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# Synthesis And Characterization Of PEDOT, an intrinsically conductive polymer

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**Abstract.** Poly(3,4-ethylenedioxythiophene) (PEDOT) is a highly valuable polymer material for modern electronics due to its impressive electrical conductivity (up to  $1000 \text{ S.cm}^{-1}$ ). Combined with poly(styrenesulfonate) (PSS), PEDOT can be processed into thin film for a multitude of applications [1]. However, the introduction of PEDOT in melt-state processes of the plastic industry is still challenging because PEDOT is infusible and only commercially available as highly diluted aqueous solutions. Nevertheless, previous study showed that extrusion processing of PEDOT:PSS solutions with PEO as a melting carrier is possible but sophisticated pre/post-treatments are mandatory to maintain high level of electrical conductivity up to  $5 \text{ S.cm}^{-1}$  [2]. In this context, the goal of this study is to synthesize electrically conductive polymeric particles of PEDOT. An oxidative chemical polymerization of EDOT was carried out using two different oxidants:  $\text{Fe}_2(\text{SO}_4)_3$  and  $\text{FeCl}_3$ . Resulting polymeric particles were studied thanks to SEM observations and resistivity measurements. The influence of parameters such as the ratio (monomer/oxidant), the polymerization time or the use of surfactants on the conductivity of PEDOT particles was studied. Interestingly, as-prepared PEDOT particles display conductivities between  $0.1$  and  $10 \text{ S.cm}^{-1}$  without any post treatment. This result is nearly 1000 times higher than previously reported by Jiang *et al.* [1]. A first explanation can be the presence of the oxidant/surfactant combined with PEDOT particles and acting as a dopant. Besides, comparison between the samples allows us to highlight the impact of the monomer-oxidant ratio on the electrical conductivity of the pellets. To better understand these results, correlations between (i) the polymerization process, (ii) the particles morphology and (iii) final electrical properties are currently being investigated.

## INTRODUCTION

With the development of Molded Interconnect Devices (MID) and flexible electronics, intrinsically conductive polymers are intensively studied [3, 4, 5, 6]. Conductive polymers present many advantages like flexibility, easy chemical modifications, and nontoxicity [7]. Thanks to these characteristics, conductive polymers are used in many different applications such as antistatic coatings, liquid crystal displays (LCDs), organic light emitting diodes (OLEDs), touch panel displays, sensors, solar cells, and printed circuit boards for example [4, 8, 9].

Polyacetylene, discovered in 1977, was the first intrinsically conductive polymer [10, 11]. Since this period, conductive polymers showed an intense interest because of various characteristics including combination of properties of metals and polymers [8]. This interest occurred with the synthesis of various other conjugated polymers like polyaniline (PANI) [9, 12, 13], polypyrrole (PPy) [9, 14] and polythiophene (PTh) [9, 15].

However, by comparison with poly(3,4-ethylenedioxythiophene) PEDOT, many conductive polymers showed a low stability [16] and poor processability [8]. That is the reason why, many studies focused on PEDOT [1, 2, 17, 18].

The objective of the present work was to develop a conductive thermoplastic material. Currently, one way to develop this type of materials is to use polymers filled with carbon or metallic particles [2]. These filled thermoplastics displayed drawbacks such as high rigidity, toxicity, high viscosity, etc. [19] and a potential solution was proposed by Duc *et al.* [2] with the use of intrinsically conductive polymers. However, the thermomechanical treatment during the process had a strong impact on the conductivity of the poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS) [2]. Moreover, PEDOT is only commercially available with PSS (poly(styrene sulfonate) as a very expensive highly diluted aqueous solution. The use of this commercial solution involves an additional step of freeze drying. The present study deals with the synthesis of conductive PEDOT particles in order to incorporate them into

thermoplastic matrix, without using a commercial solution of PEDOT:PSS or carbon or metallic objects and then propose innovative conductive polymeric materials.

## EXPERIMENTAL

### Chemical Polymerization of EDOT

3,4-Ethylenedioxythiophene (EDOT, 99%, Acros Organics), iron (III) sulfate hydrate ( $Fe_2(SO_4)_3$ , 97%, Sigma-Aldrich), iron (III) chloride ( $FeCl_3$ , 97%, Sigma-Aldrich), sodium dodecyl sulfate (SDS, 98.5%, Sigma-Aldrich), were used for the synthesis.

Synthesis of PEDOT was performed by chemical oxidation polymerization of EDOT as described in Table I [1]. Sodium Dodecyl Sulfate (SDS, 21.05 mol) was dissolved into 50 mL of demineralized water. EDOT was added dropwise into the surfactant solution and the solution was stirred for 2 hours.  $Fe_2(SO_4)_3$  or  $FeCl_3$  was then added into the solution. Proportions of the different elements for each synthesis are indicated in Table I.

