GENERAL SYMPOSIA | POLYMER COMPOSITES

Formulation of Highly Electro-Conductive Thermoplastic Composites using PEDOT-based Fillers with Controlled Shape Factor

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DOI: https://doi.org/10.51573/Andes.PPS39.GS.PC.2

December 2024

Formulation of Highly Electro-Conductive Thermoplastic Composites using PEDOT-based Fillers with Controlled Shape Factor

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Abstract: The objective of this study is to develop a new conductive thermoplastic material with superior electrical properties. Currently, conductive polymers are typically filled with carbon or metallic particles [1]. However, these filled thermoplastics exhibit drawbacks such as high rigidity, toxicity, and high viscosity [2]. An alternative approach investigated in this work is to substitute these fillers with intrinsically conductive polymers like Poly(3,4-ethylenedioxythiophene) (PEDOT). PEDOT can achieve exceptional electrical conductivities (over 1000 $S.cm^{-1}$) when combined with polymeric dopants like poly(styrene sulfonate) (PSS) and is frequently used in thin films or gels in medical and energy applications [3]. However, incorporating PEDOT into the conventional hot melt processes of the plastic industry remains challenging [1].

Keywords: Conductive Polymers, PEDOT, Oxidative Polymerization, Conductive Composites, Extrusion, Electrical Conductivity, Shape Factor

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Introduction

In a previous study, we synthesized electro-conductive PEDOT particles for incorporation into a polyethylene oxide (PEO) matrix via an extrusion process [4]. Composites with notable conductivities of up to 12 $S{\cdot}cm^{-1}$ were achieved, but a high amount of PEDOT fillers was required to reach the electrical percolation threshold. To reduce this percolation threshold, this work investigates a new approach based on a supported polymerization process. The goal is to control the shape factor of the synthesized conductive PEDOT particles by using different fillers, such as silica, graphene, or clays, for EDOT polymerization. The objective is to coat these fillers with a conductive PEDOT shell and then study the impact of various shape factors on the electrical percolation threshold of the resulting composites. Relationships between the process, morphology, and properties were analyzed using SEM, X-ray tomography, and four-probe resistivity measurements. Percolation curves for different shape factors were also obtained and compared to the initial curve obtained with micrometric PEDOT particles.

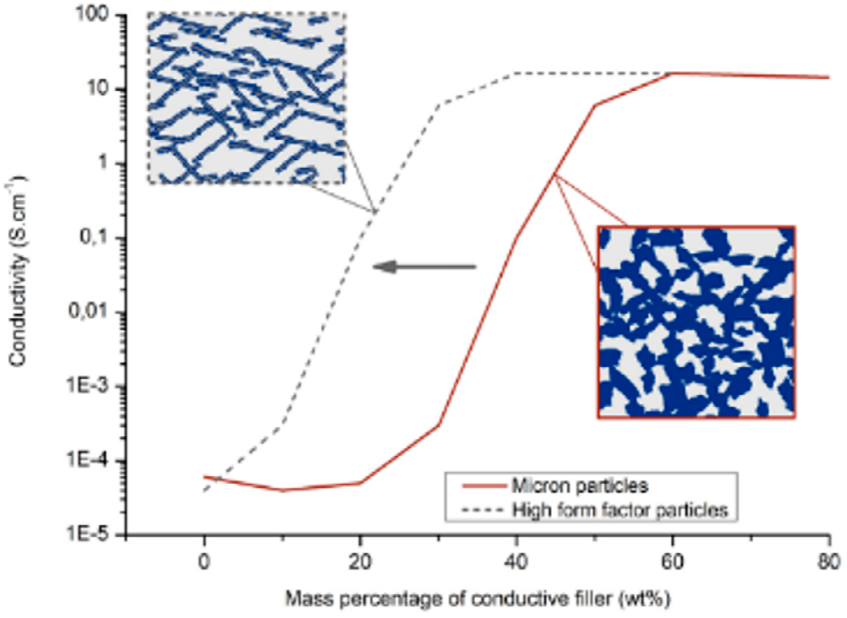

Figure 1. Illustration of the objective of reducing the percolation threshold by optimizing the form factor of the fillers.

