

Fabrication, Thermal, Morphological and Rheological Studies on Novel Organic-Inorganic Hybrid Composites of Cetylpyridinium Chloride-Modified Montmorillonite Incorporated PEO/PMMA Blend

¹Mohammad Saleem Khan, ^{1,2}Sabiha Sultana, ³Imran Rehan, ⁴Kamran Rehan, ⁵Noor-ul-Amin ¹Gul Tiaz Khan and ¹Abdul Shakoor

¹National Centre of Excellence in Physical Chemistry, University of Peshawar, Pakistan.

²Department of Chemistry, Govt. College Women University, Faisalabad, Pakistan.

³Department of Applied Physics, FUUAST Islamabad, Pakistan.

⁴Wuhan Institute of Physics and Mathematics, UCAS China.

⁵Department of Chemistry, Abdul Wali Khan University Mardan, Pakistan.

saba_rehan2006@yahoo.com*

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Summary: Ion-conducting thin film polymeric electrolytes were synthesized by mixing high molecular weight Poly(ethylene oxide) (PEO), poly(methyl methacrylate) (PMMA) as a polymer matrix, Cetylpyridinium chloride (CPC) modified montmorillonite (MMT) as a filler, and with varying content of LiClO₄ by solution casting technique. The thermal, morphological and rheological properties of the electrolytes were evaluated by using (Thermogravimetric / Differential Thermal Analysis (TG/DTA), Quick Thermal Conductivity Meter (QTM), Scanning Electron Microscopy (SEM), and Rheometer techniques respectively. The addition of CPC-modified clay to the polymeric electrolytes showed better dispersion at 3.5 wt. % of salt and resulted in enhanced thermal performance. The thermal conductivity of thin films was found to be very sensitive to the amount of clay addition in the system, and showed a linear decrease with the increasing clay content in the system. High MW PMMA incorporation at 50 wt. % to the composite system of PEO resulted in the agglomeration of clay particles in the composite system.

Keywords: Poly(ethylene oxide), Poly(methyl methacrylate), Cetylpyridinium chloride, Montmorillonite, Rheological properties, Thermogravimetric / Differential Thermal Analysis, Quick Thermal Conductivity Meter, Scanning Electron Microscopy

Introduction

The hunt for superior materials has introduced a huge number of new materials. Now-a-days polymers enjoy major position though they have been introduced very recently in the field of material sciences. In uniqueness of their performance, application scenario and multiplicity, composite materials offer innovation and flexibility which is hard to find in conventional materials. Composite are engineered substances resulted from multiple constituents with quite different chemical or physical properties. These properties remain distinct and separate within the finished material. Overall performance characteristics of composites exceed the characteristics properties of individual components. The properties of constituents have high impact on composite properties. The component which is normally in excess is called the matrix while the other components present in small proportions are called reinforcement. The factors affecting the properties of composites are fiber dispersion and their aspect ratio (geometry and orientation) within the composites, volume fraction of fiber and interface quality between the matrices and reinforcing fibers [1, 2]. Combining properties of organic and inorganic

components in a composite material is a new challenge in the field of nanotechnology. These composites have been expected to find applications in many fields including optics, electronics, biology, Ionics, mechanics, membranes protective coatings, catalysis, sensors [3-5]. The development of new polymers, blends, composites and advanced materials becomes necessity for modification of mechanical, electrical, optical and thermal properties to fulfil the required characteristics. An extensive literature on the synthesis and characterization of different polymeric composites are available and many more are being in progress [6]. Montmorillonite can advance successfully the thermal performance and toughness of polymeric matrix [7]. That is why composite of PEO/clay has been studied in detail from time to time. However, to our knowledge the published literature shows that no experimental data regarding the effect of Cetylpyridinium Chloride (CPC) modified Montmorillonite (MMT) clay on the thermal, morphological and rheological studies of PEO/Salt and PEO/PMMA/Salt system has been reported so far. In the present study, therefore, we focused on the synthesis of the subject materials

*To whom all correspondence should be addressed.

under different concentrations of inorganic particles, and devised an optimum composition for the electrolyte system. This work is believed to explore new ways of technological applications of these composites.

Experimental

Materials

Poly (methyl methacrylate) (PMMA) and Poly (ethylene Oxide) (PEO) (MW 6×10^5 g/mol) were procured from BDH and Acros chemicals correspondingly. Montmorillonite (clay) Of K10 grade with CAS #1318-93-0 (CEC 89 meq/100g and surface area 220-270 m²/g) was supplied by Aldrich chemicals. (Lithium Perchlorate) (LiClO₄) of high purity (Research grade) was purchased from Acros chemicals. All these chemicals and polymers were not subjected to further refinement. Acetonitrile (CH₃CN) being a superior solvent for polymers (PEO and PMMA), montmorillonite and salt, was employed as a solvent.

