

# Synthesis and Characterization of Polymer–Nanoclay Conductive Nanocomposites

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**ABSTRACT:** Polymer–clay nanocomposites based on poly(3,4-ethylenedioxythiophene)/polystyrene sulfonate (PEDOT) : PSS and nanoclay montmorillonite were synthesized and characterized. The doping of PEDOT with polystyrene sulfonate made it water dispersible (PEDOT–PSS). Sodium dodecyl benzene sulfonate (SDBS) and ionic liquid were used to increase the interlayer spacing and the conductivity of the nanocomposites, respectively. The nanocomposite was characterized by various techniques, such as X-ray diffraction (XRD), TEM, surface resistivity, and thermogravimetric measurement analysis. Interlayer spac-

ing increased as a result of the addition of SDBS, and this was confirmed by the 2 $\theta$  shift observed via XRD analysis. The surface morphology of the conductive coated clay was examined by TEM analysis. Good electrical surface conductivity, interlayer spacing, and polymer coating were observed for the material prepared using the surfactant and conductive ionic liquid. © 2009 Wiley Periodicals, Inc. *J Appl Polym Sci* 116: 314–319, 2010

**Key words:** conductive clay; nanocomposites; surfactant; morphology; conductive ionic liquid

## INTRODUCTION

In recent years, there has been increased focus on polymer/clay nanocomposites to develop structural materials with enhanced mechanical, thermal, and gas barrier properties as well as new hybrid materials providing functional properties such as electrical conductivity.<sup>1–3</sup>

Electrically conductive polymer–clay nanocomposites are of great interest as they may be applied as electro-active components in different electrochemical devices, such as solid state batteries, fuel cells, or electrochemical sensors.<sup>3–11</sup> As the properties of the materials are directly related to the morphology of these systems, the dispersion of the clay inorganic phase plays an important role.<sup>12,13</sup>

Clay minerals find almost innumerable applications, and the diversity of uses is still increasing. The reason for this is the large variety of clays and clay minerals and the facilities with which these materials are modified. Swelling behavior, adsorption properties, colloidal and rheological phenomena can be optimized and adjusted for the intended application. Clay minerals normally occur as crystals

of colloid size, in which parallel silicate layers about 7–14 Å thick are stacked. These layers are negatively charged because of ionic substitutions at various sites within their structures, and as a result exchangeable cations are adsorbed on their surfaces. Clay minerals and clays are more and more involved in materials studies and are parent materials of organic–inorganic composites.

Two materials, montmorillonite (MMT) and poly(3,4-ethylenedioxythiophene) (PEDOT) are the primary components of the nanocomposites used in this study. MMT is hydrated alumina-silicate clay composed of units made up of two silica tetrahedral sheets with a central alumina octahedral sheet. PEDOT was first synthesized by Heywang and Jonas.<sup>14</sup> It is now considered an excellent conjugated conducting polymer when positively doped because of its relatively high conductivity, thermal stability and the fact that it is more environmental friendly than other conjugated polymers.<sup>14–17</sup> The main problem with PEDOT is its poor solubility, which makes the processing of this material very difficult, and represents the major barrier to its commercial applications.<sup>18</sup> A good aqueous dispersion of PEDOT can be obtained by using dopant poly(styrene sulfonate) sold under the trade name of Baytron P<sup>®</sup>. As the dispersion of the clay is important in determining the subsequent hybrid materials preparation, it is essential to improve the interaction between the clay and the polymer matrix to produce a useful polymer

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nanocomposite. Here, sodium dodecyl benzene sulfonate (SDBS) has been used to increase the inter-layer spacing of the clay, which can result in improvement in the electrical conductivity of the nanocomposite.

In this work, new conductive polymer/clay nanocomposites are prepared by the interaction of PEDOT : PSS with MMT. The conductivity of the composites was aided by the addition of SDBS and a conductive ionic liquid.

## EXPERIMENTAL

### Materials

SDBS having a critical micelle concentration value of 732 mg/L was furnished by Aldrich (South Korea) and used as received. A proprietary ionic liquid (containing metallic ions) was used as received from Shinil Chemical Industry. PEDOT : PSS (molecular weight average 7000 Da) was procured from Aldrich and used as received. De-ionized water was used to prepare the corresponding solution. The natural MMT clay (cloisite Na<sup>+</sup>) was purchased from Southern Clay and was used without any treatment.

