

Short communication

Nanocomposite electrolytes with fumed silica in poly(methyl methacrylate): thermal, rheological and conductivity studies

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Abstract

Composite polymer electrolytes (CPEs), were prepared by adding hydrophilic fumed silica in different proportions upto 5 wt.% to gel polymeric electrolyte (GPE) comprising liquid electrolyte (1M LiClO₄ in propylene carbonate) immobilized with 15 wt.% poly(methyl methacrylate) (PMMA). The effect of fumed silica content in the CPEs on the ionic conductivity and viscosity over a wide temperature range was investigated. The resultant CPEs showed room temperature conductivity (σ_{25}) as high as 3.8 mS cm⁻¹ along with viscosity value of 3700 P for 2 wt.% SiO₂ addition. Fumed silica addition both to the liquid electrolyte and to the GPE exhibits similar conductivity behaviour and this suggests a passive role of PMMA. The shear thinning behaviour, pointing towards easy processability, high thermal stability and low volatility, makes these CPEs potential candidates as solid-like electrolytes for electrochemical devices.

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1. Introduction

Solid polymeric electrolytes are widely investigated because of their potential applications in a variety of electrochemical devices like solid state batteries, electrochromic windows (ECWs), sensors, fuel cells, etc. [1,2]. The solid polymeric electrolytes can potentially eliminate leakage, negate the need of the separator and moreover be amenable to low cost manufacturing technologies. Gel polymeric electrolytes (GPEs) that are prepared by immobilizing lithium salts dissolved in plasticizing solvents in a polymer matrix have been examined and are shown to be characterized by many desirable properties that include: high ionic conductivity, (>10⁻³ S cm⁻¹) comparable to that of liquid electrolytes, and stability over wide operational temperature and electro-

chemical windows [3]. Extensive efforts have been focussed on GPEs based on PMMA and polyacrylonitrile (PAN) [4]. In particular PMMA based gel polymeric electrolytes due to their very high transparency in the visible region are preferred solid electrolytes in ECWs [5,6].

The most significant drawback of the gel polymeric electrolytes is their poor dimensional stability. Although they appear solid-like they exhibit flow properties [7,8]. Composite polymeric electrolytes (CPEs) offer the best solution to overcome this drawback. CPEs with promising electrochemical properties, e.g. Conductivity, interfacial stability, ionic transport properties and mechanical properties, e.g. viscous and elastic modulus, and yield stress, are viable in many electrochemical devices, especially in lithium battery applications [9]. Most CPEs reported in the literature are formed by dispersing ceramic fillers (e.g. Al₂O₃, TiO₂, SiO₂) into high molecular weight (M_w) polyethylene oxide (PEO) polymers doped with lithium salts LiX (X = ClO₄, CF₃SO₃). The addition of ion conducting fillers (e.g. γ -LiAlO₂, Li₃N) and even inert ceramic fillers, enhances the conductivity of a high

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M_w PEO electrolyte. The effect induced by inert fillers is attributed to an increase in the volume fraction of the amorphous phase, which is a prerequisite for higher conductivity. However the ionic conductivity of such CPEs at ambient temperature is 10^{-4} to 10^{-5} S cm $^{-1}$, which is too low for commercial applications.

There have been some attempts to develop CPEs by dispersing fumed silica in low molecular weight PEO [10]. Unlike high M_w PEO composites, the solid state structure is dictated by the filler instead of PEO chains. CPEs consisting of fumed silica, poly(ethylene glycol) dimethylether oligomer (PEGdm, $M_w = 250$) and lithium salts, are promising in terms of their high conductivity (10^{-3} S cm $^{-1}$ at 25 °C) and good mechanical strength (elastic modulus $>10^5$) [11].

It is well accepted that fillers play an important role in Li $^+$ transport, however different trends in conductivity due to addition of fillers are observed, e.g. an increase, decrease or no change in conductivity all have been reported, but the observed effect is much less than the addition of extra polymer in GPE. This apparent discrepancy can partially be ascribed to the difference in electrolyte materials (polymers, salt, filler type), their concentration, preparation condition and thermal history of the materials and the polymer electrolytes.