Modification of Clay

One shortcoming associated with MMT is its hydrophilic nature for applications in polymeric electrolytes. One way to evade this problem is its cationic modification. Organic cations are being investigated by the scientists to explore their capability to formulate organophilic compounds from hydrophilic clays. In our system clay was subjected to organic modifications by taking 50 ml of millipore water and 1g of MMT in a beaker (100 ml) containing 780 mg of n-hexadecylpyridinium chloride monohydrate [C₂₁H₃₈N⁺ Cl].H₂O also known as cetylpyridinium chloride (CPC). This mixture was agitated briskly for eight h and then strained and rinsed with millipore water. The modified MMT (CPMMT) was dried out at 60 °C in a vacuum oven for 24 h [8]

Fabrication of PEO Composite and PEO Blend Composite Films

2% solution of polymers (PEO, PMMA) was prepared by dissolving these polymers singly in CH₃CN. Different volumes of 1 M LiClO₄ and CPMMT were incorporated with constant volume of 2% polymer solutions, following uninterrupted stirring at 60 °C for 24 h. These solutions were then shifted to Petri dishes of standardized diameter, kept on flat and level surfaces, sheltered with lids at room temperature for transforming into uniform smooth films of PEO / CPMMT (3.3 wt. %) / LiClO₄ (2.1,

3.5,5 wt. %) and PMMA / PEO (50 wt. %) / CPMMT (3.3 wt. %) / LiClO₄ (2.1, 3.5,5 wt. %) coded as PCS1, PCS2, PCS3 and PPCS1, PPCS2, PPCS3 respectively. For rheological study 7% polymer solution (P0) was mixed with LiClO₄ and CPMMT in acetonitrile in proportions as PEO/ LiClO₄ (2.1, 3.5 and 5 wt. %), PEO/ CPMMT (3.3 wt. %) /LiClO₄ (2.1, 3.5, 5 wt. %) coded as PS1.PS2 and PS3 and PCS1, PCS2, PCS3 respectively.

Morphological Study

Scanning Electron Microscopy was done by SEM instrument Micro analyzer Model JSM 5910. The surfaces of the film were made conducting by coating with gold (Au). The samples were viewed through the microscope, and were then analyzed using computer software. The elemental analyses were conducted by energy dispersive X-ray analyzer (EDX) Inca Oxford. A suitable magnification was chosen for obtaining micrographs.

Thermal Stability and Thermal Conductivity Analysis

Table-1: Thermal conductivities of reference substances.

S No.	Reference Substances	Thermal Conductivities (Wm ⁻¹ K ⁻¹)	
		Reported value	Measured value
1	Silicon	0.22-0.26	0.2385
2	Polyethylene	0.10-0.21	0.0395
3	Quartz	1.39-1.49	1.4156

Thermal characterization was carried out in the temperature range of 0°C to 650°C with a heating rate of 10 °C/ min using Thermal Gravimetric Analyzer (TGA) Perkin Elmer Model 6300. QTM was employed for determination of thermal conductance (TC) of a specimen. The principle of TC analysis is variation in thermal conductance which varies with alteration in temperature by decreasing or increasing the magnitude of electric current. The study was conducted at room temperature. For this purpose films were cut into 50 mm X 100 mm rectangular forms. TC measurement was conducted using QTM (Model SOFT_QTM 5EW, Japan). TC of each specimen was examined utilizing three standard materials of known TC. The standards utilized for this function are given in Table-1.

Rheological Analysis

The shear viscosity studies were undertaken using Physica MCR 301, with temperature range (°C) of -150-1000, Torque resolution (nNm) of 0.1 and measuring system of PP25/PP50 with 1mm of measuring gap, and Frequency range of 10⁻⁵ to 100 Hz. All calculations were done by Rheoplus software installed in the system under internally controlled thermal conditions.

