Investigation of Enhanced Thermal and Optical Properties of TiO_2 Nanofiller-Incorporated Lithium-Based PVC/PMMA Nanocomposite Polymer Electrolytes

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Abstract

In this study, PVC + PMMA + Li_2Co_3 + TiO_2 Nanocomposite Polymer electrolytes synthesized using solution casting method. Differential Scanning Calorimetry (DSC) and UV-Visible spectroscopy are the techniques utilized to characterise that synthesized material to analyse their thermal and optical properties of prepared samples. The thermal properties ware analysed by using Differential Scanning Calorimetry (DSC) characterization technique that indicates about Glass Transition (Tg), Crystallization Temp (Tc) and Melting Temp (Tm) of synthesised material. The optical properties of the prepared samples were analysed by using UV-Visible spectroscopy which gives information about absorption edge, direct and indirect band gaps of the PPLT. It has been noted that using TiO_2 nanofillers in lithium-ion batteries enhances their thermal, optical and electrical properties.

Keywords

Polymer, PVC, PMMA, Salt Li_2Co_3, Nano filler TiO_2, DSC and UV-visible etc.

I.Introduction

The tremendous growth in portable electronics, flexible displays, and energy storage technologies has intensified the demand for advanced electrolytes that are both reliable and versatile [1&2]. Traditional liquid electrolytes provide excellent ionic conductivity; however, they suffer from critical drawbacks such as leakage, flammability, and poor mechanical endurance, particularly under flexible or harsh operating conditions [3]. To that end polymer electrolytes have put forth as a better and more flexible option which is what we see today for improved safety and mechanical performance [4]. We also note that in terms of types of polymer electrolytes we have solid, gel, and composite which present unique benefits which play to the specific requirements of the application at hand [5–7]. In that regard we see that among the group of composite polymer electrolytes (CPEs) there has been great interest in them because of which we see in they are able to include inorganic nanofillers into the polymer structure. What this does is enhance ionic conductance also at the same time improve thermal stability and device performance [8&9].

The incorporation of titanium dioxide (TiO_2) monolayers has dazling photocatalytic activity alongside the inability to slide over one another polymer–salt matrices that helps eliminate the discrete layers of polymer–salt crystallinity and helps to increase the amorphous fraction and ion mobility [11&12]. In addition, the unique structural and chemical characteristics of TiO_2 nanosized material used as polymer–TiO_2 salts framework improve the spatial confinement of polymer composites within the swollen state that can result in core–shell polymer–salt composites. [13&14]. This set of properties renders the TiO_2 monolayers as multifunctional fillers to TiO_2 systems that can improve optical and electronic coupling to and from the fillers with little added to the polymeric backbone. Such monolayers can resolve gaps in device integration electronics with energy storage systems. The integration of such monolayers fabricates elastic optoelectronic devices augmented with energy stowage systems. Such devices can profoundly reduce the weight of solar energy stowage devices.[15].

This research evaluates polymer blend electrolytes made from PVC/PMMA with lithium carbonate and dispersed TiO_2 nano fillers. The choice of host matrix is strategic: PVC provides the structural integrity while PMMA provides the optical clarity and flexibility which gives an equilibrium hybrid system [4]. Lithium carbonate provides the lithium ions and the TiO_2 nanoparticles act as functional fillers to enhance the polymers thermally and optically [5&13] To make the films, the solution was cast and the resulting homogeneous structures were characterized using Differential Scanning Calorimetry (DSC) and UV-Visible spectroscopy. The purpose is to extend the multifunctional polymer electrolytes to contemporary advanced uses by determining the effect of nano TiO_2 on the film's thermal stability and the films optical band gap.

