Hindawi Publishing Corporation
Journal of Nanoparticles
Volume 2013, Article ID 690407, 4 pages
http://dx.doi.org/10.1155/2013/690407

Research Article

Conductometry and Size Characterization of Polypyrrole Nanoparticles Produced by Ball Milling

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Received 14 January 2013; Revised 28 March 2013; Accepted 28 March 2013

Academic Editor: Xiangwu Zhang

Polypyrrole (PPy), one of the most extensively investigated conducting polymers, has attracted a great deal of interest because of its good electrical conductivity, environmental stability, and easy synthesis. PPy films were produced by polymerization of pyrrole and tosylate (TsO^-) as dopants in the presence of oxidant $FeCl_3$ and polyethylene glycol (M_w 8000) at -5°C for 48 h. High energy milling was carried out at 850 rpm in the dry media with the balls of 10 mm. Particles were then characterized by Scanning Electron Microscope and Dynamic Light Scattering techniques for size distribution, and it was found that the size of PPy particles is a decreasing function of time of milling. Electrical conductivity was measured by preparing a homogenous aqueous dispersion of PPy particles and found as exponential decreasing function of time of milling. The changes occurred in PPy after milling was analyzed by Differential Scanning Calorimetry (DSC) and Fourier transform infrared spectroscopy (FTIR).

1. Introduction

Polypyrrole (PPy), one of the most extensively investigated conducting polymers, has attracted a great deal of interest because of its environmental stability and easy synthesis along with its good electrical conductivity [1]. Along with its other applications, PPy can be used as conducting filler in insulating polymer matrices in preparation of electrically conducting composites. These composites offer potentials in electronic packaging, EMI shields, display devices, electrodes, and other thermal applications [2–5]. Distribution of PPy particles in polymer matrices, however, becomes an issue. It has been reported that PPy nanoparticles can be effectively dispersed due to large surface area for reactions and highly porous in sol form [6, 7] and then they provide good conductivity.

Recent studies also showed that the addition of polymers can influence the conductivity by steric stabilization of the polypyrrole chains [8]. To this end, water-soluble polymers of molecular masses over 20,000 $g\cdot mol^{-1}$, such as methyl cellulose, poly(vinyl alcohol-co-acetate), poly(ethylene oxide), poly(vinylpyrrolidone), poly(2-vinylpyridine), and poly(vinylmethylether), were studied. When using these additives, conductivities of a broad range (1×10^{-9}–12 $S\cdot cm^{-1}$) have been obtained [8]. Specifically, for poly(ethylene oxide) with a molar mass of 130,000 $g\cdot mol^{-1}$, a conductivity of 2×10^{-3} $S\cdot cm^{-1}$ was found [9]. For this reason PEG 8000 was added in the preparation of PPy.

Currently, various ways to produce PPy nanoparticles have been presented which can provide better electrical conductivity of surface coatings, when applied on any substrate by bottom-up techniques. Their application is based on empirical evidence, and prediction based on their size and electrical conductivity is still very limited. This limits the design of nanocomposite structures with the purpose of their use. The purpose of this study is to produce the nanoparticles of PPy by top-to-bottom technique that is ball milling and characterize their size and electrical conductivity.

2. Materials and Methodology

Pyrrole (99%) was distilled three times before use. *p*-Toluenesulfonic acid (PTSA) as dopant, $FeCl_3$, and polyethylene

