

# Thermal and electrical behaviors of PMMA/PEG/LiClO<sub>4</sub>/MWNTs blend polymer electrolyte nanocomposites

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**Abstract**– Nanocomposites blend polymer electrolyte film based on PMMA/PEG (60:40) incorporated with 15wt% lithium perchlorate salt (LiClO<sub>4</sub>) and varying amount of multi-walled carbon nanotubes (MWNTs), have been fabricated by solution casting technique. The interaction between (LiClO<sub>4</sub>/MWNT) with functional groups in blend matrix was confirmed by FTIR spectroscopy. The surface morphology of films was probed by SEM, where the result showed roughness increased with increasing fillers content in composite films. The reduced in thermal T<sub>g</sub>, as well as the percent of crystallinity with increasing ratio of fillers in composite films was observed, which indicate to increase the amorphous portions. Dc-conductivity data showed a significant improved from 1.74X10<sup>-12</sup> S/cm for PMMA/PEG into 1.38X10<sup>-7</sup>S/cm for formulation of PMMA/ PEG/15wt% LiClO<sub>4</sub>/0.4wt%MWNTs. The increased dc-conductivity for composite films as a result to increased temperatures accompanied with reduced activation energy has noticed. That denotes to reduce the potential barriers and facilitate mobility of charge carriers through the blend matrix.

**Index Terms**– MWNTs; nanocomposites; SPEs; T<sub>g</sub> ; dc-conductivity.

## 1. INTRODUCTION

### 1.1 Background

Solid electrolytes are known as ion conducting solids or fast ion conductors which are any substances that has a high ionic conductivity, typically in the range  $\sim 10^{-8}$ - $10^{-1}$  Scm<sup>-1</sup> and negligible electronic conductivity [1, 2]. Solid electrolytes have enormous technological applications in the areas of energy storage, energy conversion, environmental monitoring and so on [3-5]. Recently, a wide range of materials have been investigated on their capability to use as super ionic conductivity in solid phase includes crystalline salts, ceramics, glasses, composites, polymers, etc., [6-8]. Polymer electrolytes are one of the most widely studied solid electrolytes. The composition of the film with the desired mechanical, thermal and electrochemical stability makes the polymer electrolytes more attractive than conventional liquid electrolytes and the brittle crystalline/polycrystalline, composites and glassy solid electrolytes. Solid polymer electrolytes (SPEs) with considerable ionic conductivity have been the subject of many recent investigations because of

their potential applications in solid state lithium ion rechargeable batteries, electrochemical devices, such as electric double-layer capacitors, solar cells and sensors [9-11]. SPE has desirable features, including their safety, high energy density, high specific energy, good reliability, high ionic conductivity, solvent-free conditions, light weight, and wide electrochemical stability windows [12, 13]. The traditional SPEs are essentially polymer-salt complexes prepared by dissolving suitable salts/acids into high molecular weight polymers which act as a matrix. Polymer electrolytes support variety of ions, such as  $\text{Li}^+$ ,  $\text{Cs}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Al}^{3+}$  etc., for transport. There are numerous polymers which are used as matrices like polyethylene oxide (PEO), polypropylene oxide (PPO), poly methyl methacrylate (PMMA), poly vinyl pyrrolidone (PVP) and poly vinyl alcohol (PVA) and so forth. The electrical application of virgin polymers is limited because the most polymers are partially crystalline in nature, which is an unfavorable property for achieving appropriate ionic conductivity due to lower segmental motion of the polymer network, which leads to a lower ionic conductivity at ambient temperature. The ion transport in these polymer electrolytes is governed by local relaxation as well as segmental motion of the polymer chains, which are more favored by high degree of amorphousness in the host polymers [14]. The ionic conductivity of the solid polymer electrolyte could be improved by integrating different additives such as lithium salt, nanofillers and plasticizers into the polymeric matrices. PMMA have been extensively studied as candidates for polymer electrolytes because of their high solvation capability for many types of salts with good mechanical properties, colorless or transparent polymer with good resistance to acid and high dielectric strength (2.6 at 1MHz). However, PMMA is insulating polymer in nature ( $1 \times 10^{-15} \Omega^{-1}$ ) at room temperature with high thermal transition degree ( $T_g \sim 115-125^\circ\text{C}$ ). S. Ahmad [15] mentioned that PMMA has amorphous phase (random arrangement of the asymmetrical carbon atom) by nature and flexible backbone chains which leads to improve ambient-temperature conductivity. E. T. Eugenia et al [16] reported that the embedded 5wt%  $\text{TiO}_2$  NPs leads to partially improved electrical properties of PMMA to few orders even up to  $6.3 \times 10^{-9} \text{Scm}^{-1}$ . L. Othman et al [17] revealed that ionic conductivity of [PMMA-EC]-35wt%  $\text{LiBF}_4$  system was improved to about  $4.07 \times 10^{-7} \text{Scm}^{-1}$ . Therefore, in this current work, an attempt has been made to fabricate a series of SPE-NCs by casting insulating PMMA with PEG as blend matrix embedded with 15wt%  $\text{LiClO}_4$  and small quantities of MWNTs as nanofillers to investigate thermal behavior and conduction process of such system.