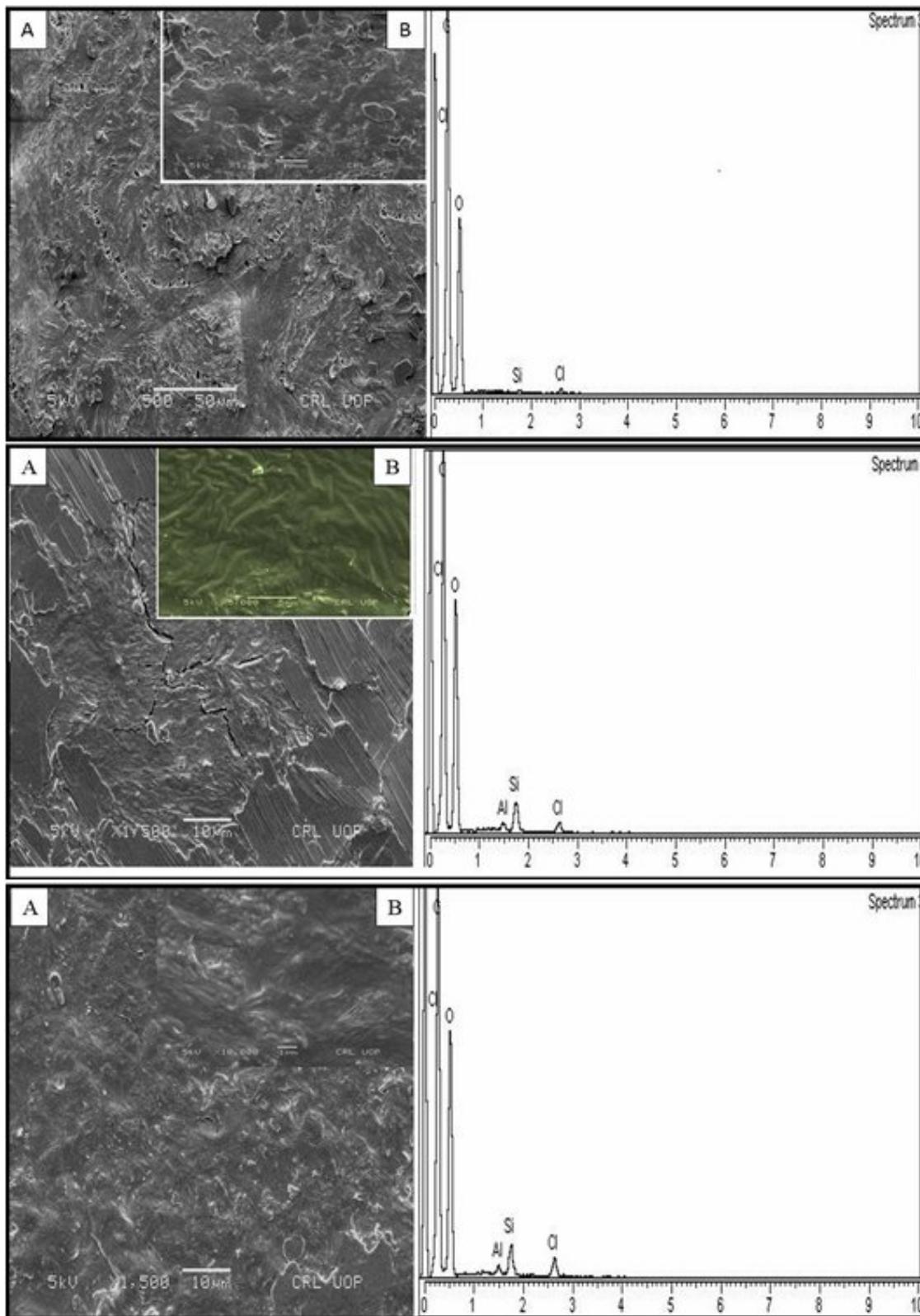


Fig 1: EDX/SEM Scan of PCS1, PCS3 and PCS2 composite system inset showing high magnification scan (From Top to Bottom).

Results and Discussion

EDX/SEM Analysis of PEO/CPMMT/Salt Composite System

EDX/SEM of PEO/CPMMT/Salt composite system is shown in Fig. 1. The EDX spectra (right side of the Fig) confirm the presence of salt and clay particles in the polymer matrix. Some Signal's existence in the EDX can be snubbed as they arise from the analytical procedure. EDX/SEM image of neat PEO film shows distinctive crystal morphology with dense and ordered branched shaped structure [9]. Fig. 1 shows the SEM images of PCS1, PCS3 and PCS2 composites from top to bottom at different magnifications. The bright entities are the silicate organo-clay layers and the dark areas are the polymer matrix. At low magnification the SEM images of PCS1 and PCS3 composites showed splinter surfaces which are microscopically coarse and three dimensional, pinpointing of crack branching showing that there is a crystalline structure in the network, which appear as cracks. At higher magnification, a smooth appearance of the particle surfaces protruding above the fissure plane is a clear sign that bonding between the fillers and the matrix is poor. At low magnification the SEM image of PCS2 composite show smooth morphology with little crack formation showing minimum crystallinity of PEO and better adhesion between the components of the composite at this composition. At higher magnification, the image show better dispersion of silicate layers of CPMMT, responsible for better ionic and thermal performance [10].

EDX/SEM analysis of PEO/PMMA/CPMMT/Salt blend composite system

EDX spectra (Fig. 2) confirm the presence of salt and clay particles in the polymer matrix. Fig. 2 shows lower and higher magnification SEM images of PPCS1, PPCS3 and PPCS2 composite system from top to bottom respectively. It can be seen clearly that after the addition of PMMA to the composite system of PEO, both the polymers are not fully miscible as the phase separation is pretty markedly noted for the system. The appearance of the spherical particles is due to the agglomeration of CPMMT and PMMA-rich phase because of its greater affinity toward PMMA in a blend system of PEO/PMMA. This trend is fully supported by the literature reported earlier [11, 12]. At higher magnification, Fig. 2 showing crack surface due to the increased crystallinity of the PEO for PPCS1 and PPCS3 loadings. The SEM analysis is completely supported by the XRD, TGA and AC impedance as reported earlier [10].