Sample	Oxidant type	EDOT:Oxidant ratio	Volume of the solution (mL)	Mass of EDOT (g)	Mass of oxidant (g)	Mass of surfactant (g)
1	$Fe_2(SO_4)_3$	1:1	50	0.5	1.406	0
2	$Fe_2(SO_4)_3$	1:2	50	0.5	2.812	0
3	$Fe_2(SO_4)_3$	1:3	50	0.5	4.218	0
3bis	$Fe_2(SO_4)_3$	1:3	50	0.5	4.218	0
3ter	$Fe_2(SO_4)_3$	1:3	50	0.5	4.218	0
4	$Fe_2(SO_4)_3$	1:10	50	0.5	14.062	0
5	$FeCl_3$	1:3	50	0.5	1.711	0
6	$Fe_2(SO_4)_3$	1:3	50	0.5	4.218	0.73
6bis	$Fe_2(SO_4)_3$	1:3	50	0.5	4.218	0.73

TABLE I. Parameters of synthesis.

The solution was then placed in the oven at 50°C under magnetic stirring during 48 hours for polymerization.

The polymerized solution was after centrifuged (9000 rpm, 23 min) and washed two times with acetone:methanol and ethanol:water respectively (volume ratios). After the three steps of centrifugation, the supernatant liquid was removed with a syringe. After a last centrifugation step, PEDOT was dried at 60°C for 48 hours.

The EDOT polymerization is followed by a quick changing of color of the solution. EDOT is a liquid translucent product and PEDOT is a dark blue powder, insoluble and infusible, in suspension into the polymerization solution.

### Characterizations

The conversion rate was calculated by weighing and morphological analysis was performed by SEM using a Hitachi SU 8010 with a working distance of 5 mm and an acceleration voltage of 5 kV.

To perform electrical conductivity measurements, PEDOT powder had to be compressed into pellets. Infra-red equipment normally intended for making KBr pellets was used. The powder was compressed at 45 bars during 30 seconds.

Pellets were then placed into a home-made four probes system developed specially for this study, with a constant pressure for resistance measurement. In order to perform the measurements a multimeter Agilent 34461A was used.

Accounting for pellet thickness, resistance was converted into conductivity using the formula described in Eq. 1 [20]:

$$\rho = G \frac{V}{l}. \quad (1)$$

with I, the current passed through the sample, V, a measured voltage and G, a correction factor depending on tested sample shape and dimensions, and on the arrangement of electrical contacts

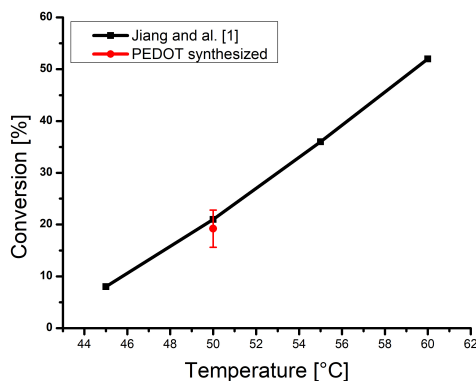
## RESULT AND DISCUSSION

### Conversion measurements

The conversion rate was estimated by the measurement of the polymer weight. The quantity of PEDOT was compared with the mass of EDOT introduced in the system. For a 48h polymerization at 50°C, a conversion rate of  $19.2 \pm 3.6\%$  was obtained.

As a function of the oxidant type and the EDOT:Oxidant ratio, different conversion rates were obtained. In fact, the use of  $FeCl_3$  as oxidant allowed to reach 27% of conversion. With the  $Fe_2(SO_4)_3$ , the best conversion rate was obtained with the (1:3) EDOT:oxidant ratio. The yield was only 14.6% for the (1:1) EDOT:oxidant ratio and 11.8% for the (1:2).

Figure 1 shows the evolution of the conversion rate as a function of the temperature [1]. By comparison with results obtained by Jiang *et al.* [1], using the same experimental conditions of polymerization, the yield is quite similar.

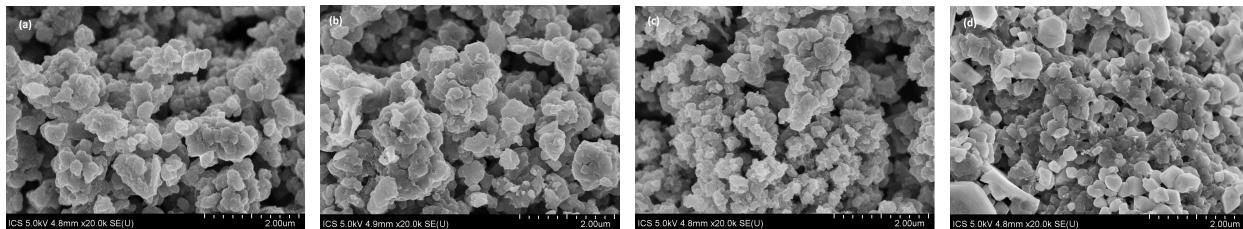


**FIGURE 1.** Effect of polymerization temperature with reaction time of 48h on conversion of EDOT [1] and comparison with the conversion of our sample.