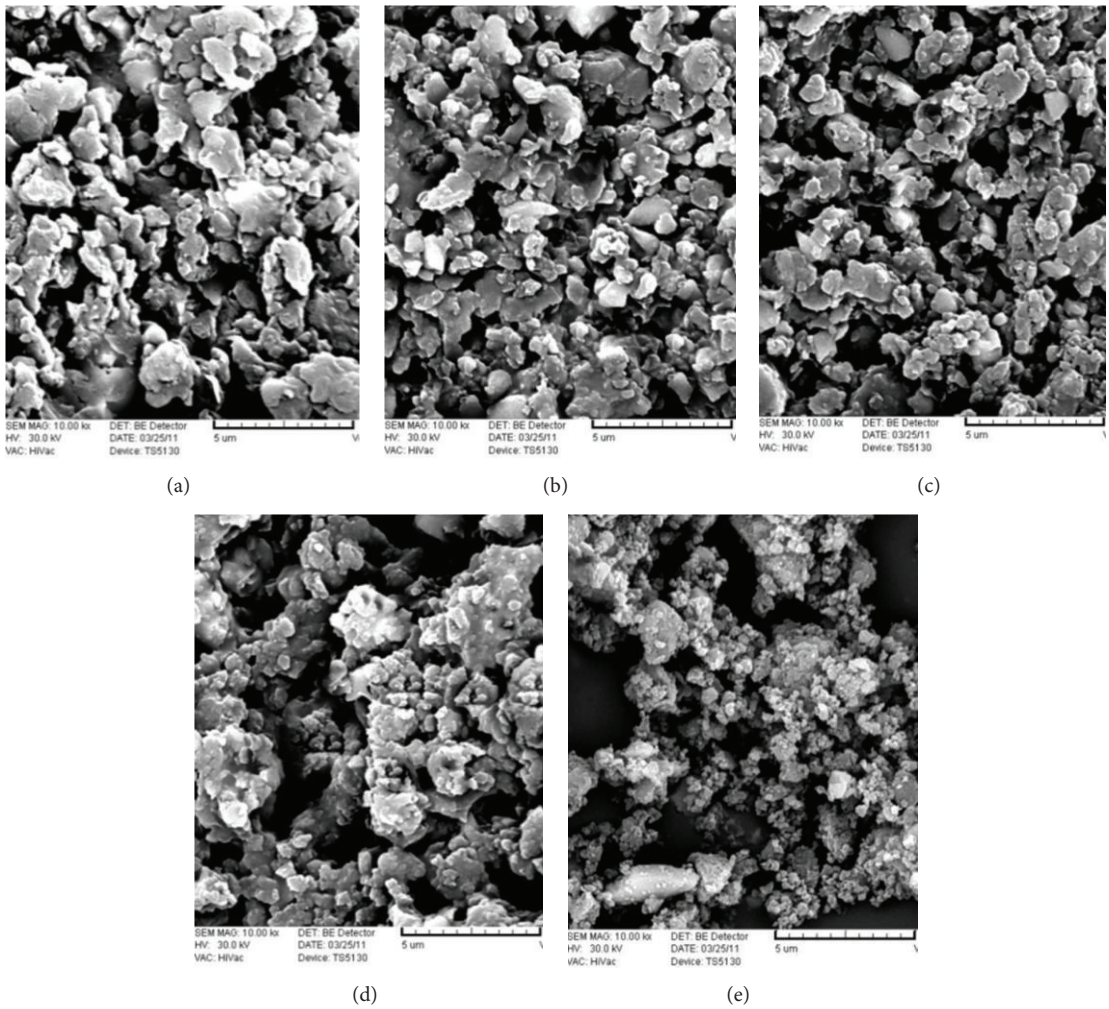

Figure 1: SEM images of PPy particles taken after (a) 60 min, (b) 120 min, (c) 180 min, (d) 240 min, and (e) 300 min.

glycol (PEG) 8000 were used as received. All of the chemicals were obtained from Sigma-Aldrich.

The molar ratio of monomer (pyrrole), oxidant ($FeCl_3$), and dopant (PTSA) was kept at 1 : 2 : 2. $FeCl_3$ and PTSA were dissolved separately in 50 mL of distilled water at 0°C under constant stirring with gradual addition. After complete dissolution, both solutions are mixed together and temperature was reduced below 0°C. PEG 8000 (20 g) was also dissolved in 30 mL of distilled water at 25°C. Solution of PEG was added in it in single step. After 10 min of severe stirring, distilled pyrrole was added drop by drop with constant high stirring. Temperature was kept around −5°C for 48 h with constant stirring. Polymer was filtered and washed with distilled water several times and finally 3 times with acetone. The polymer was then dried under vacuum.

Milling was carried out in Planetary Ball Milling machine (FRITSCH PULVERISETTE7 *premium line*) at 850 rpm at room temperature. Keeping reverse rotations on, milling can be achieved with much more homogenization. Sintered corundum—99.7% Al_2O_3—with steel casing bowls (FRITSCH) and Zirconia balls (FRITSCH) of 10 mm diameter were selected in this experiment. Bowls were cooled down to room temperature after each 2-minute milling cycle. Ball-to-mass ratio was kept as 6 : 1. Samples were collected for analysis each after 60 minutes of milling till 300 minutes.

Each sample was characterized by SEM by putting the particles on double-sided tape and placed on specimen mount. Specimen mount was then coated with gold particles before recording the images. For precise size distribution measurement 0.1 g from each milled sample was dispersed in distilled water Bandelin SONOPULS ultrasonic homogenizer for 5 min and analyzed by DSL (Malvern Instruments' Zetasizer *Nano series*).

Dispersions of PPy particles in distilled water were prepared under ultrasonic homogenizer for 30 minutes at ambient temperature. Electrical conductivity of the dispersions of 0.5% to 3% with gap of 0.5% was measured by conductometer.