Literature survey demonstrates that although a large volume of research papers based on PEO is available, publications related to CPEs based on PMMA are scarce. In the report [12] dealing with the ion and solvent dynamics in PMMA based gel as a function of the loading of nanosized TiO $_2$ particles, the ionic conductivity decreased in contrast with the pristine gel electrolyte at low loadings but at higher (8 wt.%) loadings the conductivity was close to that of the unfilled sample.

Fumed silica as a filler is of special interest because of its branched primary structure and the ability to tailor the surface functionalities. CPEs based on fumed silica were shown to be highly transparent in the visible region and to have a wide electrochemically stable potential window [7]. In this communication we report our findings on the effect of fumed silica on a PMMA based electrolyte, investigating ion transport and rheological properties of the resultant CPEs. Experiments were also carried out to examine thermal stability of the synthesized CPEs, a detailed analysis of which is presented here.

2. Experimental

2.1. Materials

PMMA (molecular weight 996,000) and lithium perchlorate (LiClO $_4$) were supplied by Aldrich and used after drying at 100 °C in a vacuum oven overnight. Synthesis grade propylene carbonate (Merck, Germany) was used after drying over 4 Å molecular sieves. Hydrophilic fumed silica (CABOSIL, A-200) from Cabot India Ltd. was used after drying in a vacuum oven for 72 h at 120 °C.

2.2. Sample preparation

The fumed silica nanocomposite electrolytes were prepared first by dissolving 1 M LiClO $_4$ in PC. In the liquid electrolyte thus made the fumed silica particles were dispersed in different weight percentage and stirred with the help of magnetic bar, till homogeneity was attained. After obtaining a homogenous mixture, 15 wt.% PMMA was added slowly while heating at 55 °C, until a transparent CPE was obtained. CPEs of various weight percentage i.e. 1–5 wt.% of fumed silica were made from the above compositions under controlled laboratory conditions. The conditions were kept constant through out. The obtained CPE can also be used as a solid film, by means of a solution casting method dissolving it in acetonitrile or tetrahydrofuran.

2.3. Instrumentation

Electrolyte conductivities were measured using Metrohm 712 conductometer over the temperature range 20–70 °C controlled by a Paar Physica circulating water bath after standard calibration. Rheological measurements were carried out on Anton-Paar DV2P digital viscometer equipped with a temperature controlled circulating water bath. A concentric cylinder was used to measure the viscosity under shear rate 0.17–68 s $^{-1}$. The lowest measurable viscosity value is 20 P. DSC data were obtained between 25 and 450 °C using DuPont TA-2000 scanning calorimeter under nitrogen atmosphere at a heating rate of 10 °C min $^{-1}$.

3. Results and discussion

3.1. Fumed silica effect on liquid electrolyte

We first consider the effect of fumed silica on the conductivity of the liquid electrolyte 1 M LiClO $_4$ in PC. Hydrophilic fumed silica (A-200) does not form gel, because of the similar solubility parameter of PC and fumed silica, which is supported by its very low viscosity (<20 P) and therefore could not be measured with our viscometer. Fig. 1 illustrates variation of conductivity values as a function of fumed silica concentration. As can be seen conductivity demonstrates a general trend of increase, though by small amount with respect to the parent liquid electrolyte. The most noticeable feature is the maximum in conductivity at an optimum content (2 wt.%) of added fumed silica, which is broad at low temperature but is relatively sharp at higher temperature (70 °C). This is likely to be due to the greatest degree of network formation at 2 wt.% of fumed silica, while at higher wt.% entanglement in the network structure occurred. The conductivity increment relative to the parent liquid electrolyte for 2 wt.% fumed silica changes from 13% at 20 °C to 32% at 70 °C. The Arrhenius plots for the liquid electrolyte and the liquid electrolyte with 2 wt.% fumed silica shown in Fig. 2 shows increase in conductivity with temperature.

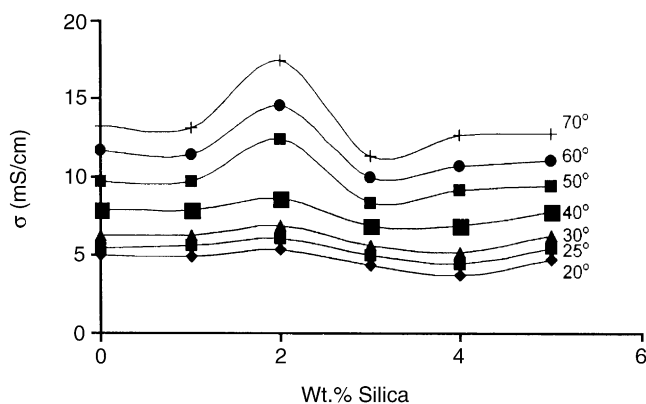


Fig. 1. Ionic conductivity of silica immobilized liquid electrolyte (1 M) as a function of fumed silica content.