### Preparation routes

Four preparation methods were carried out to determine the appropriate synthesis route of polymer/clay nanocomposites.

#### Method 1

Two grams of clay was dispersed in 200 mL of water, and the suspension was stirred for 30 min at room temperature. After the dispersion of the clay, different quantities of PEDOT : PSS (1, 1.4, and 2 g) were added drop wise using a dropper or a pipette. The suspension was again stirred for 6 h at room temperature and was then sonicated for 1 h. The water was evaporated using a rotary vacuum evaporator, and the material was then kept in an oven overnight at 70°C to remove the remaining moisture. Finally, the product was ground and then sieved through a 250 μm mesh.

#### Method 2

In this experiment two different amounts of surfactant were used. Clay (2 g), SDBS (0.06 and 0.1 g), and ionic liquid (2 g) were added into 200 mL of DI water. The suspension was stirred for 30 min following sonication for 1 h, and 2.0 g of PEDOT : PSS was added drop wise using a dropper or pipette. The suspension was again stirred for 6 h. Water removal, drying, grinding, and sieving were performed as described earlier in Method 1.

#### Method 3

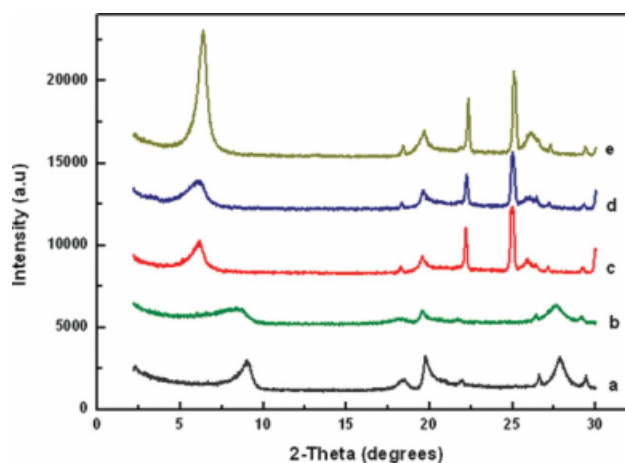
In this method, different amounts of PEDOT : PSS were used. Clay (2 g), SDBS (0.06 g), and Ionic liquid (2 g) were added into 200 mL of DI water. The suspension was stirred for 30 min following sonication for 1 h, and then different amounts of PEDOT : PSS (0.4, 0.6, 0.8, and 1.0 g) were added drop wise using a dropper or a pipette. The suspension was again stirred for 6 h. Water removal, drying, grinding, and sieving were performed as described earlier in Method 1.

#### Method 4

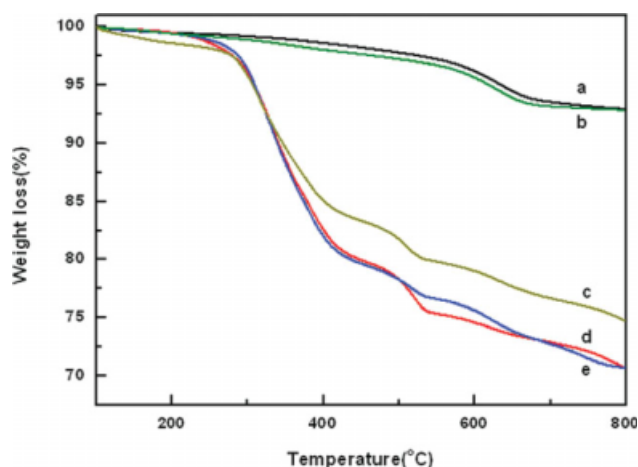
In this experiment, the effect of ionic liquid alone was studied, i.e., without the addition of the polymer (PEDOT : PSS). Clay (2 g), SDBS (0.06 g), and Ionic liquid (2 g) were added into 200 mL of DI water. The suspension was sonicated for 1 h. The suspension was then stirred for 6 h. Water removal, drying, grinding, and sieving were performed as described earlier in Method 1.