PPy powder after 300 minutes of milling was analyzed by Differential Scanning Calorimetry (DSC) from Perkin Elmer for the glass-transition temperature. Heating rate of 15°C/min and nitrogen flow rate of 20 mL/min were set throughout the

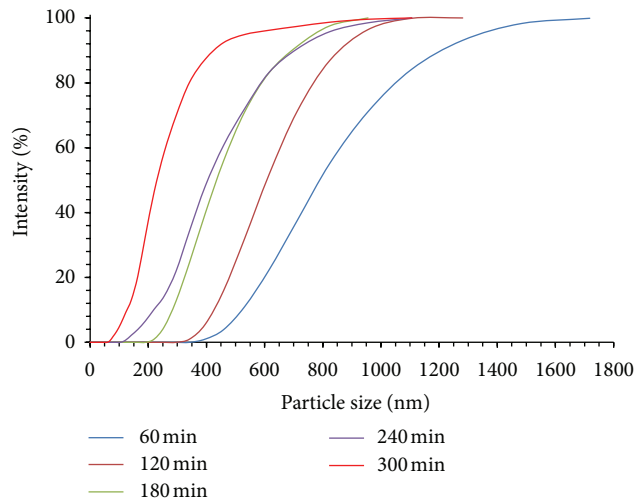

Figure 2: Undersize distribution of particles after ball milling.

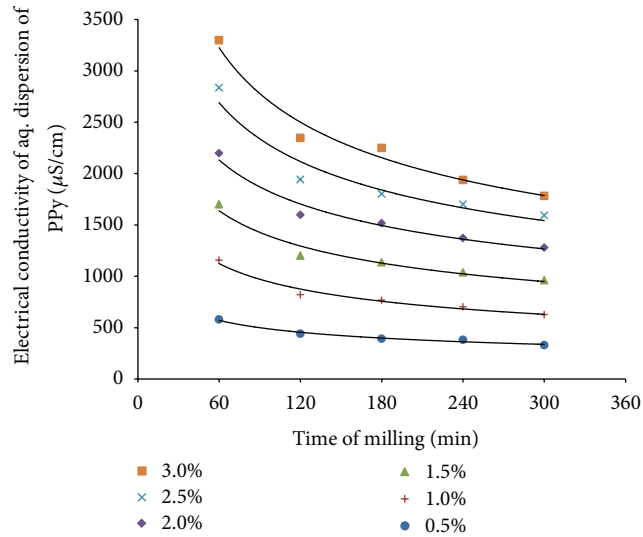

Figure 3: Conductometry of milled samples at different concentrations.

experiment. The samples are sealed in a standard aluminum pan, and the measurement is done in the temperature range of 25–150°C. The weight of each sample is about 10 mg. The DSC heat flow and temperature values are calibrated with a standard Indium.

The powder after 300 minutes of milling was also analyzed by FTIR spectroscopy in order to observe the changes that occurred due to high energy milling and compared with PPy without milling.

3. Results

3.1. Size Characterization. PPy powders were collected after 60, 120, 180, 240, and 300 min of milling and cooled down to room temperature, that is, 25 ± 1°C at 65% relative humidity. Small sample from each milled powder was analyzed by SEM as shown in Figure 1.

SEM measurement reveals that the resulting PPy particles size continuously reduces during milling and these have non-spherical morphology with 60–90 nm in average diameter after 300 minutes of milling.

Decrease in particle size can also be observed from undersize curves of all 5 samples of PPy after milling as shown in Figure 2.

However, the PPy nanoparticles tended to form an aggregation since the average particle size, measured by a DSL nanosizer, was found to be in the range of 78–1100 nm after 300 minutes of milling. This value was much larger than the particle size observed from SEM images.

3.2. Conductometry. Figure 3 shows an exponential decreasing function of liquid electrical conductivity with increasing milling time of PPy. The relation which has found can be written as

$$\mathrm{Lc} = K \cdot t^{-0.343}. \quad (1)$$

The exponent (−0.343) is found to be valid for all 5 samples with standard deviation of 0.017. Lc is the liquid electrical conductivity, t is the time of milling, and K is the constant depending upon the concentration of the PPy particles in an aqueous dispersion which is for this experiment found as

$$K = 4662.7\ C. \quad (2)$$

After 300 minutes of milling, electrical conductivity decreased approximately by 2 times. For example, electrical conductivity of 3% w/v aqueous dispersion of PPy particles after 60 min of milling was 3298 μS/cm whereas it was measured to be 1783 μS/cm for 300 min milled powder.

3.3. DSC Analysis. Figure 4 shows the DSC of unmilled PPy and particles of PPy after 300 min of milling. Pure PPy shows a broad endothermic crust at 92.3°C, which might be the glass-transition temperature (T_g) of PPy. The milling of PPy till nanoparticles does not have an effect on the T_g of PPy. The second cycle of heating till 150°C clearly shows that there were major changes happening during milling.