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Experimental Section

Materials

3,4-Ethylenedioxythiophene (EDOT, 99%, Acros Organics), iron (III) chloride ($FeCl_3$; 97%, Sigma-Aldrich), sodium dodecyl sulfate (SDS, 98.5%, Sigma-Aldrich), natural clays with interesting shape factor (L/D ratio > 50) were used as received for the synthesis of PEDOT-Clay particles. Poly(ethylene oxide) (PEO, 100.000 g/mol, Sigma-Aldrich) was used as received for the extrusion of PEO / PEDOT-Clay composites.

Synthesis of PEDOT-Clay Particles Using Oxidative Polymerization Process

The synthesis of PEDOT-Clay was performed by chemical oxidative polymerization of EDOT in the presence of clay particles, as presented in a previous work [4]. The clays were dispersed in 100 mL of demineralized water, and Sodium Dodecyl Sulfate (SDS, 0.00056 mmol) was dissolved in the solution. EDOT (0.007 mol) was added dropwise, and the solution was stirred for 2 hours. The oxidant (FeCl3, 0.0023 mol) was then added to the solution. The solution was placed under magnetic stirring for 48 hours to allow polymerization at room temperature.

The polymerized solution was filtered using a Büchner funnel and filter paper. During suction, the PEDOT-Clay particles were retained by the filter paper and the oxidizing solution was collected in the vacuum flask. The polymerized particles were washed twice on the filter paper during suction, first with acetone:methanol (3:10) and then with ethanol:water (1:1). The PEDOT-Clay particles were dried at 60°C for 48 hours.

Incorporation of Synthesized PEDOT-Clay Particles into the PEO Matrix by Twin Screw Extrusion

The result of the polymerization step, which is a dry dark blue powder, is directly used as a filler for the twin screw extrusion process. Agglomerates of synthesized PEDOT-Clay particles were separated using a mortar and then blended with PEO powder. The proportions of PEDOT-Clay in PEO were varied from 10 wt.% to 40 wt.%. The blended dry powders were then introduced into a twin screw extruder at a temperature of 100°C and a screw rotation speed of 30 rpm. The microcompounder (Haake Minilab 2, Thermo Fisher Scientific) was used in direct extrusion mode. Under these conditions, the residence time of the material inside the microcompounder is approximately 1 minute.

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Characterizations

Conductivity Measurements on PEDOT-Clay Particles and Extruded PEO/PEDOT-Clay Composites

To perform electrical conductivity measurements, the PEDOT-Clay powder was compressed into pellets. Infrared equipment normally used for making KBr pellets was employed for this purpose. The pellets were compressed at 45 bars for 30 seconds. With this method, all the samples are 13 mm in diameter, but with varying thicknesses. The thickness of each pellet was measured with a slide caliper.

The composite strip could be used immediately after the extrusion step. The width and thickness of the strip were also measured with a slide caliper. Both the PEDOT-Clay pellets and the extruded strips were then placed in a homemade four-probe system, developed specifically for this study and equipped with a Keithley 2611B multimeter, with constant pressure applied for resistance measurements.

Morphological Analyses by SEM and X-Ray Tomography

The morphology of PEDOT-Clay powders and extruded PEO/PEDOT-Clay ribbons was analyzed primarily by scanning electron microscopy (SEM, Hitachi SU 8010). The extruded ribbons were also subjected to X-ray tomography using an EasyTom 150/160 apparatus (RX Solution, voltage 100 kV, spatial resolution 5 µm) for better visualization of the aggregation state of PEDOT-Clay particles within the PEO.