These observations can best be explained by considering possible interactions between LiClO_4 , PC and fumed silica. The choice of PC as a solvent amongst many other desirable properties for electrolyte application hinges upon its high dielectric constant ($\epsilon = 64$)₂₅ much higher than that of fumed silica ($\epsilon = 4.1$)₂₅. This facilitates high dissociation of the salt with consequent high ionic conductivity. The chosen concentration (1 M) in addition to the highest ionic conductivity is characterized with negligible ion pairs formation in the liquid electrolyte. Dissociation of LiClO_4 in PC has been shown earlier [13] to have Li^+ ions strongly solvated while ClO_4^- ions to coordinate and solvate poorly, affecting the structure and dynamics of the solvent. The solvation of Li^+ with PC is shown to take place via its coordination with C=O group of PC. The first coordination sphere of Li^+ in PC is assumed to contain four or more PC molecules depending on the concentration [14] forming a “solvation shell” around it. Outside this region most of the electrostatic force from the ions is screened off. The cations thus experience lower diffusion coefficient/transference number [15] than the bulky anion.

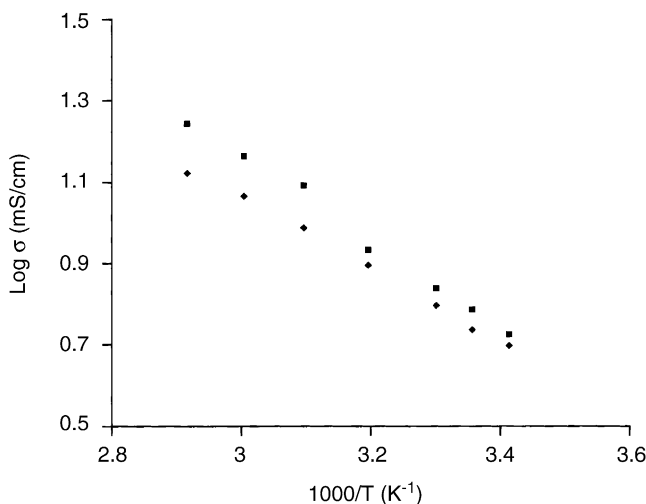


Fig. 2. Arrhenius plots of conductivity for liquid electrolyte (◆) and with 2 wt. % fumed silica immobilized liquid electrolyte (■).

Dispersion of fumed silica in PC changes the ion transport properties in the resultant system due to interactions between LiClO_4 , PC and fumed silica. The hydrophilic nature of fumed silica is well known to control also the rheological properties of the medium in which it is dispersed. Fumed silica is amorphous and non-porous in nature. Its small particles form three-dimensional branched chain aggregates of approximate length 0.2–0.3 μm , having surface area as large as $200 \pm 25 \text{ m}^2 \text{ g}^{-1}$. This complex aggregated structure is responsible for the unique properties of fumed silica, in particular its ability to impart high viscosity to the medium in which it is dispersed [16]. The surface silicon atoms of fumed silica have hydroxyl groups that are capable of forming hydrogen bonds between its aggregates. When a sufficient amount of fumed silica is thoroughly dispersed in any system at rest it can form a network due to hydrogen bonding. The degree of network formation, which fumed silica is able to produce and as a result the viscosity it can impart to any medium, in addition to its content is dependent on the properties of the medium.

When PC is the dispersion medium, its highly polar C=O groups interfere the hydrogen bonding of the aggregates of fumed silica extensively. As a result fumed silica cannot impart high viscosity to the system. The possible interaction of the surface hydroxyl groups of silica and the C=O groups of PC is represented in Fig. 3.

With fumed silica as the filler in the liquid electrolyte under consideration, the interactions are likely to be more complex. The solvent PC can have interactions via its C=O groups with Li^+ ions and additionally with Si–OH surface groups of fumed silica. Do these possible interactions modify the so called “solvation shell” of Li^+ ion and as a result its mobility and transference number? Some of these questions have been addressed earlier and their explanations have been offered.