3.4. FTIR Analysis. The PPy powders prepared after 4 h of milling and films without milling were analyzed by FTIR as shown in Figure 5. FTIR spectra showed the main characteristic peaks at 1546 cm^{-1} and 1421 cm^{-1} corresponding to the fundamental vibrations of polypyrrole ring. The band at 1311 cm^{-1} corresponds to C–H deformation. Other low intensity peaks are observed at around 2892 cm^{-1}–2846 cm^{-1} which can be attributed to aromatic C–H stretching vibrations and shows the presence of TsO^- doping agent in the structure. However this peak almost vanished in the case of milled PPy powder which confirms the loss in doping agent during milling process. The peaks at 1546 and 781 cm^{-1} represent C=N and C–N bonds, whereas the bond of C–H in plane deformation vibration is situated at 965 cm^{-1} in our spectrum. The overlapped peaks at 1054 cm^{-1} and 1033 cm^{-1} can be credited to the sulphonate group present in TsO^-

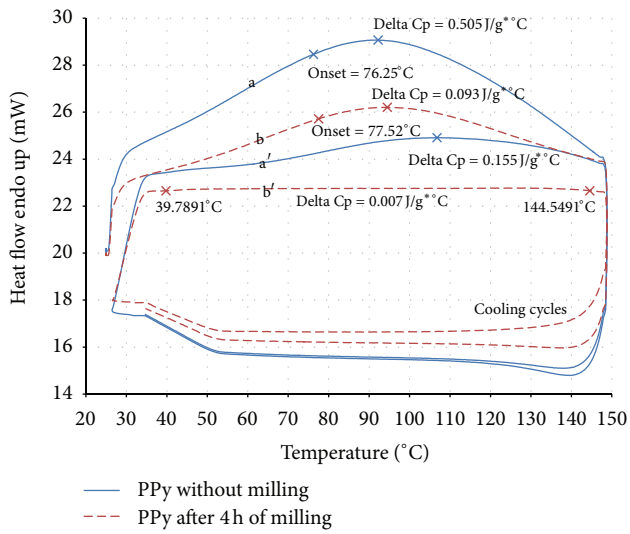

Figure 4: DSC plots of unmilled PPy and PPy powders after 4 h of milling, (a) and (a′) are first and second heating cycles of unmilled PPy, (b) and (b′) are first and second cycles of heating of milled PPy particles, respectively.

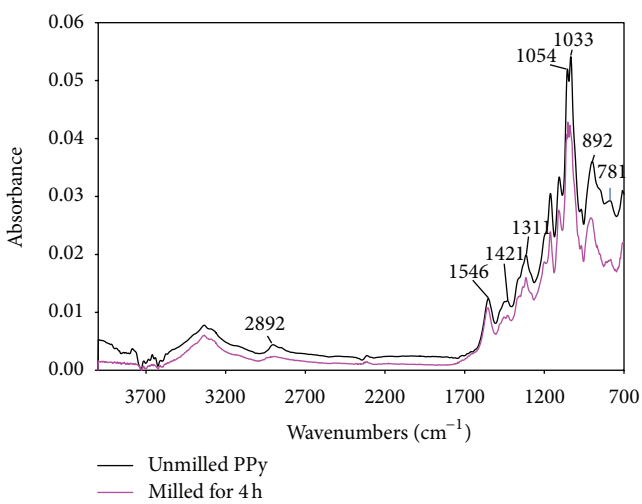

Figure 5: FTIR analyses of unmilled PPy and PPy particles after 4 h of milling.

which is observed to be lost absorbance considering milled PPy.

4. Conclusion

The use of PEG during oxidative polymerization gave much more electrical conductive PPy. After planetary ball milling of PPy polymer pallets up till 300 minutes, nonspherical shaped nanoparticles can be obtained. The disadvantage of achieving the size of the particle in nanometer range is the exponential loss of electrical conductivity of PPy particles. This might happen due to loss of dopant during rise in temperature of milled material in the process of high energy milling as observed in FTIR analysis. Differential Scanning Calorimetry was also found to be a useful tool to explore this fact, but from DSC analysis it can also be concluded that ball milling does not change the T_g of PPy.

Planetary ball milling method is still the simplest, easiest, and cheapest method to produce nanoparticles, but results show that size distribution is very broad as well as there is a high chance of agglomeration when bringing particles into ambient conditions. This happens due to dry conditions in the milling process of PPy. Planetary ball mills are useful for small amounts of nanoparticles. These are energy intensive, but the rate of acquisition of the product is much higher compared to other milling machines. The loss of electrical conductivity after milling can be gotten back by redoping and information provided in (1) could be very helpful for it. Nonconductive PPy nanoparticles can be used as thermal transducer of NIR radiation in hot-melt adhesives [10].

Acknowledgment

This work was financed by Student Grant Scheme (SGS) at the Technical University of Liberec, Czech Republic.

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