TG/DTA Analysis of PEO and PEO/PMMA/CPMMT/Salt blend Composite system

Fig. 3 depicts the TG / DTA investigation of pure PEO dissolved in acetonitrile solvent. From TGA curve it is clear that pure PEO starts single step decomposition at 330 °C. The region from (325-400) °C is attributed to the residual combustion and decomposition of PEO [13]. DTA analysis also supports the same trend showing clearly observable endothermic peak at 68 °C for the melting of crystalline PEO with characteristics irregular exothermic peaks and an endothermic peak at high temperature for the pyrolysis [14]. The DTA curve shows an endothermic peak near 390 °C which may be attributed to the evolution of carbonaceous deposits left on the surface. Fig. 4 show characteristic TG/DTA thermogram of PPCS2 blend composite illustrating that when PMMA is loaded in to the PCS system, it decreases the thermal stability. The composite system shows onset of weight loss beneath 200 °C attributable to the elimination of water, followed by a rapid weight loss starting around 300 °C, lower than pristine polymer. This low thermal stability of the system is caused by the poor dispersion of the clay due to its agglomeration associated with PMMA, caused by the incompatibility of the blend in the proportion used for the synthesis of the composite system. This is in conformity with the result reported in literature earlier [15-17]. TGA analysis shows that the degradation is a multi-stage process, which is fully supported by the DTA analysis. The agglomeration of the silicate particles associated with PMMA is confirmed by our SEM result. Observed findings suggest that PPCS composites profitably can be maneuvered up to 250 °C. These composites are therefore favored in the lithium polymeric batteries as their working temperature is generally (40 to 70) °C [18].

TC Analysis of PEO/CPMMT/Salt Composite system

Table-2 shows the result of thermal conductivities of PCS composite system. It is clear from the table that the thermal conductivity goes on increasing with increasing salt concentration. Like the previous system here PCS2 is the critical concentration at which the system has attained maximum value of thermal conductivity. The reason of this high thermal conductivity for PCS2 is the better dispersion of CPMMT in the system at this concentration as indicated by our SEM analysis. In the stated system the initial increase in the value of thermal conductivity may be due to the higher TC of the added CPMMT.