## 2. EXPERIMENTAL DETAILS

### 2.1 Materials

Poly (methyl methacrylate) (PMMA) ( $M_w \sim 350,000 \text{ g mol}^{-1}$ ) was supplied by Aldrich, Poly (ethylene glycol) (PEG) ( $M_w \sim 4500 \text{ g mol}^{-1}$ ) was obtained from Scharlu, Tetrahydrofuran (THF) (Aldrich) with purity 99.9% HPLC grade was used as reagent grades without further purification, while multi-walled carbon nanotubes (MWNTs) with diameter 10nm, length 0.1–10micron and purity 90%, was supplied by Nanocyl S.A. Lithium perchlorate ( $\text{LiClO}_4$ ) (Merck) with purity >99 % was dried for 24 h at  $120^\circ\text{C}$  before used.

### 2.2 Fabrication of blend polymer electrolyte nanocomposite films

The films were prepared by solution casting techniques [18, 19], where the blend PMMA/PEG with ratio (60:40) was dissolved in THF under continuous mechanical stirring overnight with covered the top of beaker. Then, blend

solution poured into glass dishes and allowed to evaporate slowly at room temperature. For SPE film, 15wt% of  $\text{LiClO}_4$  has been incorporated into blend solution of PMMA/PEG (60:40) in THF and stirring to completely dissolve salt in solution followed by casting the film into glass dishes. For NCs-SPE film, the different ratios 0.2, 0.4, 0.6 and 0.8wt% MWNTs was added into solution of PMMA/PEG(60:40)-15wt%  $\text{LiClO}_4$  with vigorously stirred for 1hr followed by sonicated for 30min to get good dispersion of MWNTs in solution. The NC-SPE films were casted in glass dishes and the solvent was evaporated gradually at room temperature.

### 2.3 Instruments and measurements

Thermal behaviors of films was probed by DSC measurements (DSC-60, Shematzu, Japan), where films heated at a scanning rate of  $10^\circ\text{C}/\text{min}$  from  $20$  to  $300^\circ\text{C}$  under a nitrogen gas. The mutual effects between components in composite films were investigated by FT-IR spectra (Varian 800 FT-IR Spectrometer, Scimitar). SEM images are used to examine the surface morphology and microstructure of films by (JEOL, 100-S), room temperature; under pressure  $10^{-6}$  Torr, coating with gold, magnification about 1600X. The dc-conductivity is evaluated by measuring electrical resistance at different temperature range ( $293\text{--}353^\circ\text{K}$ ) using the (Keithley electrometer type 2400). Then dc-conductivity ( $\sigma_{dc}$ ) values were calculated as  $\sigma_{dc}=L/(R_b/A)$  where,  $R_b$  is the resistivity,  $L$  and  $A$  are the thickness and the surface area of the film in contact with the stainless steel disc electrode, respectively.

## 3. RESULTS AND DISCUSSION

### 3.1. Morphological studies

The SEM image of pure PMMA electrolyte is shown in Figure1 (a). It can be noticed a small craters on the surface of film caused by the rapid evaporation of THF solvent.