II.Experimental setup and methodology

Materials

PVC and PMMA polymers of analytical grade were purchased and not purified. The active fillers were the salt dopant lithium carbonate (Li_2CO_3) and spaced TiO_2 nanoparticles. Tetrahydrofuran (THF) and acetone were used as solvents in order to allow adequate dissolution and mixing of the ingredients. The reasons of using PVC and PMMA are in their complementary nature; one material has rigidity and chemical resistance (PVC), and other processes and transparency (PMMA). The ionic carriers needed are introduced by Li_2CO_3; TiO_2 takes the responsibility of thermal stabilizer and optical modifier.

Preparation of Nanocomposite polymer electrolytes:

Solution casting technique was used in the creation of polymer blend films as it is known to generate smooth thin films. PVC and PMMA were weighed in 7:3 percent mass ratio in the initial step and then dissolved in 50mL of THF with continuous stirring until homogeneous mixture. Then, 0.3g of Li_2CO_3 was added and fully dissolved. TiO_2 nanoparticles were added in changeable concentrations 0.1 g (PPLT10), 0.15 g (PPLT15), and 0.2 g (PPLT20). All of the mixtures were stirred long to dispersive the nanofillers in the polymers-salt matrix. The solutions thus obtained were mattered into clean Petri dishes which were left to evaporate at the room temperature. Consistent thickness had been achieved and solid films were obtained after 24 hours and kept in desiccators and then before characterization. Prepared samples were labelled as shown in Table 1.

Table 1: Represents the weight of materials that used in preparation of sample

S. No	Sample name	PVC	PMMA	Li_2Co_3	TiO_2
1	PPLT10	0.7g	0.3g	0.3g	0.1g
2	PPLT15	0.7g	0.3g	0.3g	0.15g
3	PPLT20	0.7g	0.3g	0.3g	0.2g

III.Result and discussion

Thermal Studies by DSC:

The DSC thermograms showed explicit reliance on concentration of TiO_2 as shown in Figure 1. In the case of the PPLT10 sample, the Tg was noted at around 61.3 ºC and derivatively Tc/Tm was 174.8 ºC/221.6 ºC. When the TiO_2 content was raised, significant improvements portions were obtained: PPLT15 and PPLT20 had the highest stability, namely, Tg, Tc, and Tm 70.1ºC, 192.5 ºC and 235.9 ºC respectively as shown in Table 2. This evolution is indicative that TiO_2 nanoparticles operate as thermal reinforcers, constraining the mobility of polymer chain and pin solidifying crystalline domain. Also, superior filler gives sharper endothermic peaks ensured a higher crystallinity level. The existence of covalent cover layers at filler interface must have also contributed to such thermal improvements by suppressing segmental relaxation and favouring ordered packing. Therefore, the obtained readings of DSC confirm that the concentration of TiO_2 improves the electrical stability of thermal qualities and crystallinity of PVC/PMMA/Li_2CO_3.

