from an electron source is accelerated at a selected energy and directed onto the sample surface using electromagnetic lenses. The interaction between the incident electrons and the sample atoms produces various signals, including backscattered electrons and secondary electrons. Backscattered electrons arise due to the deflection of incident electrons by atomic electric fields, whereas secondary electrons are emitted from the sample surface following electron collisions.

Simultaneously, the electron–matter interaction results in the emission of characteristic X-ray photons, which are analyzed to determine the chemical elements present within the irradiated region. The obtained X-ray spectra

provide qualitative as well as quantitative information, including elemental concentrations in atomic percentage and weight percentage. In addition, elemental mapping can be performed to visualize the spatial distribution of different elements across the sample surface. Figure 5 presents the EDAX spectra of the prepared samples, while Table 2 summarizes the elemental composition in terms of weight percentage. The obtained results confirm the successful incorporation of PS/PCZ/TiO_2 components within the electrospun nanofibres.

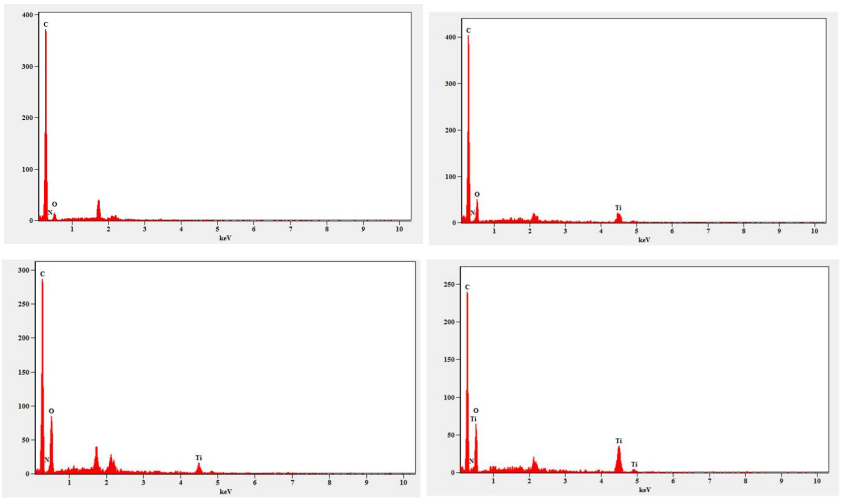


Fig 5: EDAX images of the samples with a) 0wt% b)10 wt% c)20wt% and d) 30wt%

TABLE II: THE CHEMICAL COMPOSITION IN WEIGHT % OF DIFFERENT SAMPLES

Samples	Elements	Weight %
T0	C, N, O	75.64,14.65, 9.70
T1	C, N, O, Ti	71.11, 0.00, 23.16, 5.74
T2	C, N, O, Ti	53.07, 7.12, 37.30, 2.51
T3	C, N, O, Ti	54.71, 1.59, 34.88, 8.83

C. FTIR Analysis

Fourier Transform Infrared Spectroscopy (FTIR) is a widely employed analytical technique used to identify functional groups present in gaseous, liquid, and solid materials through the interaction of infrared radiation with chemical bonds. The technique measures the absorption of infrared energy by molecular bonds, producing a spectrum generally represented as percentage transmittance versus wavenumber (cm^{-1}). Figure 6 illustrates the FTIR spectra obtained for the prepared materials and various sample compositions. FTIR analysis primarily investigates molecular vibrational behaviour, where specific functional groups exhibit characteristic absorption bands corresponding to their fundamental vibrational modes. These absorption peaks provide valuable information regarding the chemical structure and bonding characteristics of the samples.