Results & Discussions

Processing of PEO/PEDOT Composites

Previous work by our team demonstrated the synthesis of conductive PEDOT particles and their incorporation into a thermoplastic matrix [5]. Electrically conductive PEDOT particles were obtained through chemical oxidative polymerization. Using these particles as fillers, electrically conductive thermoplastic composites were manufactured by twin screw extrusion to determine the electrical percolation threshold and the maximum conductivity of the composite. PEDOT particles were blended with PEO having a molecular weight of 100,000 $g.mol^{-1}$ at a processing temperature of 100°C, which is compatible with the maximum processing temperature of PEDOT, close to 170-180°C [5]. At approximately 30 wt.% PEDOT, the electrical conductivity begins to increase, reaching a maximum conductivity of around 12 $S.cm^{-1}$ with 60 wt.% of conductive particles.

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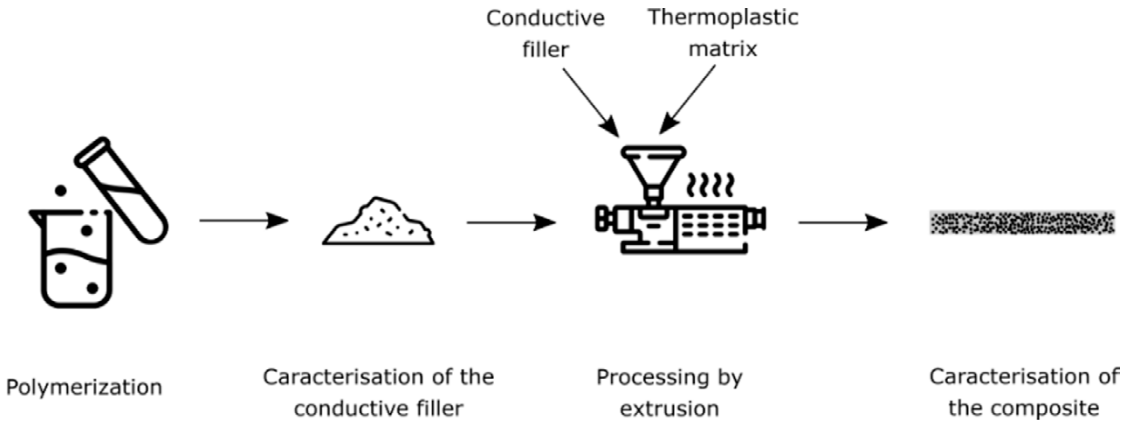

Figure 2. Schematic representation of the electrically conductive thermoplastic composite processing.

Influence of the Form Factor on the Percolation Threshold

Interesting properties were obtained in the previous study, but a high percolation threshold was observed, which can lead to certain issues. In fact, aside from cost concerns, a high percolation threshold results in high viscosities and a reduction in the mechanical properties of the composite [6]. Therefore, reducing the percolation threshold is necessary while maintaining the electrical properties of the composite materials. To this end, some studies have demonstrated the influence of the form factor and aspect ratio on the percolation threshold. Audoit and Matthews, for example, showed that the higher the form factor of the filler, the lower the percolation threshold [7,8].

Supported Polymerization of PEDOT in Literature

To modify the form factor of PEDOT, using a polymerization support to obtain a core-shell structure with controlled morphology is a promising strategy. To achieve a very high form factor, Chen et al. and Zhang et al. demonstrated the possibility of polymerizing EDOT onto polypropylene fibers or glass fibers [9,10]. Supported oxidative polymerization on graphene particles has also been presented in literature, as shown by the work of Xu et al. [11], leading to the formation of 2D particles. This method can also be used to synthesize coated nanoparticles, such as silica@PEDOT nanoparticles [12] or carbon black@PEDOT [13].