An increase in transference number from 0.19 in pure liquid electrolyte to 0.25 in fumed silica immobilized liquid electrolyte [15] is a clear cut evidence of more free motion of Li^+ cations in silica immobilized liquid electrolyte. A broad maximum in conductivity at 22 °C with fumed silica observed by Fritz et al. [17], which is similar to our current investigation can be ascribed as an “electroosmotic” phenomenon.

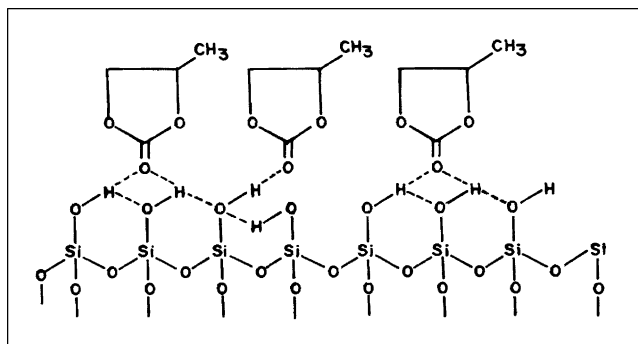


Fig. 3. Formation of H-bonding (---) between PC and Fumed silica.

Formation of a preferential distribution of anions at the silica – solvent interface is the cause of the observed conductivity maximum. Much higher dielectric constant of PC compared with that of fumed silica is responsible for the formation of a highly conductive interfacial region, as a result Li^+ can move more freely. At sufficient large weight fraction of fumed silica, it is the volume filling that decreases the conductivity.

3.2. Fumed silica effect on composite polymeric electrolytes

3.2.1. Conductivity

Our earlier studies have shown that the addition of a polymer-like PMMA lowers the conductivity of the liquid electrolyte by a factor [18] that is higher in comparison with the addition of the filler as mentioned in Section 3.1. In GPEs the macroscopic mechanical stability of a polymer is combined with liquid like microscopic dynamics of a low molecular solvent. The gel polymeric electrolyte can be viewed as free liquid electrolyte encaged in a polymer matrix [19]. To verify this and to investigate the ion conduction mechanism as well as the local coordination, these gels have been probed by Raman, FTIR, NMR and relaxation process studies [20,21]. Some recent studies by ab initio calculations and Raman spectroscopy [22] led to conclude that the lithium ions prefer strongly to coordinate to the solvent molecules as ligands with dominance of $[\text{Li}(\text{solvent})\text{Li}]^+$ complex. Further for the PMMA gels, a temperature increase is shown not to inflict any serious changes as compared to liquid electrolyte. The PMMA gel is thus aptly described only as a “bystander”. With such passive role of PMMA in a gel electrolyte, gel electrolytes are expected to exhibit behaviour similar to the parent liquid electrolyte especially with respect to conductivity and viscosity. Indeed our experimental results have proved these expectations. The trends observed on addition of fumed silica to GPE are similar to those exhibited by the liquid electrolyte. This effect supports the idea that the addition of ceramic filler does not impede the mobility of lithium ions in the polymer matrix.

Fig. 4 illustrates conductivity Arrhenius plots of the CPEs obtained by addition of fumed silica in different amounts to GPE. The temperature dependence of the conductivity of these CPEs shows non-Arrhenius behaviour typical of amorphous materials and can best be related by the Vogel–Tamman–Fulcher (VTF) equation [1]. The addition of fumed silica does not appear to affect the mechanism of ionic transport, since all the profiles have similar curvature, i.e. the apparent activation energy is unaffected. It also exemplifies an increase in conductivity with temperature and for different amounts of fumed silica, though by a small amount. Conductivity plotted against the filler content (inset Fig. 4) leads to realization that there exists a maximum in conductivity at all temperatures, but becomes more pronounced at higher temperatures.