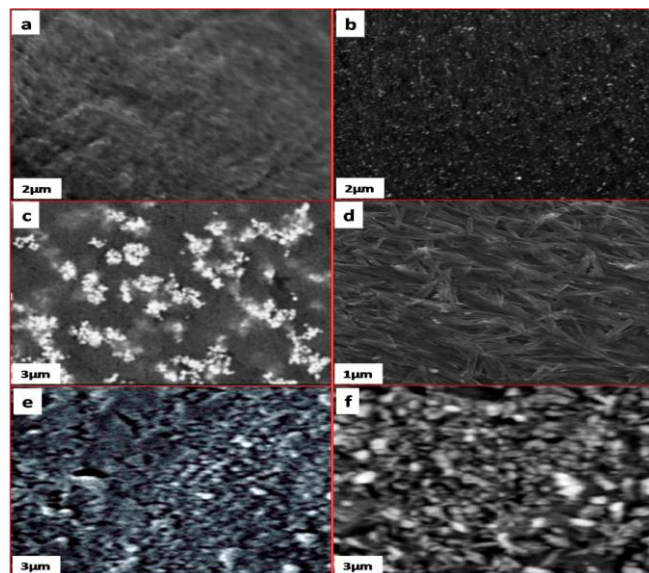
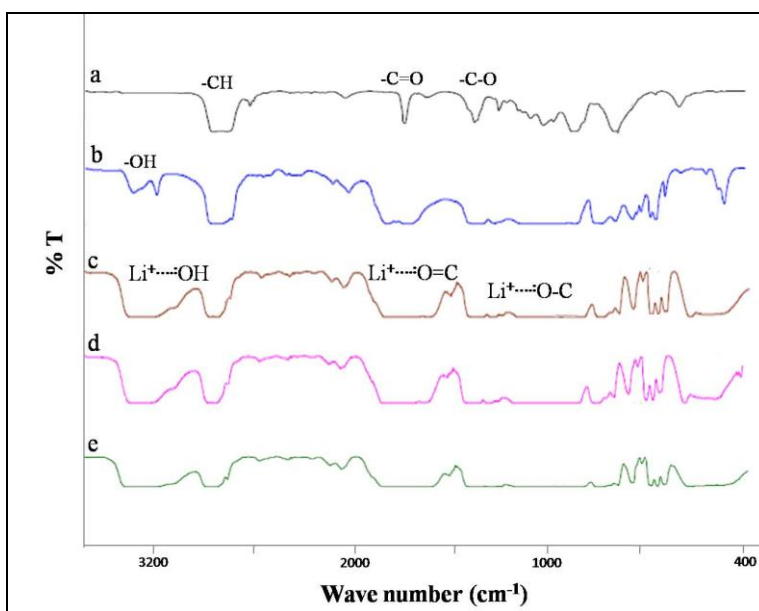


Figure1: SEM photomicrographs of a) PMMA, b) PMMA/PEG, c) PMMA/PEG-15wt% $\text{LiClO}_4$ , d) pure MWNTs, PMMA/PEG-15wt% $\text{LiClO}_4$ with e) 0.4 and f) 0.8wt% MWNTs

Figure1 (b) displays the cloudy semi-homogeneous and porous film for PMMA/PEG (60:40). The porosity in the film indicates the surface microstructure has become slightly rougher. This inferred that addition PEG tends to disorder the structure and increase the amorphous region in blend. Besides, the surface morphology of blend is changed due to the addition  $\text{LiClO}_4$  salt, where the dispersed semi-spheres particles inside the blend film were observed (Figure1(C)). Figure1 (d) presents the fibrous-like structure for pristine MWNTs which formations three dimensional networks. As MWNTs increasing up to 0.8wt% in PMMA/PEG-15wt%  $\text{LiClO}_4$ , the dispersed grains are getting closer to each other leads to agglomerate being built and the surface of composite becomes more roughness (Figure1(e, f)).

### 3.2. FTIR studies

FTIR spectroscopy is used to analyze the mutual effect and interaction between components inside blend system. Figure2 show FTIR spectrum of pure PMMA, blend PMMA/PEG (60:40) and its SPES films.