### Characterization techniques

X-ray diffraction (XRD) measurements were performed using Rigaku Rotating Anode X-ray diffractometer equipped with Cu K $\alpha$  radiation (0.15418 nm) 50 kV, 100 mA. XRD patterns are shown in Figure 1. The basal spacing or  $d_{001}$ -spacing of the samples were calculated using the Bragg equation ( $\lambda = 2d\sin\theta$ ). Thermogravimetric analysis (TGA) of the polymer nanocomposites was performed using a TGA Q5000IR instrument, operating at a heating rate of 10°C/min under nitrogen atmosphere. TEM analysis of the polymer-based nanocomposites was



**Figure 1** XRD patterns of (a) Neat clay, (b) Method 1 (1 g PEDOT : PSS), (c) Method 2 (0.06 g SDBS), (d) Method 2 (0.1 g SDBS), and (e) Method 4. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]



**Figure 2** Thermal gravimetric diagrams: (a) Method 1 (2 g PEDOT : PSS), (b) Method 1 (1.4 g PEDOT : PSS), (c) Method 4, (d) Method 2 (0.06 g SDBS), and (e) Method 2 (0.1 g SDBS). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

carried out using a JEOL JEM-4010 transmission electron microscope. Surface resistivity of the samples was measured using a HIOKI 3453 M-ohm Hi TESTER at room temperature with 50% of humidity.

## RESULTS AND DISCUSSION

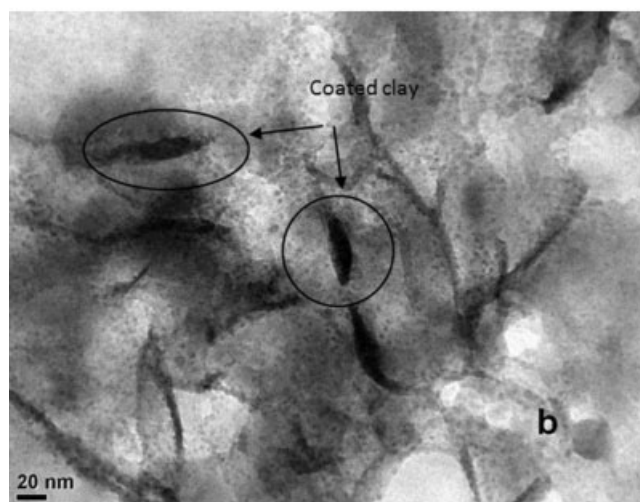
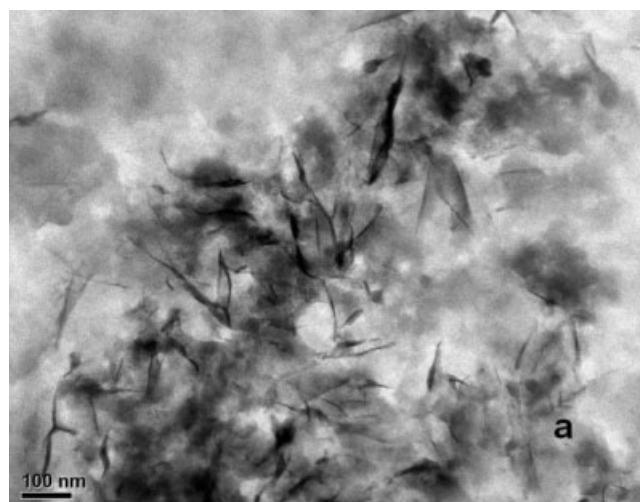
In these experiments, evaporation (rotary vacuum evaporator) is used instead of centrifuging to remove the water, while the remaining moisture was removed in an oven at 70°C. Centrifuging did not prove to be effective in case of PEDOT : PSS because PEDOT : PSS is water-soluble and it is washed away along with the water during centrifuging.

### X-ray diffraction

XRD is a suitable method for the characterization of the clay layers in polymer. It is not only easy but also inexpensive. Figure 1 represents almost harmonic series of diffraction peaks, in which the clay dispersed at the nano-scale in the polymer, is still present in the form of layered structure. Intercalation of PEDOT : PSS polymer between the clay layers can be deduced by comparing the basal spacing ( $d_L$ ) from the XRD curve of the layered clay with the nanocomposites. Upon treatment of the MMT with the SDBS and the PEDOT : PSS, the XRD of the resulting nano-hybrid material shows a very good shift of  $2\theta$  to the left. The basal spacing ( $d_L$ ) for the neat clay was found to be 0.98 nm, whereas the sample intercalated with PEDOT : PSS and SDBS results in a basal spacing of 1.42 nm. The use of surfactant helped in the exfoliation of the