A small but significant enhancement of lithium ion mobility in PMMA gel electrolytes with the addition of nanopartic-

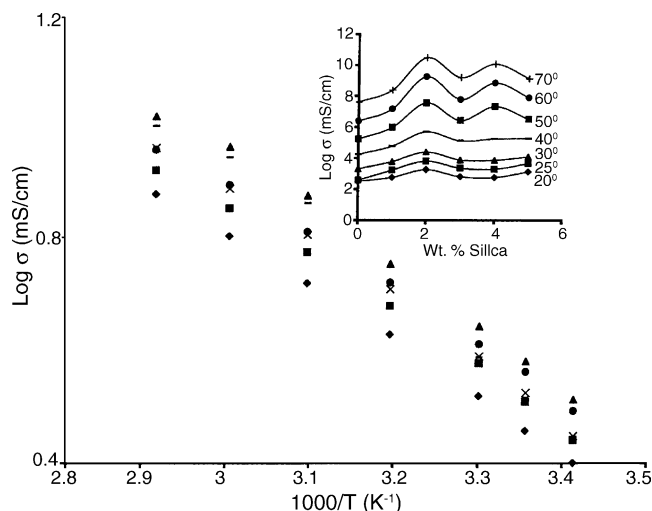


Fig. 4. Arrhenius plots of conductivity for CPEs with 0 wt.% (◆), 1 wt.% (■), 2 wt.% (▲), 3 wt.% (×), 4 wt.% (–) and 5 wt.% (●) fumed silica.

ulate TiO_2 has been shown [12] to be neither due to enhanced solvent diffusion determined by pulsed field gradient-NMR technique nor to an increased fraction of free ions with the addition of filler. It was suggested to be due to creation of new pathways for the lithium ions with the addition of filler particles leading to decreased overall conductivity. It was discussed in terms of anion filler interaction although anion diffusion coefficient was not determined. Such mechanisms explain the experimentally observed results.

3.2.2. Viscosity

Fig. 5 depicts log viscosity versus $1000/T$ plots for varying amount of fumed silica added to gel polymeric electrolyte. The viscosity increases monotonically with filler content. It is very obvious that the viscosity is not seen to follow Arrhenius behaviour, and the curved profiles are as of amorphous materials. Thus thermal dependence of viscosity can also be

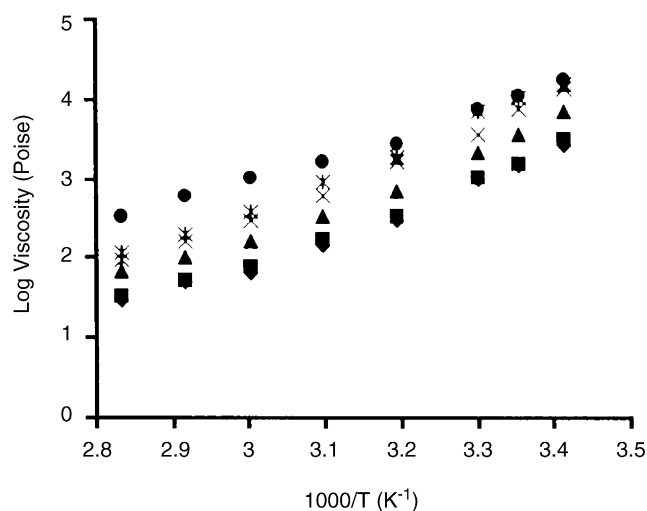


Fig. 5. Arrhenius plots of viscosity for CPEs with 0 wt.% (◆), 1 wt.% (■), 2 wt.% (▲), 3 wt.% (×), 4 wt.% (×) and 5 wt.% (●) fumed silica.

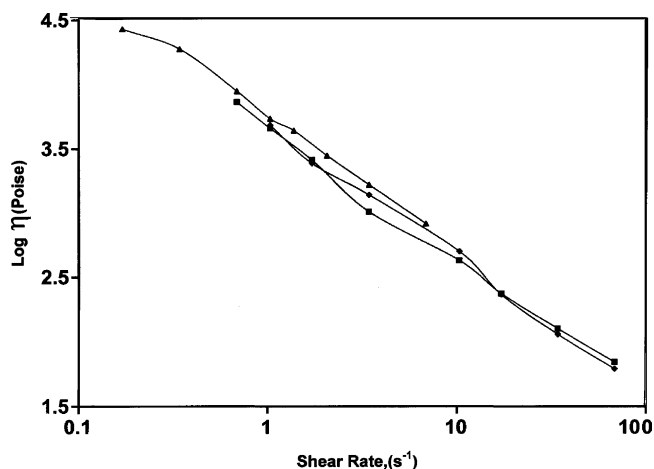


Fig. 6. Viscosity of CPEs as a function of shear rate for 0 wt.% (◆), 2 wt.% (■) and 5 wt.% (▲) fumed silica.