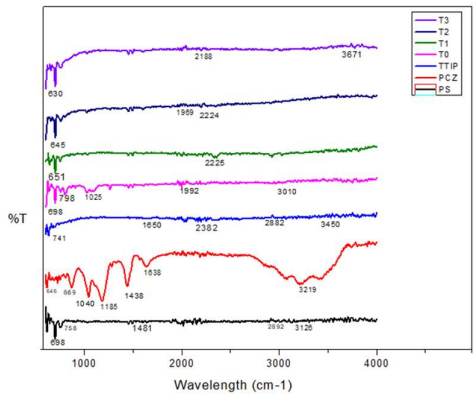


Fig 6: FTIR analysis of the samples

D. XRD Analysis

X-ray Diffraction (XRD) analysis of crystalline materials typically produces diffraction patterns containing sharp, narrow, and well-defined peaks that correspond to their ordered crystal structures. In contrast, amorphous materials generally exhibit broad humps, diffuse peaks, or noisy patterns due to the absence of long-range structural order. Many polymeric materials display semi-crystalline characteristics and therefore generate halo-like diffraction patterns accompanied by partially defined peaks. XRD analysis can also be employed to evaluate the degree of crystallinity by comparing the integrated intensity of the amorphous background with that of the crystalline diffraction peaks. Figure 7 illustrates the XRD patterns obtained for the different prepared samples

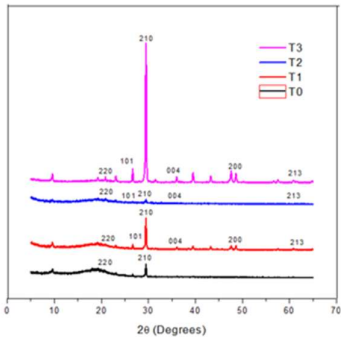


Fig 7: XRD of the samples

E. UV – Vis Analysis

UV-Vis (Ultraviolet-Visible) spectroscopy is a widely used analytical technique for measuring the absorbance or transmittance of light by a sample in the UV (200–400 nm) and visible (400–700 nm) regions of the electromagnetic spectrum. Figure 7(a) shows the absorbance with respect to wavelength of the samples electrospun. When photons of energy hν (where h is Planck's constant and ν is frequency) hit a semiconductor, If hν≥Eg electrons absorb the photon energy and jump from the valence band to the conduction band. The absorption edge (sudden increase in absorbance) is related to the band gap energy. To determine the band gap energy from UV-Vis data, the Tauc relation given in equation 1 is used

$(\alpha h\nu)^n = A(h\nu - Eg)$.....(1)

α = absorption coefficient

hν = photon energy (in eV)

A = constant

Eg = optical band gap

n = exponent depending on the nature of the transition

Fig 7(b) shows the indirect band gap of the samples w.r.t the wavelength. The **Tauc equation** for an indirect band gap is

$(\alpha h\nu)1/2 = A(h\nu - Eg)$.....(2)

Where α = absorption coefficient

hν = photon energy (in eV)

A = constant

Eg = optical band gap

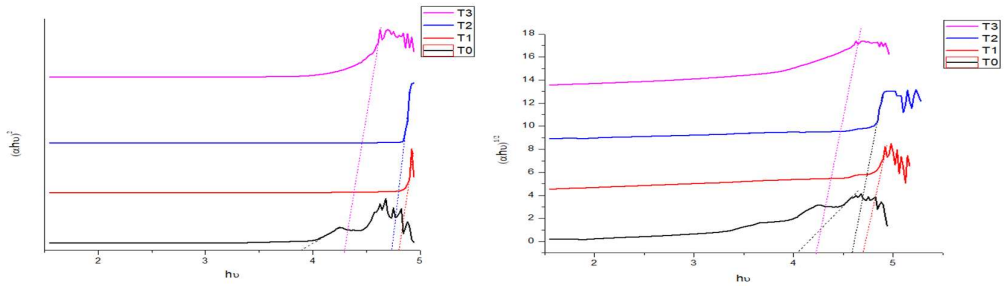


Fig 7: Direct band gap and indirect band gap energy Plot for Samples

TABLE III: COMPARISON OF DIRECT AND INDIRECT BAND GAPES

Nanofiber Samples	Direct band gap Eg (eV)	Indirect band gap Eg (eV)
T0	3.85	4.009
T1	4.87	4.73
T2	4.82	4.72
T3	4.32	4.37

The samples exhibit similar values of direct and indirect band gaps. Choosing a direct or indirect band gap material is based on how the application uses or manipulates light or carriers, not just on the band gap value.