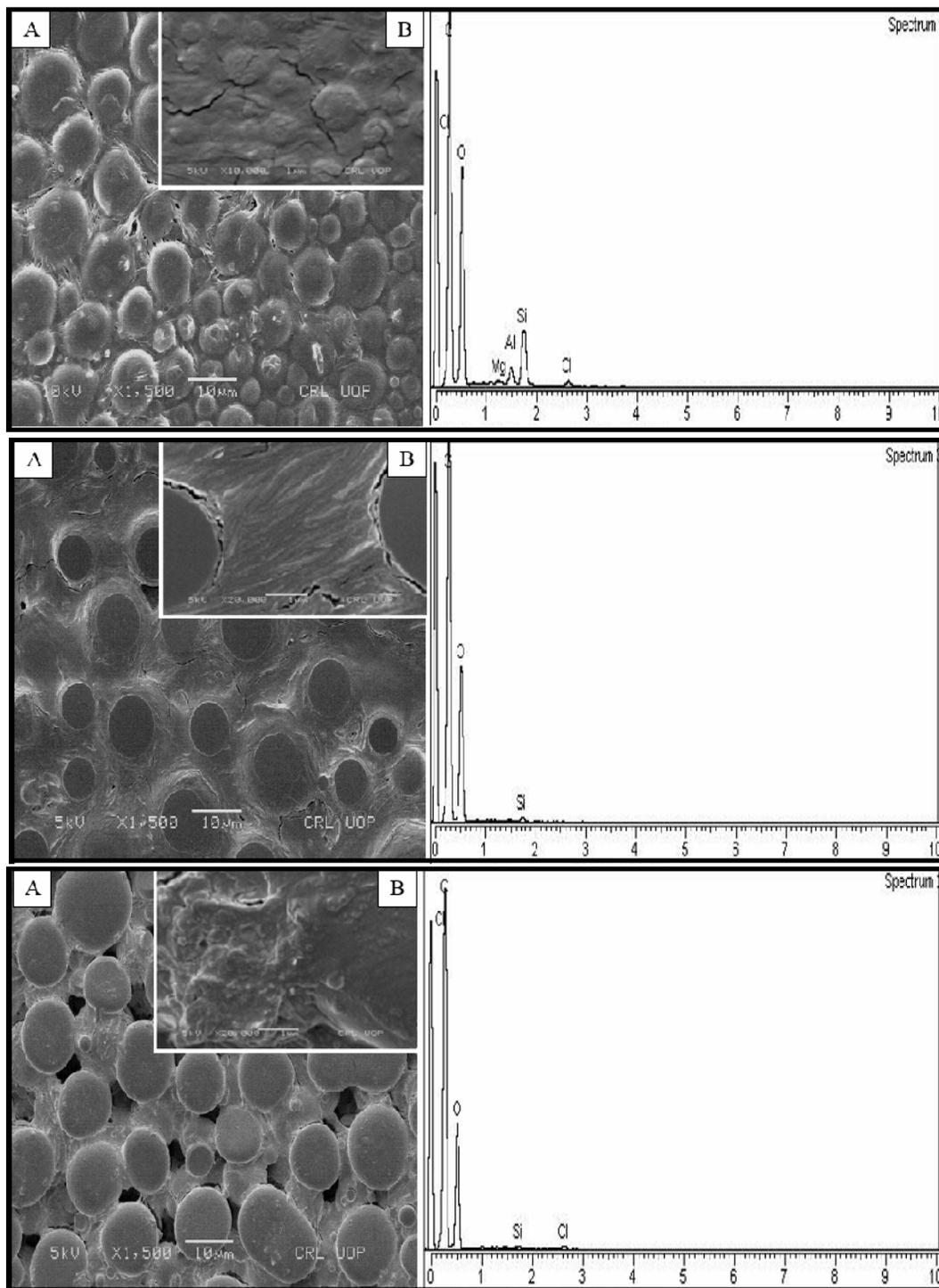


Fig. 2: EDX/SEM Scan of PPSC1, PPSC3 and PPCS2 blend composite system inset showing high magnification scan (From Top to Bottom).

Table-2: Thermal conductivity variation PCS system with varying salt concentration.

PCS system Code	Thermal Conductivity (W / m K)
P0	0.19200
PCS1	0.2036
PCS2	0.2578
PCS3	0.2331