Supported Polymerization of PEDOT on High Form Factor Clays

To reduce the percolation threshold of our PEO/PEDOT thermoplastic composites and lower the material cost, a supported polymerization of PEDOT on clay particles with a very high aspect ratio (L/D > 50) was performed. Figure 3 shows the morphology of PEDOT/clay particles obtained by

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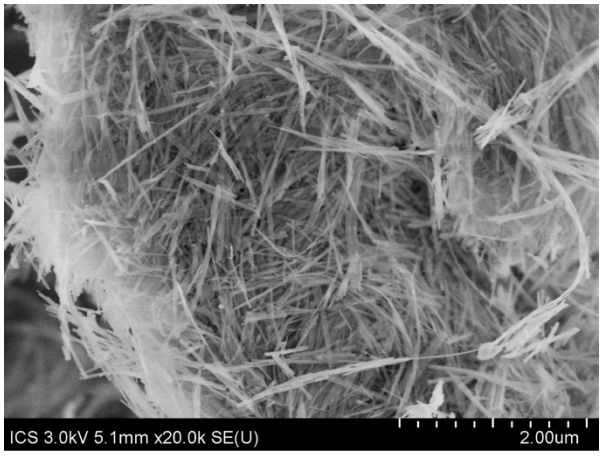
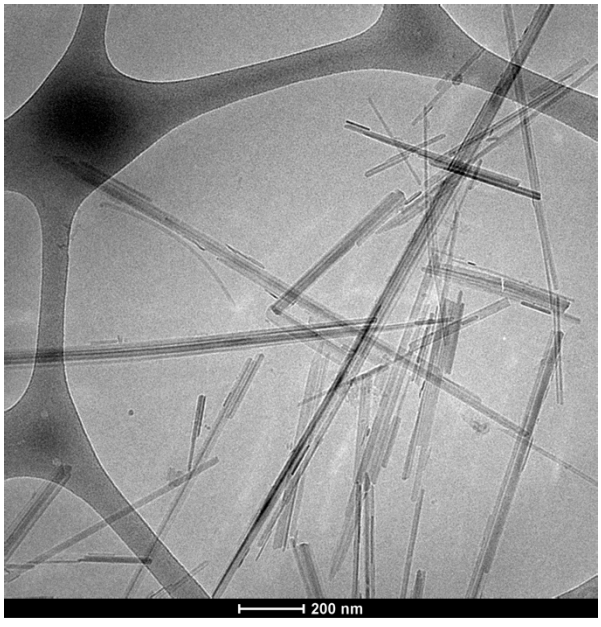
chemical oxidative polymerization of EDOT in water at 20°C. SEM and cryo-TEM images illustrate the clay particles before polymerization ([a] and [c]) and covered by a PEDOT shell ([b] and [d]).

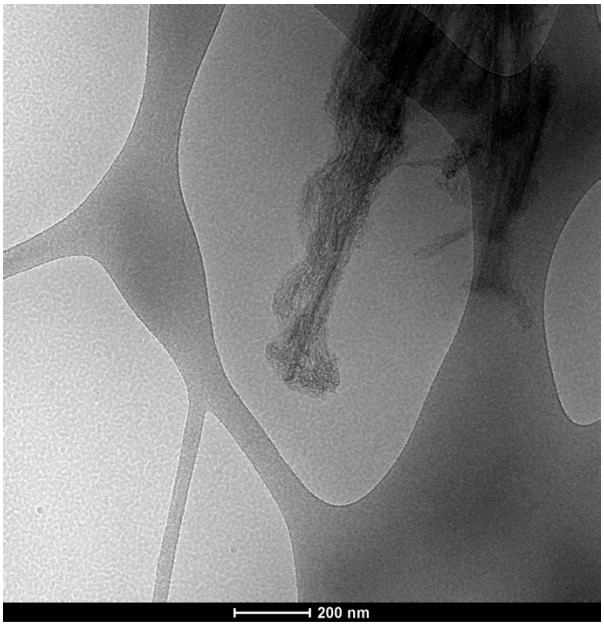


(a) Pure Clay – Before polymerization

(b) Clay-PEDOT – After polymerization



(c) Pure Clay – Before polymerization



(d) Clay-PEDOT – After polymerization

Figure 3. SEM images of clay particles before polymerization (a) and after supporting EDOT (b); cryo-TEM images of clay particles before polymerization (c) and after supporting EDOT (d).