F. Contact angle measurement

Contact angle measurement is an effective way to investigate solid surface properties. The surface wettability is inversely proportional to the contact angle and reduction in the contact angle improves the surface wettability leading to a CHF (critical heat flux (CHF) enhancement. Contact angles can provide information about surface hydrophobicity, heterogeneity, roughness, liquid surface tension and line tension.

$$CHF \propto \boldsymbol{cos}(\theta) \ldots (\mathbf{2})$$

Equation 2 gives relation between CHF and contact angle. As θ decreases, cos(θ) increases, enhancing CHF and vice versa. Figure 8 shows the images of different samples for contact angle measurement. The samples exhibited hydrophobicity with contact angle values 115.38, 126.98,109.37, 106.54 respectively.

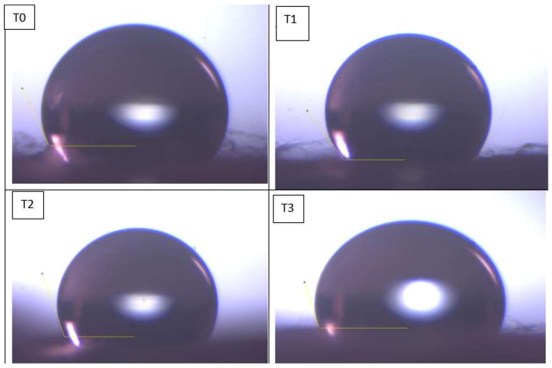


Fig 8: Contact angle measurement of different sample ratios

G. EIS (Electrochemical Impedance Spectroscopy).

Electrochemical Impedance Spectroscopy (EIS) is an effective analytical method used to obtain kinetic and mechanistic information from a wide range of electrochemical systems. The technique has been extensively applied in areas such as corrosion analysis, semiconductor research, energy storage and conversion devices, chemical and biosensors, as well as non-invasive diagnostic applications. EIS operates as a transfer-function-based technique in which the response signal, either alternating current (AC) or alternating voltage, is analyzed with respect to the applied AC excitation over a broad frequency range.The linear portion observed at higher values of the real impedance component (Z′) is generally attributed to diffusion-controlled electrochemical processes occurring within the material or at the electrode–electrolyte interface.

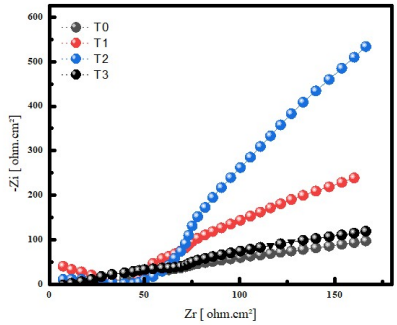


Fig 9: EIS of the samples

H. VI Characteristics

The VI characteristics (Voltage-Current characteristics) of polymer samples refer to how the current (I) flowing through a polymer material varies with the applied voltage (V). This relationship can reveal the electrical behavior of the polymer — whether it behaves like an insulator, conductor, or a semiconductor. The current and voltage are linear for the samples T0,T1,T2 but T3 exhibits some non- linear behaviour. This is may be because of the DC input. The Ohmic region of a material's VI characteristics is where the current increases linearly with voltage, following Ohm's Law. The conductive materials in nanocomposites can be used for gas sensing applications.