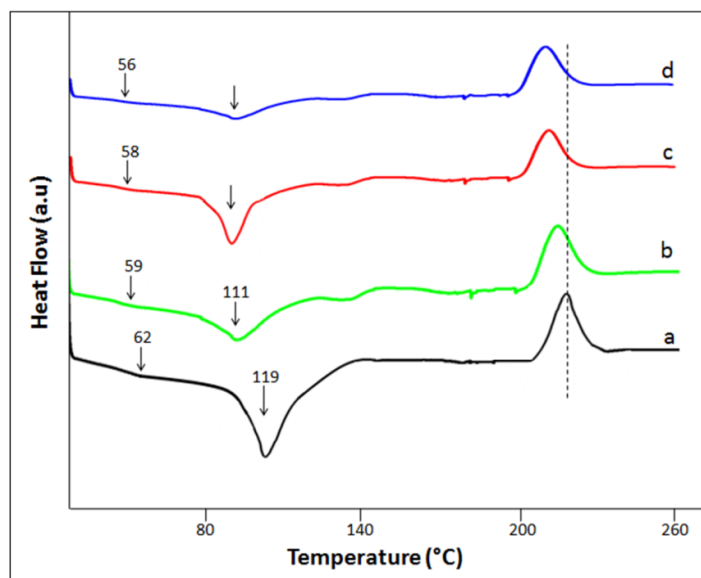
**Figure2: FTIR of a) PMMA, b) PMMA/PEG, c) PMMA/PEG-15wt% $\text{LiClO}_4$ , PMMA/PEG-15wt% $\text{LiClO}_4$ with d) 0.4 and e) 0.8wt% MWNTs**

From Figure2(a), the stretching vibrational peaks at  $2951\text{-}2922$ ,  $1722$ ,  $1240$  and  $1191\text{cm}^{-1}$  are assigned to CH, C=O, O-C-O and C-O, respectively in the chemical structure of pure PMMA. Whilst, in Figure2 (b) can be notice new stretching vibrational peak at  $3300\text{-}3450\text{cm}^{-1}$  which refer to OH groups from PEG in the blend system. In addition, it can be also observed the vibrational peaks of C=O, O-C-O and C-O of PMMA were converted from sharp to wide peaks by the effect of presence PEG which leads to form H-bonds between functional groups ( $\text{HO}\cdots\text{O}=\text{C}$  and  $\text{HO}\cdots\text{O}-\text{CH}_3$ ). Figure2 (c) shows the addition of 15wt% $\text{LiClO}_4$  caused to significant changed in FTIR spectra of PMMA/PEG. The disappeared of splitting/shoulder OH peak at  $\sim 3300\text{cm}^{-1}$  as well as broaden sharp OH peak at  $\sim 3350\text{-}3450\text{cm}^{-1}$  may attributed to ion-dipole interaction between ( $\text{Li}^+\cdots\text{OH}$ ). It can be notable the same behavior for the peaks at  $1722$  and  $1240\text{-}1050\text{cm}^{-1}$  where peaks becomes broaden in SPE film due to the interaction of ( $\text{Li}^+\cdots\text{O}=\text{C}$  and  $\text{Li}^+\cdots\text{O}-\text{C}$ ) [20]. The embedded MWNTs into PMMA/PEG-15wt% $\text{LiClO}_4$  leads to drastically reduced intensity of the

peaks at  $\sim 3300$ - $3450$ ,  $1722$  and  $1240$ - $1050\text{cm}^{-1}$ , which it tends to be vanish with increasing dosage of MWNTs from 0.4 to 0.8wt% in SPE films (Figure2 (e, d)). Similar trends were also reported for other polymeric nanocomposites in literatures [21, 22].

### 3.3. Thermal behavior

Thermal characteristics of polymeric films was estimated through DSC thermograms to determine phase transitions such as glass transition temperature ( $T_g$ ) which represents the amorphous phase and melting ( $T_m$ ) temperatures indicates to crystalline portions inside film. Figure 3 illustrates the DSC thermograms of blend PMMA/PEG and its SPE films with 0.4 and 0.8wt% MWNTs.