### Structural and morphological characterizations

Figure 2 shows that each polymerization with different EDOT:oxidant ratios results on PEDOT particles. We can note that all the samples show similar morphologies. Synthesized PEDOT have a grain structure with a particle size of approximately 0.5 to 1  $\mu m$ . The particle size seems to decrease as a function of the augmentation of the concentration of oxidant. Smaller particles were obtained for the (1:3) EDOT:oxidant ratio. In all cases, aggregates of particles were formed. On Fig 2d, the size of the aggregates appears to be larger.

Moreover, structure of the synthesized PEDOT samples is very close to that shown by Jiang *et al.* [1]. In Fig. 2d, presence of excess oxidant compared to the amount of PEDOT is consistent with the EDOT:oxidant ratio of 1:10 during synthesis.



**FIGURE 2.** SEM pictures of PEDOT samples synthesized with different EDOT:oxidant ratio mol : (a) 1:1, (b) 1:2, (c) 1:3, (d) 1:10

## Electrical conductivity

With the results of electrical conductivity measurements, we can see the influence of different parameters.

### *Influence of the oxidant type on the conductivity*

During synthesis, the influence of two different oxidants  $Fe_2(SO_4)_3$  and  $FeCl_3$  is compared. Better conductivity values are obtained with  $Fe_2(SO_4)_3$  (Fig. 3a). Actually, using  $Fe_2(SO_4)_3$  an average conductivity of  $12.9 \pm 3.6 S.cm^{-1}$  was obtained and. However, with  $FeCl_3$  the measured conductivity is close to  $4.9 \pm 1.3 S.cm^{-1}$ . Moreover, Jiang *et al.* [1] explained that  $FeCl_3$  hydrolyzed severely. This phenomenon can be an explanation of the poorer performances of this oxidant.

### *Influence of the EDOT:oxidant ratio on the conductivity*

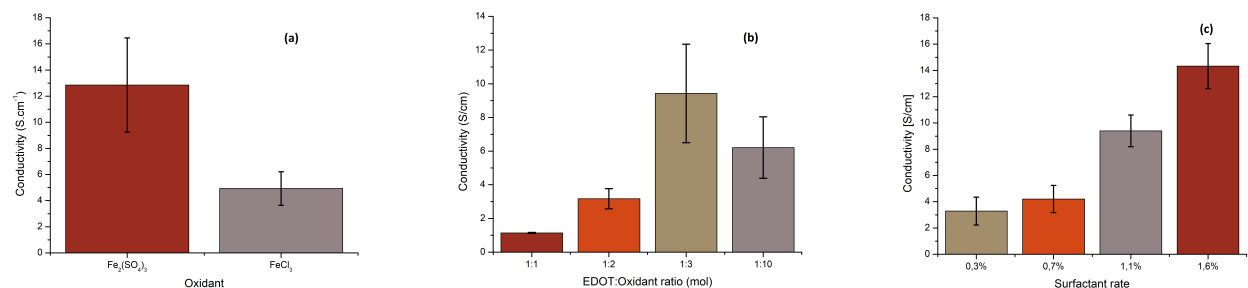
Figure 3b describes the evolution of the conductivity as sample as a function of EDOT:oxidant ratio. The conductivity is observed to reach a peak with the (1:3) ratio and then decreased for higher ratio. This specific evolution has already been described by Kudoh *et al.* [17]. In fact, they showed an increase of the conductivity as a function of the  $Fe_2(SO_4)_3$  concentration, with an optimal value and then a decrease with the concentration. They explained that the "side reactions brought about by the excess oxidant were responsible for this decrease of conductivity" [17].

All our future samples will be made with an EDOT:oxidant ratio of (1:3).

### *Influence of the use of surfactant on the conductivity*

The influence of the use of surfactant on conductivity was also studied (Fig 3c). An increase of conductivity is noticed as a function of the augmentation of the surfactant concentration. In fact, the conductivity was around  $3.3 \pm 1.1 S.cm^{-1}$  with 0.3% of surfactant and reached  $14.3 \pm 1.7 S.cm^{-1}$  with 1.6%.

However, Ouyang showed that this conductivity reached a maximum with a defined molar ratio [8]. An augmentation of the surfactant concentration in our samples can therefore results on a better conductivity. In fact, use of surfactant seems to be reducing the distorsion of PEDOT chain. This conformation allows to improve the conductivity [8].



**FIGURE 3.** Conductivity of synthesized PEDOT samples as a function of the type of oxidant used (a), the EDOT:oxidant ratio (b), the surfactant rate (c)

## CONCLUSION

The main objective of the present study was to synthesize, with an oxidative polymerization, conductive PEDOT particles in order to incorporate them into thermoplastic matrices. In one hand, easily scalable and cheap polymerization process was performed, without PSS or post treatment. The as-prepared PEDOT powders exhibit conductivities close to  $20 \text{ S.cm}^{-1}$ . The influence of oxidant type, EDOT:Oxidant ratio and concentration of surfactant was also studied. Higher conductivities were obtained with the use of  $\text{Fe}_2(\text{SO}_4)_3$ , an EDOT:oxidant ratio of 1:3 and Sodium Dodecyl Sulfate (SDS) as surfactant.

## ACKNOWLEDGMENTS

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