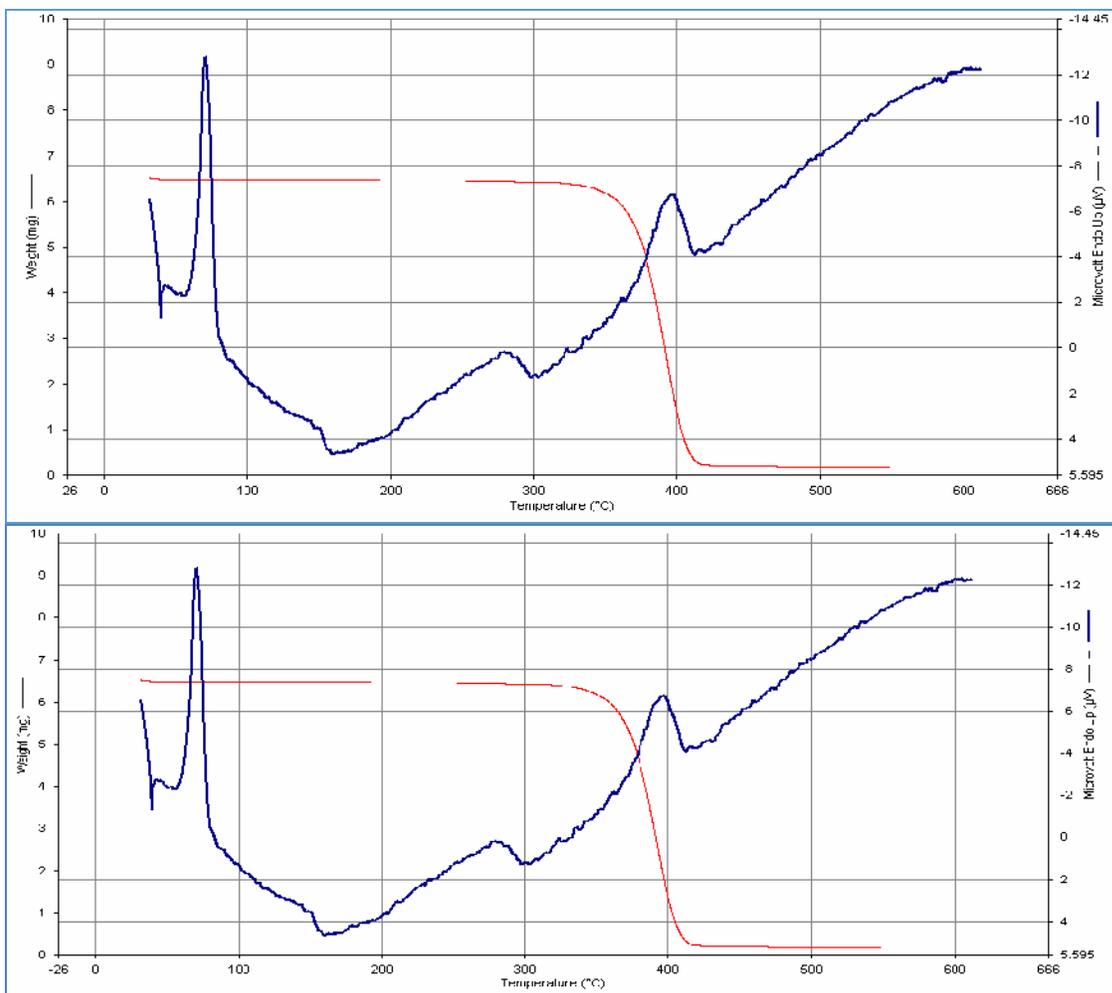


Fig. 3: TG/DTA thermogram of pure PEO film in acetonitrile

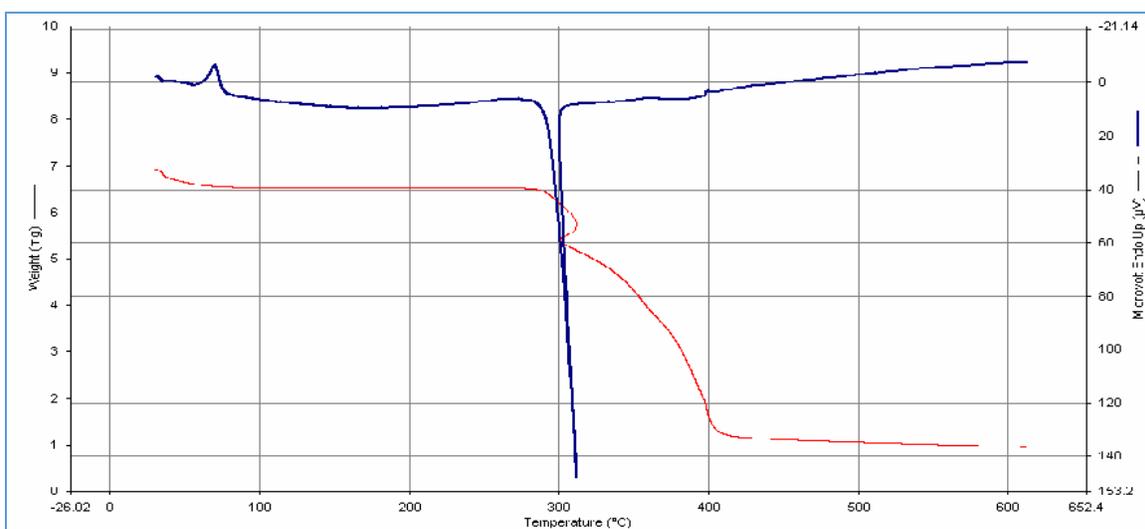


Fig. 4: TG/DTA thermogram of PCS2 Composite System.

Thermal Conductivity Analysis of PEO/PMMA/CPMMT/Salt blend Composite system

PPCS blend composite systems show reduction in the value of Thermal Conductivity (TC) for PPCS1 followed by an increase in TC for PPCS2. Here again 3.5 wt. % of LiClO₄ (PPCS2) is the critical concentration. The results of thermal conductivities shown by PEO/LiClO₄ and PPCS blend composite system are shown in Table-3. It is apparent from the results of TCs that for the addition of same amount of salt as that of PEO/LiClO₄, the thermal conductivity of PEO increases when it is blended with PMMA. These results also depict that in the presence of salt the crystallinity of PEO increases when it is blended with PMMA. This effect has been confirmed by our XRD of PEO/PMMA and PEO/PMMA/LiClO₄ blend composite system [10]. This means that PMMA is not fairly miscible with PEO in all proportions. This is in close agreement with already reported literature [19].

Zero Shear Viscosity (ZSV) Analysis of PEO/ LiClO₄ (PS) Composites against Temperature with varying Salt

The zero shear viscosity values for PS composites at different temperatures and concentrations are given in Fig. 5, a glance at these values show that when salt was added to the system of PEO at higher concentration it increases zero shaer viscosity due to the agglomeration of salt at higher loading posing resistance to the flow of polymer by increasing crystalline fraction, while for 2.1 and 3.5 % wt of salt, initially the zero shaer viscosity increases but at higher temperature it starts declination, a decreasing trend in the values of zero shear viscosity, is prominent for 2.1 and 3.5 % wt of salt, which confirms that lithium perchlorate salt act as a plasticizers at lower concentration, which increases the fluidity of the system with a subsequent

decrease in the value of η_0 . This behavior of salt is in complete harmony with the trend shown in the UTM results (not given here) where the ductility of the system increases with the increasing salt concentration. The abnormal increase in η_0 at 30 °C with 3.5 wt. % of lithium perchlorate (PS2) may be due to the better dispersion and interaction of salt at this temperature and also by the removal of more solvent. Acetonitrile is employed as a solvent, which is low boiling solvent and hence increases the zero shear viscosity [20].