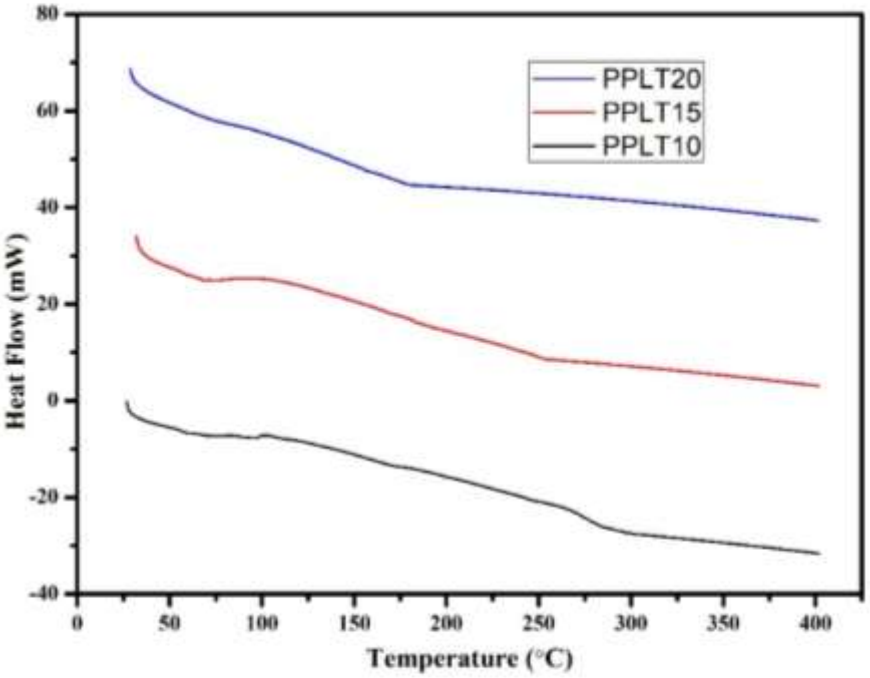

Figure 1: DSC curves of PPLT10, PPLT15, and PPLT20 samples.

Sample	Glass Transition (Tg)	Crystallization Temp (Tc)	Melting Temp (Tm)
PPLT10	61.3 °C	174.8 °C	221.6 °C
PPLT15	65.7 °C	183.2 °C	228.4 °C
PPLT20	70.1 °C	192.5 °C	235.9 °C

Table 2: Represents the Glass Transition (Tg), Crystallization Temp (Tc), and Melting Temp (Tm) of PPLT10, PPLT15, and PPLT20 samples

UV–Visible Spectroscopy

The optical absorption spectra showed that there was great UV absorbance in all the samples with the maximal reducing in the visible region. Sample with the greatest TiO_2 (PPLT20) exhibited greatly high TiO_2 absorbance, in line with the innate property of TiO_2 to block UV and its amplified consequential scattering, in the polymer network. Absorption edges were analysed and its systematic decrease was seen as 2.62 eV (PPLT10) to 2.35 eV (PPLT20), revealing characteristic band gap narrowing as shown in Table 3. The direct bandgap dropped to 2.45 eV instead of 2.56 eV and the indirect bandgap dropped by 1.90 eV rather than 2.18 eV. Such red shifts are explained by the augmentation of structural chaos and upgraded filler polymer connections that make sideways electronic conditions close to the bands edge. These changes are beneficial in photovoltaic and optoelectronic applications since these materials expand the spectral responsive region of the material. The UV Vis analysis, together as a network, indicates that the incorporation of TiO_2 besides increasing UV absorbance, fine tuning the electronic band structure of the composite system.

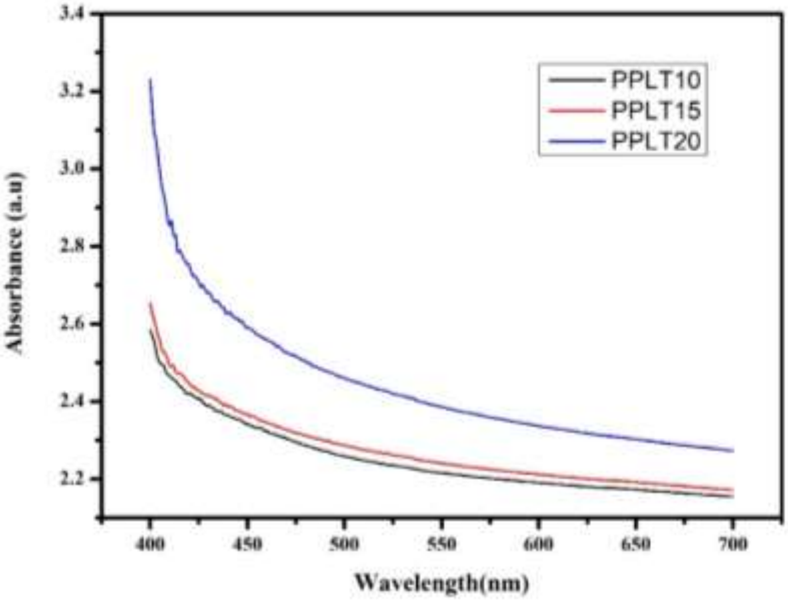

Figure 2: UV-Visible: Wavelength vs Absorbance curves of PPLT10, PPLT15, and PPLT20 samples.