described by VTF relationship. The CPEs with more than 2 wt.% fumed silica exhibit solid-like behaviour resulting in viscosity enhancement by an order or more. Viscosity increase is the direct result of fumed silica network formation through H-bonding. The polar end of the molecule is preferentially adsorbed on the silica surface, this halts further network formation at this site.

3.2.3. Shear thinning

Another interesting feature exhibited by these CPEs is their shear thinning behaviour. The viscosity follows a linear relationship with respect to shear rate. The viscosity as a function of shear rate for CPEs with various fumed silica contents is shown in Fig. 6. Over the studied shear rate the viscosity of the CPEs with 5 wt.% fumed silica is higher than that of the GPE. At low shear rate, i.e. when the sample is less deformed, it exhibits a solid-like behaviour with a high value of viscosity. This enhancement of viscosity arises from the induction of siloxane linkage in the polymer matrix leading to a network structure. At high shear rate the viscosity and shear thinning rate for the CPEs are comparable with GPE due to the preferential orientation of the siloxane linkage parallel to the flow direction. The linear profiles have typical non-newtonian behaviour characteristic of shear thinning fluids. Shear thinning occurs because the bonds composing the network structure are weak physical bonds that can be disturbed by shear [23]. Thus it may be concluded that the CPEs are physical gels due to formation of a three-dimensional network.

This property of the CPEs under consideration is very important, under shear, the viscosity becoming less resulting in a gel like consistency makes their processing relatively easy and endows good filmability. This is advantageous in fabrication of devices.

3.2.4. Thermal studies

Fig. 7 illustrates TGA and DSC traces of PMMA alone used in synthesizing the CPEs. The TGA curve indicates no

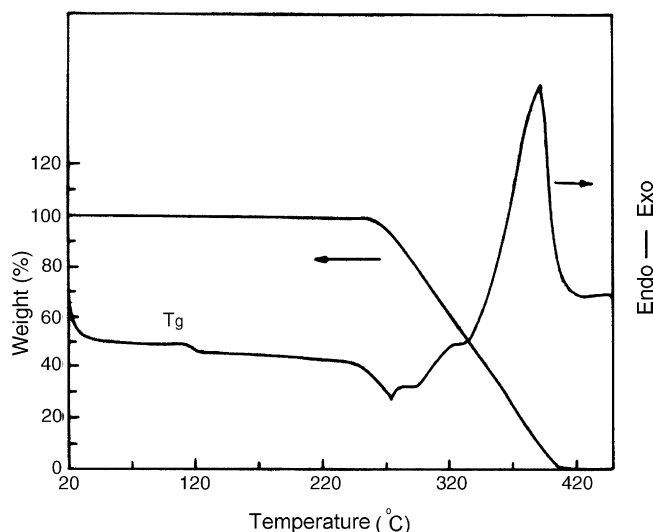


Fig. 7. TGA and DSC traces of PMMA at a heating rate of $10^{\circ}\text{C min}^{-1}$.

weight loss up to 250°C but beyond that up to about 405°C there is continuous weight loss with the same rate. In the DSC trace at low temperature T_g is well reflected at around 125°C . Corresponding to the weight loss in the TGA trace their appear two reaction stages in the temperature ranges $245\text{--}337.5$ and $337.5\text{--}420^{\circ}\text{C}$. It is clear from the TGA trace that both these reaction stages have comparable weight loss but differ in that the one at low temperature is endothermic while the other at higher temperature is exothermic. The first one, which takes place by heat absorption, is ascribed to the degradation of the polymer's unsaturated groups, in contrast the second reaction is due to unzipping initiated by the random scission produced by monomer volatilization [24,25]. Beyond 425°C PMMA is destroyed completely.