Zero Shear Viscosity (ZSV) Analysis of PEO/CPMMT/LiClO₄ (PCS) Composites against Temperature with varying Salt

The ZSV values for PCS system at different temperatures and concentrations of salt at constant CPMMT (3.3 wt. %) is given in Fig. 7. These values show that when CPMMT was added to the PS composite system, the system showed an overall increase in the ZSV. It could be caused by the polymer conformation modification and CPMMT layer orientation, under shear. Upon shear rate increase, silicate layers line up correspondingly to the flow field, thereby anticipating an alteration in intercalated chain conformation [21]. Viscosity is a complex phenomenon influenced by a variety of factors, so it is complicated to have clear idea of its variation, though this increase may also be explained by taking into account the following two reasons firstly addition of CPMMT may cause an increase in the flexibility and more retardation of rotation which in turn increases the internal resistance to flow and secondly, The addition of clay may cause interaction and overlapping of polymer molecules by intercalating the polymer in the clay galleries and thus causing an increase in the zero shear viscosity [22].

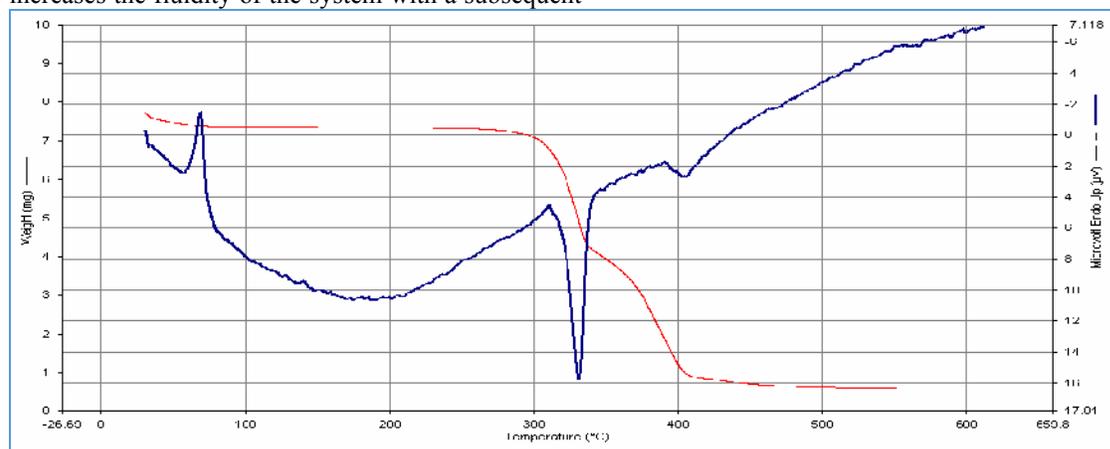


Fig. 5: TG/DTA thermogram of PPCS2 Composite System

Table-3: Variation of thermal conductivity of PS and PPCS composite system with varying salt concentration.

PEO / PMMA / LiClO ₄	Thermal conductivity (W / m K)
PEO	0.19200
PEO / LiClO ₄ (2.1 wt %)	0.1524
PEO / LiClO ₄ (3.5 wt %)	0.1949
PEO / LiClO ₄ (5 wt %)	0.1295
PEO / PMMA / LiClO ₄ (2.1 wt %)	0.2024
PEO / PMMA / LiClO ₄ (3.5 wt %)	0.2064
PEO / PMMA / LiClO ₄ (5wt %)	0.1888