The above graph shows that the absorption edge of PPLT10, PPLT15 and PPLT20 shifts at 2.62 eV down to 2.35 eV and the band gap is narrowed. This shift allows the absorption of lower-energy light, probably as a result of compositional or structural changes.

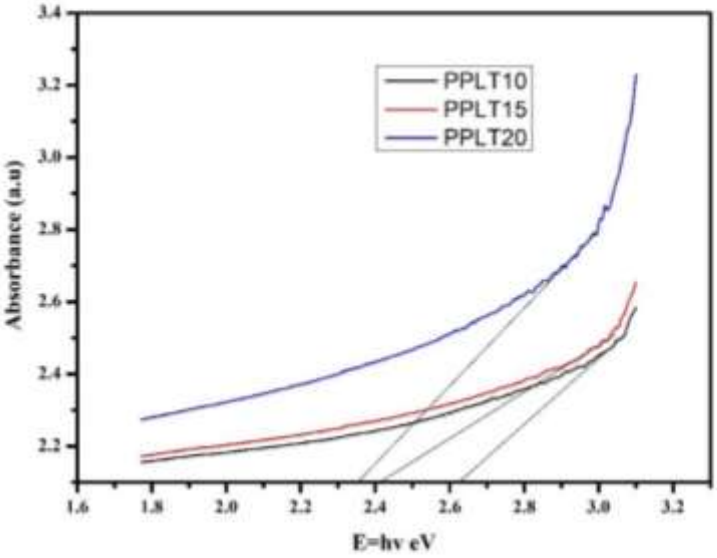

Figure 3: UV-Visible: Absorption Energy Edge vs Absorbance curves of PPLT10, PPLT15, and PPLT20 samples.

Figure 3 describes about absorbance vs photon energy (E = hv) of PPLT10, PPLT15, and PPLT20 are plotted in the graph. Absorption edges are seen at 2.62 eV (PPLT10), 2.50 eV (PPLT15) and 2.35 eV (PPLT20). This negative slope shows progressive reduction in band gap separation, PPLT20 is the lowest band gap.