**Figure3: DSC of a) PMMA/PEG, b) PMMA/PEG-15wt%LiClO<sub>4</sub>, PMMA/PEG-15wt% LiClO<sub>4</sub> with c) 0.4 and d) 0.8wt% MWNTs**

It is obvious existence three endothermic regions in the thermal curves. In first region, the baseline show slightly change in the curve at  $\sim 62^\circ\text{C}$  indicates to  $T_g$  for PMM/PEG. This low  $T_g$  value may refer to the effect of PEG which act as plasticizer and caused to increase free volume and flexibility of blend film. The presence of a single glass transition temperature  $T_g$  has been widely accepted as a demonstration of the miscibility of polymeric blends. The  $T_g$  value drastically decreases from  $\sim 62^\circ\text{C}$  for blend to  $56^\circ\text{C}$  for PMMA/PEG/15%LiClO<sub>4</sub>-0.8wt% MWNTs which denote to amorphous portions dominate in SPEs structure. Similar reduced of  $T_g$  in polymeric composites also observed in literatures [23, 24]. The second endothermic region shows as a deeper peak with centered at  $\sim 119^\circ\text{C}$  of PMMA/PEG film which may attributed to the melting of small crystalline islands in blend structure. The  $T_m$  peaks shifted to low temperature and tends to disappear with increasing MWNTs up to 0.8wt% in SPE film. The third endothermic region can be clearly noticed at  $\sim 220$ - $245^\circ\text{C}$  for PMMA/PEG. That refers to the thermal degradation process of functional groups in polymeric chains as well as LiClO<sub>4</sub> which occurred in this range. The peaks shifted to low temperature and become less intense as increasing the dopants in SPE films.

### 3.4. Electrical characteristics

The temperature-dependent dc-conductivity ( $\sigma_{dc}$ ) measurements are carried out to analyze the mechanism of conduction in the polymeric blend and its NC-SPEs. Figure 4 displays the variation of  $\sigma_{dc}$  with the reciprocal temperature for PMMA/PEG, PMMA/PEG-15wt%LiClO<sub>4</sub> without and with 0.2, 0.4 and 0.8wt%MWNTs.

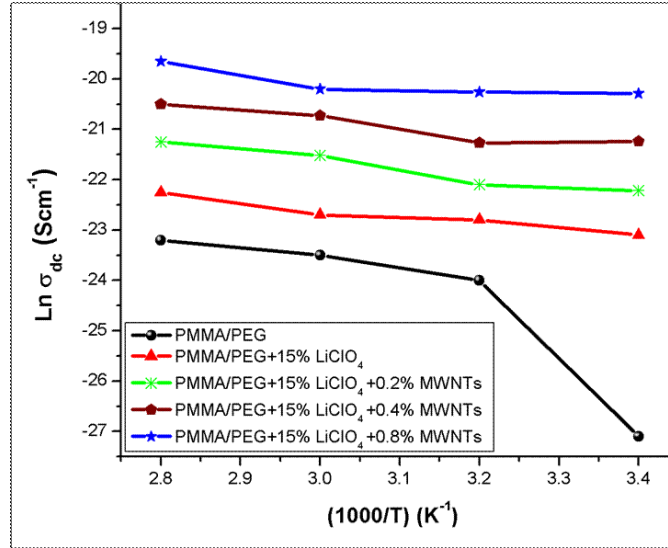


Figure4: Ln dc-conductivity as a function of temperatures

The linear variation of  $\ln \sigma_{dc}$  versus  $1000/T$  plots in Figure4 suggests an Arrhenius type thermally activated process with slightly deviation in the pure blend at higher temperature. The temperature-dependent  $\sigma_{dc}$  can be expressed as:

$$\sigma_{dc} = \sigma_0 \exp(-E_a/KT) \dots\dots\dots (1)$$

where  $\sigma_0$  is a pre-exponential factor,  $E_a$  is the activation energy,  $K$  is the Boltzmann constant and  $T$  is the absolute temperature in °K. As temperature increases, the polymer chain acquires faster internal modes in which bond rotations produce segmental motion. This, in turn, favors hopping inter-chain and intra-chain ion movements, thus  $\sigma_{dc}$  of blend SPEs becomes high [25].