Figure 3(b) shows a complete coverage of the clay particles by PEDOT, while Figure 3(d) indicates that all PEDOT chains surround the clay particles, with no PEDOT chains appearing to be independent of the clay particles. Moreover, conductivity characterizations were also performed on compressed powders, with conductivities reaching up to 47 $S.cm^{-1}$.

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Effect of Form Factor on the Percolation Threshold of PEO Composites

Electrically conductive thermoplastic composites PEO/PEDOT-Clay were manufactured by twin screw extrusion using the same process described in paragraph 1. To determine the electrical percolation threshold, extrusion experiments were conducted with varying amounts of PEDOT-Clay particles, ranging from 10 wt% to 40 wt%. Figure 4 shows that the electrical conductivity of PEO/PEDOT-Clay composites begins to increase from 20 wt% of fillers. A shift of approximately 10 wt% in the percolation threshold is observed between the percolation curves of composites loaded with high aspect ratio versus low aspect ratio particles, which is consistent with literature.

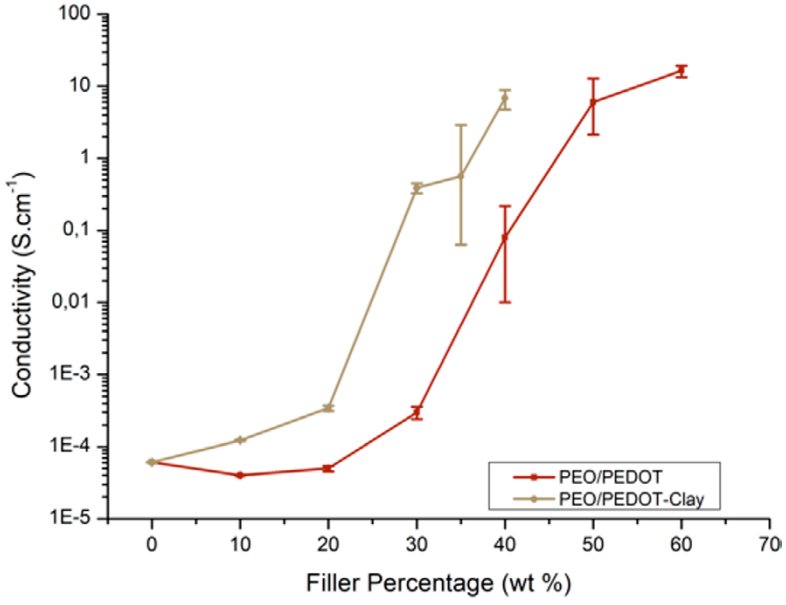

Figure 4. Evolution of the electrical conductivity of PEO/PEDOT and PEO/PEDOT-clay thermoplastic composites as a function of the PEDOT weight content (red) or PEDOT-Clay weight content (dash line).

Moreover, a drastic improvement in filler dispersion is evident from the X-ray tomography images presented in Figure 5.