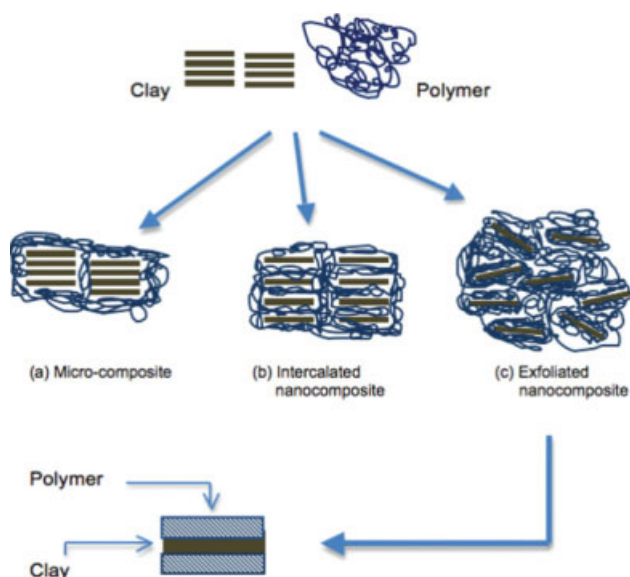
clay by entering into the layers of the clay providing a good exfoliation.

For the sample, where only PEDOT : PSS was used (Method 2), indicating that polymer has entered into the gallery, expanding the layers, the partial exfoliation is observed and the XRD pattern (1b) reveals a basal spacing in between that of neat clay (1a) and Method 2 (1c). Thus, PEDOT : PSS is not effective for increasing the interlayer spacing as compared to SDBS. XRD patterns (1c) and (1d) are for different amounts of the used surfactants, but both have the same basal spacing ( $d_L$ ), which shows that the surfactant can only open the clay plates up to a limit, which is 1.42 nm in these experiments. In curves (1c), (1d), and (1e), two high intensity peaks are observed at  $2\theta = 22^\circ$  and  $24^\circ$ , these peaks are related to the ionic liquid used in these methods and it does not affect the basal spacing of the clay. Thus, XRD analysis provides evidence for a very strong interaction of clay layers with the polymer and ionic liquid.



**Figure 3** (a) TEM of Method 2, with 0.06 g SDBS loading. (b) TEM of Method 2, with 0.06 g SDBS loading.



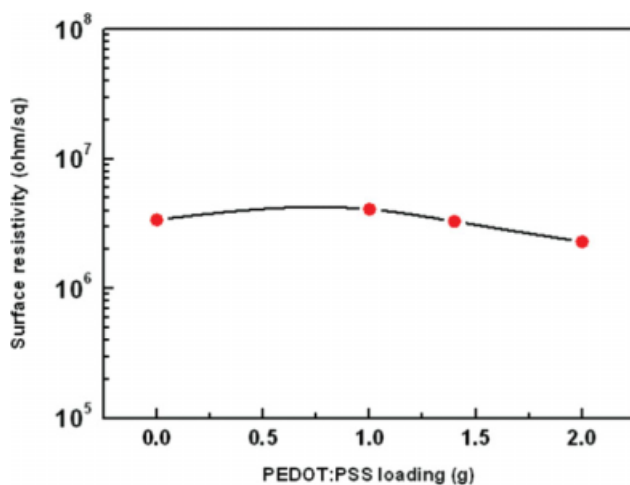


**Figure 4** Three main concepts about the polymer-clay nanocomposites. [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

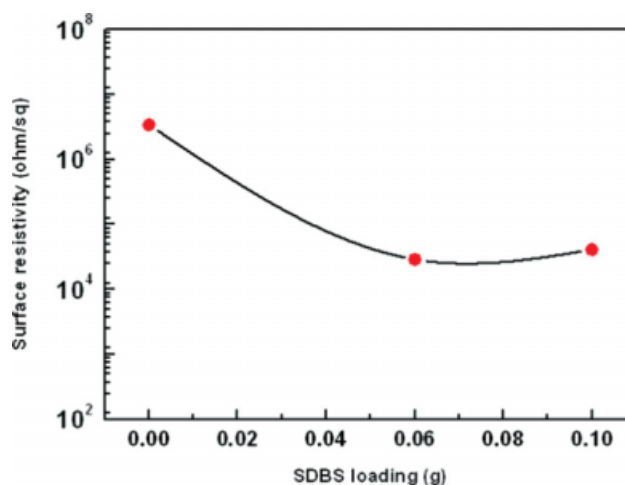
### Thermogravimetry analysis

Thermal stability of the PEDOT : PSS/clay nanocomposites was studied by TGA, which is an important method to detect the degradation behavior of synthesized materials. The bounded moisture evaporated at 100°C and this evaporation part is excluded. In Figure 2, plots "a" and "b" are of same type while the plots "c", "d", and "e" are showing the same trend.