The activation energy,  $E_a$  has been estimated from the slope of the Arrhenius plot. The  $E_a$  values of blend and its SPE films were listed in Table1. The obtained results reveal that  $E_a$  decreases effectively with addition 15wt% LiClO<sub>4</sub> and the increment ratios of MWNTs from 0.2 to 0.8wt% inside films. That may due to dipole-ion interaction between polar groups in the polymeric blend with Li<sup>+</sup> ions which enhance dissociation lithium salt into free ions, whereas existence MWNTs prevent free ions from reforming salt and built a conduction pathway inside polymeric chains. The dependence  $E_a$  and  $\sigma_{dc}$  on the MWNTs contents in SPE films were presented in Figure 5. The decrease in  $E_a$  values indicate to reduce potential barriers in front of mobility of charged carriers through polymeric chains which reflex in increase the  $\sigma_{dc}$  of SPE films. The  $\sigma_{dc}$  increased to  $1.38 \times 10^{-7} \text{ Scm}^{-1}$  for SPEs containing 8wt%MWNTs which means improved by several orders of magnitude compared with pure PMMA/PEG. It was also observed that the percolation threshold only appeared at high MWNTs contents, suggesting at low MWNTs contents the conducting filler is not fully connected and therefore the electric current is low. When the concentration of MWNTs is increased, the percolation threshold appears. At this point, the electrical conductivity will steeply rise over several orders [26, 27].

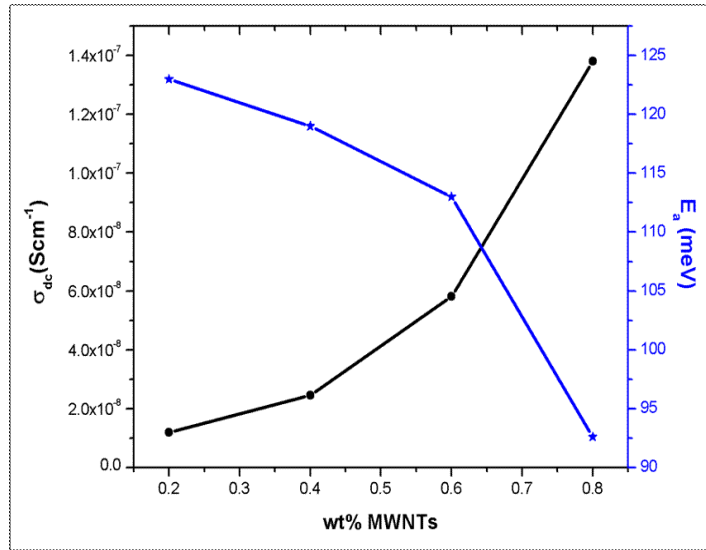


Figure5: Dc-conductivity and activation energy as a function of wt% MWNTs in SPEs

Table1: Dc-conductivity and activation energy for PMMA/PEG and its SPE-NCs

Compositions	$\sigma_{dc} \times 10^{-8}$ (Scm <sup>-1</sup> )	$E_a \times 10^2$ (m.eV)
PMMA/PEG	0.001	1.60
PMMA/PEG+15%LiClO <sub>4</sub>	0.43	1.30
PMMA/PEG+15%LiClO <sub>4</sub> +0.2%MWNTs	1.19	1.23
PMMA/PEG+15%LiClO <sub>4</sub> +0.4%MWNTs	2.46	1.19
PMMA/PEG+15%LiClO <sub>4</sub> +0.6%MWNTs	5.81	1.13
PMMA/PEG+15%LiClO <sub>4</sub> +0.8%MWNTs	13.8	0.92

#### 4. CONCLUSION

Blend polymer electrolyte nanocomposite based on PMMA/PEG/LiClO<sub>4</sub>/MWNTs films was successfully fabricated via solution casting technique. The surface morphology of the blend and its SPE films has been evaluated by SEM which indicated to predominance amorphous portions in the structure of films. FTIR showed a change in the shape and intensity peaks of distinctive functional groups in PMMA/PEG with addition LiClO<sub>4</sub> and MWNTs, which denoted to interfacial interaction between polymers and fillers. DSC thermograms exhibited reduced T<sub>g</sub> with the addition LiClO<sub>4</sub> and increase of MWNTs contents in blend films. The PMMA/PEG/15wt%LiClO<sub>4</sub>containing 0.8wt% MWNTs showed the lowest activation energy and improved dc-conductivity to 1.38X10<sup>-7</sup>S/cm at ambient temperature. These achieved results demonstrated that PMMA (a very high insulating nature) able to successfully improve its electrical conductivity and converted to semiconducting in the formulation PMMA/PEG/15wt%LiClO<sub>4</sub>-0.8wt%MWNTs film which prepared in this study.

#### ABBREVIATIONS AND ACRONYMS

SEM Scanning Electron Microscope  
FTIR Fourier Transform Infrared Spectroscopy  
DSC Differential Scanning Calorimetry

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