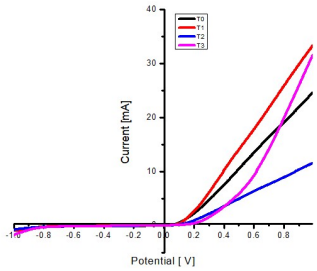


Fig 10: VI characteristics of the nano composite samples

I. Mott- Schottky Analysis

Mott-Schottky analysis is an electrochemical technique used primarily to characterize semiconducting materials, especially in photoelectrochemical (PEC) cells, solar cells, and corrosion studies. It helps determine to Flat-band potential (Vfb), Doping density (donor or acceptor concentration), Type of semiconductor (n-type or p-type). It is based on the capacitance–voltage (C–V) relationship at the semiconductor–electrolyte interface.
The Mott-Schottky equation is:

$$\frac{1}{C^2} = \frac{2}{\varepsilon\varepsilon_0 eN}\left(V - V_{fb} - \frac{kT}{e}\right) \quad \textbf{(3)}$$

Where
C=Capacitance of the space-charge region
ε=Dielectric constant of the semiconductor
ε0=Vacuum permittivity
N=Doping concentration
V=Applied potential
Vfb=Flat-band potential
K=Boltzmann constant
T=Temperature
The flat band potential of the nano composite samples are shown in the table 3. Flat band potential is a crucial parameter in designing photoelectrochemical (PEC) cells, solar cells, and semiconductor-electrolyte interfaces, as it relates to the position of the conduction and valence bands with respect to a reference electrode

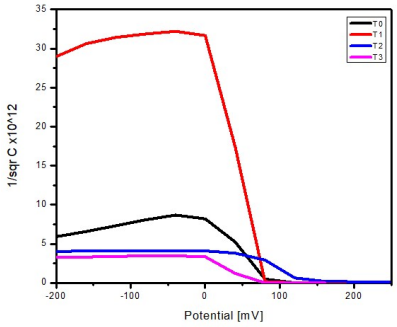


Fig 11: Mott- Schottky analysis of the samples

TABLE IV: FLAT BAND POTENTIAL OF THE SAMPLES

Sl. No	Samples	Flat band potential (Efb) (v)
1	T0	0.081
2	T1	0.079
3	T2	0.122
4	T3	0.072

J. PEC

Photoelectrochemical (PEC) analysis is a technique used to study the light-driven electrochemical behavior of semiconducting materials. It is especially useful for evaluating materials for applications like water splitting , solar cells etc. Mott-Schottky provides electronic parameters that help explain PEC behavior. Flat-band potential conveys the beginning of the PEC activity. Here the sample T1 showed a photo current value of 53.5 micrpamperes.

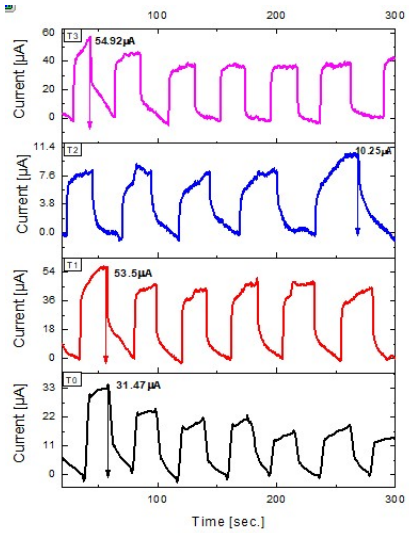


Fig 12: The graphs show a periodic pattern in the photocurrent, indicating a cyclic response to an external stimulus

V. CONCLUSION

The XRD analysis confirms the structural nature and crystallinity of the prepared material. The presence of sharp and intense diffraction peaks indicates the existence of crystalline phases, while the broad halo pattern suggests the presence of amorphous or semi-crystalline regions in the polymer matrix. The obtained diffraction pattern demonstrates that the material possesses semi-crystalline characteristics with both ordered and disordered molecular arrangements. Furthermore, the variation in peak intensity and broadness indicates changes in crystallinity due to filler incorporation and intermolecular interactions within the composite. Overall, the XRD results verify the successful formation of the composite structure and reveal its suitability for dielectric and EMI shielding applications, where controlled crystallinity and phase distribution play a significant role in determining electrical and thermal performance.

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