In case of plots "a" and "b", where only PEDOT : PSS is used, degradation of PSS started from 270°C<sup>19</sup> and the degradation of PEDOT took place above



**Figure 5** Graphical representation of surface resistivity as a function of PEDOT : PSS loading (Method 1). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

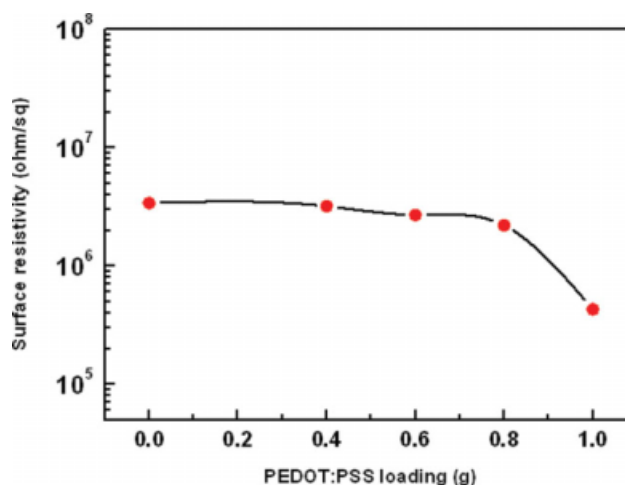


**Figure 6** Graphical representation of surface resistivity as a function of SDBS loading (Method 2). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

370°C.<sup>20</sup> The curve temperature reached up to 630°C due to the degradation of organic polymers<sup>19,20</sup> and due to the dehydroxylation from the silicate layers<sup>21</sup> and the curve became stable after 630°C.

In the case of "d" and "e", the degradation started from 240°C followed by a sharp fall in the curve, which was due to the presence of SDBS. This sharp fall was not observed in plots "a" and "b" due to the absence of surfactant in method 1. The degradation between 430–630°C is due to the elimination of hydroxyl groups from the structure of the silicate layers.<sup>21</sup>

SDBS also caused a sharp fall in plot "c", but due to the absence of the organic polymer the weight loss is less and the second curve which is from 430 to 630°C is due to the removal of hydroxyl groups.<sup>21</sup>



**Figure 7** Graphical representation of surface resistivity as a function of PEDOT : PSS loading (Method 3). [Color figure can be viewed in the online issue, which is available at [www.interscience.wiley.com](http://www.interscience.wiley.com).]

**TABLE I**  
Surface Resistivity as a Function of the Amount of PEDOT : PSS (Method 1)

PEDOT : PSS (g)	Ionic liquid (g)	SDBS (g)	Surface resistivity (ohm/sq)
1.0	0	0	$4.1 \times 10^6$
1.4	0	0	$3.3 \times 10^6$
2.0	0	0	$2.3 \times 10^6$

It can be inferred from TGA that polymer nanocomposites remain stable up to 240°C.

### Transmission electron microscopy

TEM is a very useful tool for analyzing the structure of polymer/clay nanocomposites. Figure 3(a,b) shows TEM micrographs of PEDOT : PSS/clay nanohybrids (Method 2), which indicate that the clay is unbroken and is well dispersed in the polymer matrix and that the clay is well coated with polymer. From the TEM images, the conductive coated nanoclay are exfoliated and dispersed homogeneously as further explained in Figure 4.

### Surface resistivity

The surface resistivity values observed in different experiments are shown in Figures 5–7 as a function of the amount of PEDOT : PSS, SDBS, and PEDOT : PSS, respectively. In Method 1 (Table I), the minimum surface resistivity obtained is  $2.3 \times 10^6 \Omega/\text{sq}$ , which is very close to the surface resistivity of the neat clay ( $3.4 \times 10^6 \Omega/\text{sq}$ ). This result shows that the PEDOT : PSS did not intercalate the clay, although the surface resistivity decreases in Figure 5 with the increase in PEDOT : PSS loading, but the value of surface resistivity fluctuates within  $10^6 \Omega/\text{sq}$ .