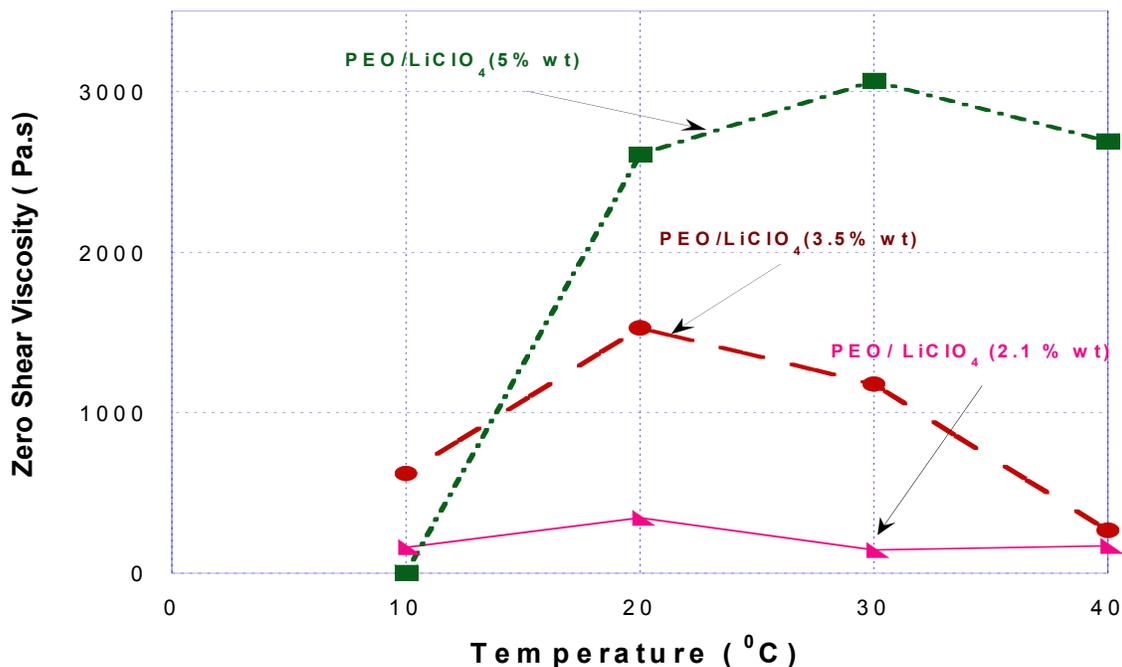


Fig. 6: Zero shear viscosity of PS composite system with varying content of salt against temperature.

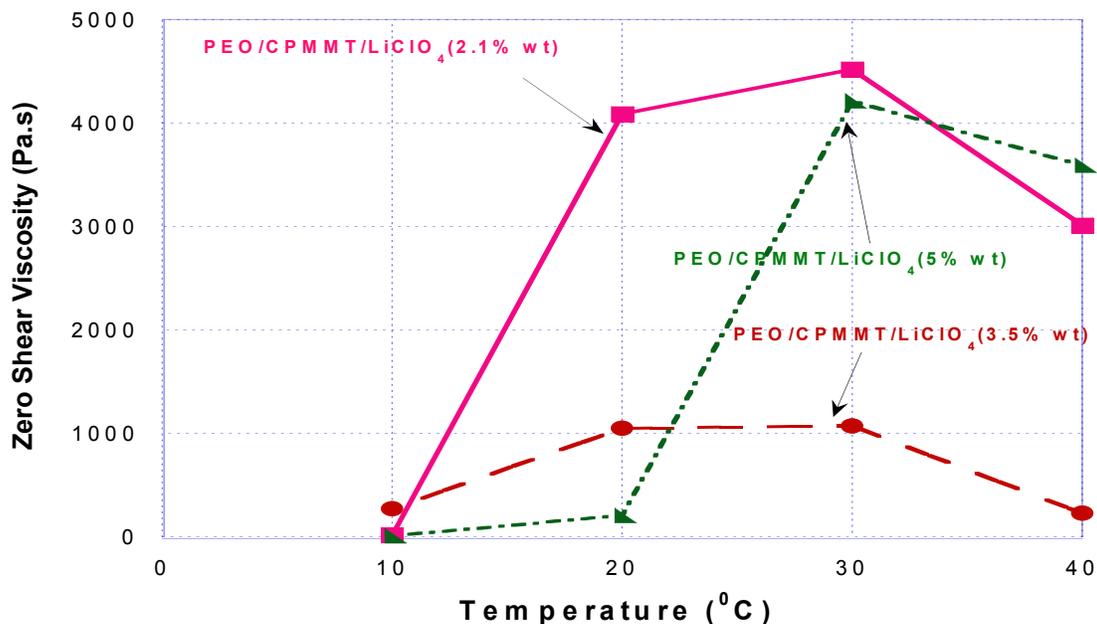


Fig 7: Zero shear viscosity of PCS composite system with varying content of salt against temperature.

Conclusion

Morphological, thermal, and rheological characteristics of PCS composites and PPCS blend composites were investigated by SEM, TG/DTA, QTM and Rheometer Physica MCR. It was observed that the addition of CPC-modified MMT improves the thermal stability and also results in sweeping effect on the rheological properties of the composite system. Thermal conductivity of thin films was found to be very sensitive to the salt and clay addition. Thermal conductivity decreased with increasing salt concentration with the exception of PCS2. It was observed that when salt was added to the system of PEO at higher concentration it increases zero shear viscosity due to the agglomeration of salt at higher loading posing resistance to the flow of polymer by increasing crystalline fraction, while for 2.1 and 3.5 % wt of salt, initially the zero shear viscosity increases but at higher temperature it starts declination, a decreasing trend in the values of zero shear viscosity, is prominent for 2.1 and 3.5 % wt of salt, The undesirable effect of PMMA addition to the PEO/PMMA blend system can be attributed to the poor dispersion and size distribution of silicate layers throughout the polymer matrix. The agglomeration of the silicate particles associated with PMMA was confirmed by the SEM result. The composites of PEO, and PEO/PMMA blend with 3.5 wt. % of LiClO₄ and 3.3 wt. % of CPMMT i.e. PCS2 and PPCS2 were found to be the optimum compositions, which exhibited better performance.

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