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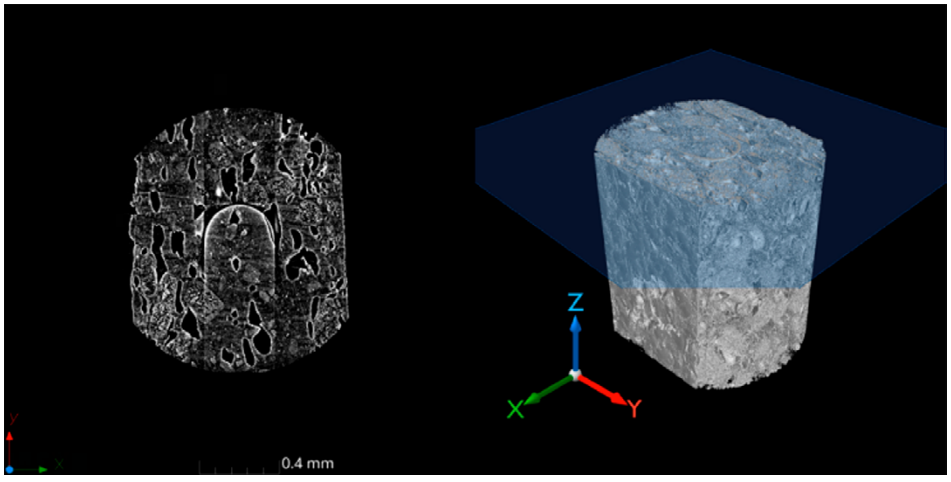
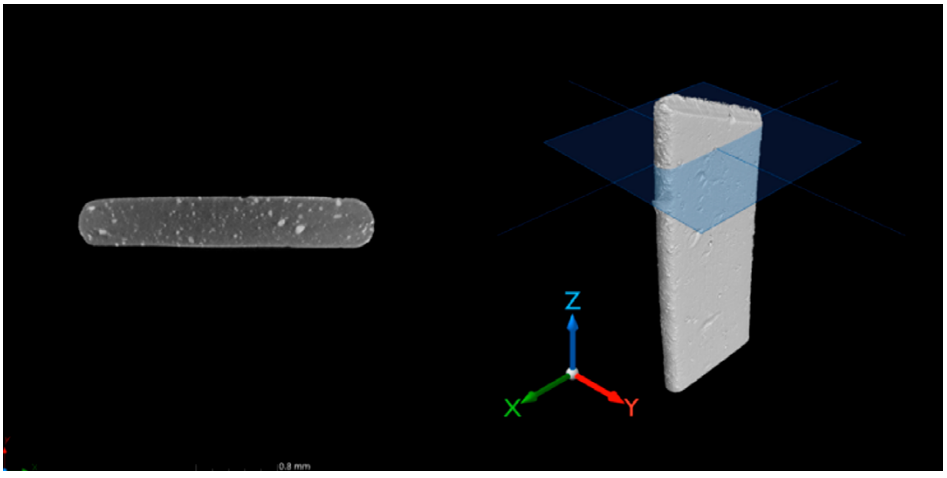


PEO/μPEDOT 60/40 wt%



PEO/CLAY-PEDOT 60/40 wt%

Figure 5. X-Ray tomography of PEO/PEDOT and PEO/PEDOT-clays thermoplastic composites filled with 40 wt% of filler.

Conclusion

Electrically conductive PEDOT-Clay particles were successfully produced, with conductivities reaching up to 47 $S \cdot cm^{-1}$. These micron-sized fillers were then incorporated into a thermoplastic matrix. PEO/PEDOT-Clay thermoplastic composites were obtained through an extrusion process, and a significant reduction in the percolation threshold was observed due to form factor optimization. Additionally, improved filler dispersion within the matrix was noted, leading to better homogeneity and enhanced mechanical resistance of the material.

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Acknowledgments

All authors acknowledge the MINAMEC platform (Antoine Egele) for conductivity measurements, X-ray tomography, and data interpretation. The authors especially acknowledge Damien Favier for the realization of the four probes conductivity measurement device. The authors acknowledge the PLAMICS microscopy facility of ICS. CS and JS particularly acknowledge the Wallonia Region/ Service Public de Wallonie (Belgium), West Vlaanderen Region (Belgium), Agentschap Innoveren Ondernemen (Belgium), and European Commission (FEDER) for the financial support regarding important chemicals in the framework of the INTERREG France-Wallonie-Vlaanderen program (BIOHARV project, GoToS3 portofolio).

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