Method 2 (Table II), with the SDBS and the ionic liquid, provided better results. The optimum value of SDBS among those, which we have used is 0.06 g (3% of PEDOT : PSS), while keeping the rest of the quantities constant. The minimum value of surface resistivity obtained with 0.06 g of SDBS was  $2.9 \times 10^4 \Omega/\text{sq}$ , which was less than the  $4.1 \times 10^4 \Omega/\text{sq}$  obtained with 0.1 g of SDBS.

Figure 6 is representing a relationship between surface resistivity and amount of surfactant. The

**TABLE II**  
Surface Resistivity as a Function of the Amount of SDBS (Method 2)

PEDOT : PSS (g)	Ionic liquid (g)	SDBS (g)	Surface resistivity (ohm/sq)
2	2	0.06	$2.9 \times 10^4$
2	2	0.1	$4.1 \times 10^4$

**TABLE III**  
Surface Resistivity as a Function of the Amount of PEDOT : PSS (Method 3)

PEDOT : PSS (g)	Ionic liquid (g)	SDBS (g)	Surface resistivity (ohm/sq)
0.4	2	0.06	$3.2 \times 10^6$
0.6	2	0.06	$2.7 \times 10^6$
0.8	2	0.06	$2.2 \times 10^6$
1.0	2	0.06	$4.3 \times 10^5$

graph is showing a decreasing trend with the increase in the surfactant loading, the graph is interpolated to form a curve, in which the lowest point is for 0.06 g SDBS loading that is corresponding to  $2.9 \times 10^4 \Omega/\text{sq}$ . In Method 3 (Table III), the same amount of clay and ionic liquid with 0.06 g of SDBS is used and conditions are also kept constant with varying amount of PEDOT : PSS to check the effect of PEDOT : PSS. The resistivity reached  $10^5 \Omega/\text{sq}$  for 1 g of PEDOT : PSS and it was found that, in the presence of ionic liquid and SDBS, the surface resistivity decreased with increasing the amount of PEDOT : PSS.

Figure 7 represents an interpolated relationship between PEDOT : PSS and surface resistivity, the main component in this experiment is the PEDOT : PSS as other components are constant. The polymer helps the composite in decreasing its surface resistivity by entering into the clay layers. The curve remains between  $10^6$  and  $10^5 \Omega/\text{sq}$  as represented by the first and last point of the plot and the lowest point of the surface resistivity is for 1.0 g loading of PEDOT : PSS.

The coating of the PEDOT : PSS on the clay created uniform and continuous morphologies, which were also confirmed by TEM. Combination of the PEDOT : PSS coating and the micro-emulsions of the ionic liquid causes the surface resistivity of the nanocomposites to decrease due to an increase in ionic mobility.

In Method 1, only PEDOT : PSS is used (no addition of SDBS or ionic liquid) while in Methods 2 and 3, SDBS and ionic liquid are used. The results demonstrated that the surface resistivity of clay decreases due to the addition of ionic liquid. Method 4 was performed to check the effect of ionic liquid alone on the surface resistivity of clay, which was found to be  $3.6 \times 10^6 \Omega/\text{sq}$  (Table IV), indicating

**TABLE IV**  
Surface Resistivity of Method 4

PEDOT : PSS (g)	Ionic liquid (g)	SDBS (g)	Surface resistivity (ohm/sq)
0	2	0.06	$3.6 \times 10^6$

that the surface resistivity of clay decreases due to the combined effect of SDBS, PEDOT : PSS, and ionic liquid not due to the addition of any individual component.

### CONCLUSIONS

Different routes have been explored to fabricate conductive coated nanoclays. Using surfactant along with ionic liquid resulted in a good basal spacing ( $d_L$ ), and also a good electrical conductivity. Surfactant not only helped in the dispersion of clay but also made it possible for the ionic liquid to form a micro-emulsion in the water. Further, the use of surfactant resulted in a good coating of the clay with the polymer. PEDOT : PSS or ionic liquid alone could not provide the improved results, but the combination of PEDOT : PSS, ionic liquid, and surfactant proved to be helpful in reducing the surface resistivity of the polymer nanocomposites.

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