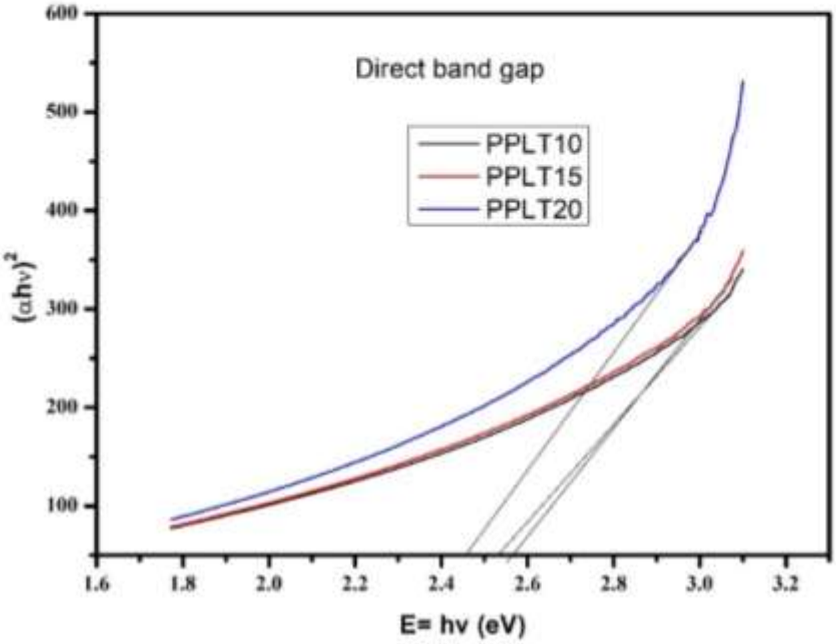

Figure 4: UV-Visible: Direct band gap of PPLT10, PPLT15, and PPLT20 samples

This figure 4 illustrates the Tauc plot $(\alpha h\nu)^n$ vs photon energy ($E = h\nu$) of PPLT10, PPLT15, and PPLT20, which is employed to obtain the direct band gap. The extrapolated linear regions cut the energy axis at 2.62 eV of PPLT10, 2.5 eV of PPLT15, and 2.35 eV of PPLT20. A decrease in band gap with the band sample variation is a gradual process and it shows greater absorption of lower energy photons.

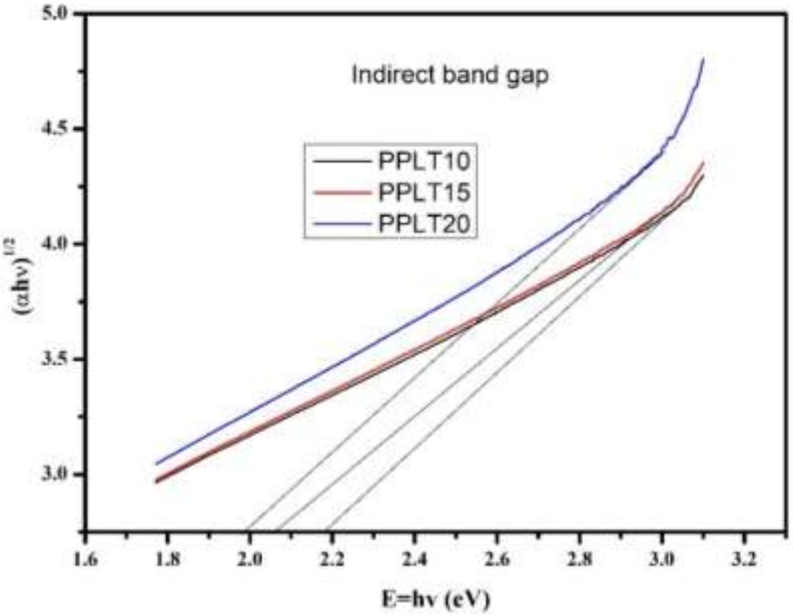

Figure 5: UV-Visible: Indirect band gap of PPLT10, PPLT15, and PPLT20 samples.

The above graph is the Tauc plot $(\alpha h\nu)^{1/2}$ vs photon energy ($E = h\nu$) of PPLT10, PPLT15, and PPLT20, to estimate the indirect band gap. The extended straight-line regions lie on the energy axis 2.45 eV (PPLT10), 2.40 eV (PPLT15), and 2.25 eV (PPLT20). Such a systematic decrease in the indirect band gap with variation in sample may indicate enhanced absorption of lower-energy photons.

Table 3: Represents the Absorption Edge, Direct band gap and Indirect band gap of PPLT10, PPLT15, and PPLT20 samples

Sample	Absorption Edge (eV)	Direct Band Gap (eV)	Indirect Band Gap (eV)
PPLT10	2.62	2.56	2.18
PPLT15	2.41	2.53	2.06
PPLT20	2.35	2.45	1.90

IV.Conclusion

On incorporation of TiO_2 nanofillers in the polymer electrolyte ($PVC/PMMA/Li_2CO_3$) thermal stability and optical characteristics are greatly enhanced. PPLT20 has the highest thermal stability of the samples tested, lower transition temperatures and a higher heat endurance as indicated by DSC, particularly in high-power applications like solid-state batteries and in flex electronics.

UV-Vis optical analysis showed increased absorbance and decreased bandgap as TiO_2 increased, as crystallinity and electronic structure were improved. This increases interaction between light and matter and collection of photons. On balance, the stability and narrow bandgaps of TiO_2-based PVC/PMMA/Li_2CO_3 electrolytes indicate their advantages in the energy storage, optoelectronics, and the flexible devices.

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