The thermograms of the parent GPE and CPEs with different amount of fumed silica are given in Fig. 8. The thermograms reveal predominant amorphous nature of all of them. Two major endothermic peaks appear in all the thermograms in the temperature range $210\text{--}310^{\circ}\text{C}$. The one at lower temperature corresponds to loss of solvent. The solvation of lithium salt in PC has lowered it down to 210°C in GPE as compared to pure PC (256°C) [26]. With addition of fumed silica however this peak has shown shift to higher temperature maximum by 50°C . The high temperature peak is identical to that of the reference PMMA (Fig. 7) at which the degradation of unsaturated groups of the polymer begins. This peak also has displaced due to addition of fumed silica and the maximum shift it has shown is by 20°C for CPE with 4 wt.% fumed silica. The incorporation of fumed silica has thus significantly enhanced the thermal stability of the polymer as well as the solvent retention ability of the CPEs.

At high temperature the reaction chain scission occurs initiated by unzipping, leading to monomer volatilization. Instead of giving a single exothermic peak it is seen to be taking place in two steps and the temperatures at which they

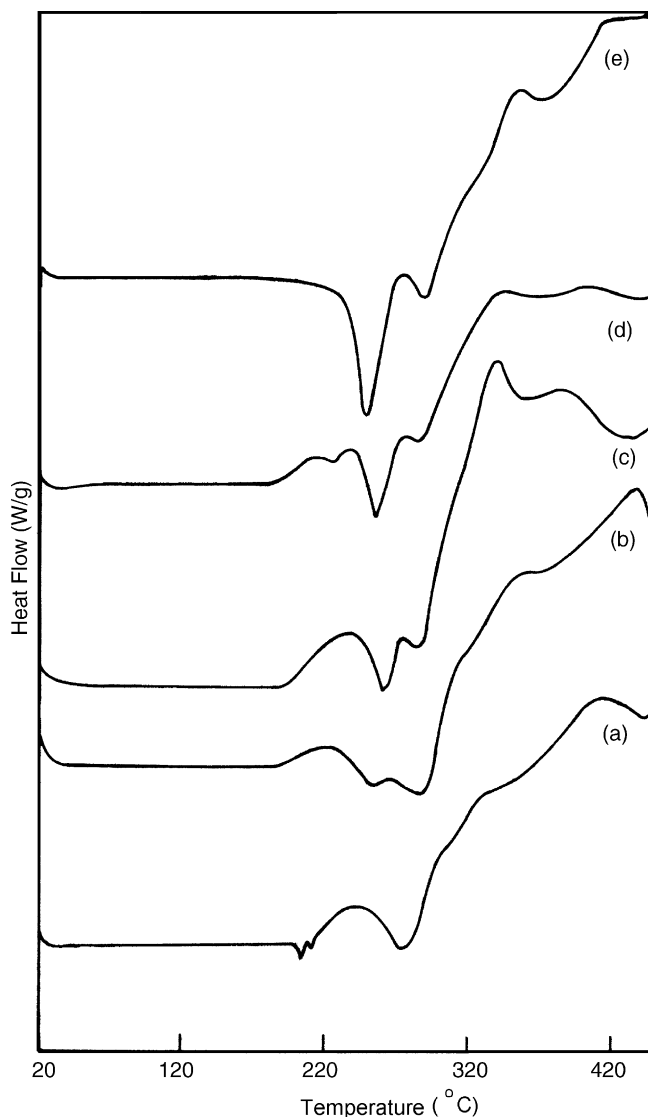


Fig. 8. DSC thermograms of CPEs with (a) 0 wt.%, (b) 1 wt.%, (c) 2 wt.%, (d) 3 wt.% and (e) 5 wt.% fumed silica.

occur differ by the presence of fumed silica, the exact cause of origin of this change is unknown however.

4. Conclusion

CPEs prepared by dispersing fumed silica in PMMA based GPE exhibit high ionic conductivity ($>10^{-3}$ S cm^{-1}) and improved dimensional stability. The effect of dispersed fumed silica content in GPE on conductivity and rheology has been examined. An enhancement in viscosity by nearly two orders of magnitude can be attained with increased conductivity at an optimum content. The maximum conductivity is 3.8 mS cm^{-1} at room temperature with corresponding viscosity reaching 3700 P. PMMA has been shown to be passive without exhibiting difference in the conductivity behaviour

of liquid and gel to which SiO_2 is added. Additionally their high thermal stability along with good rheological properties make them potential candidates as solid electrolytes for electrochemical devices.

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