# Synthesis and Characterization of Polypyrrole Nanoparticles and Their Nanocomposites with Poly(propylene)

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**Summary:** Conducting polypyrrole (PPy) nanoparticles were synthesized via microemulsion polymerization. PP/PPy nanocomposites were prepared by melt-mixing of polypyrrole with polypropylene (PP) and processed with injection molding. Tensile tests have revealed that increasing amount of PPy increased the strength and the stiffness of the nanocomposite while limiting the elongation of PP. Thermal gravimetric analysis has showed that incorporation of PPy nanoparticles has improved the thermal stability of the nanocomposites. Increasing amount of PPy nanoparticles increases the conductivity of nonconductive PP up to $2{,}4.10^{-4}$ $Scm^{-1}$. The same techniques were used to characterize nanocomposites containing 2% w dispersant. Composites prepared with dispersant have involved smaller dimension PPy nanoparticles and exhibited improvement in some mechanical and thermal properties.

**Keywords:** conducting polymers; mechanical properties; nanocomposite; polypyrrole; poly(propylene)

## Introduction

Polypyrrole (PPy) has received widespread interest due to its good environmental stability, facile synthesis and higher conductivity than many others.[1] Different synthesis routes produce polypyrrole with different forms; chemical oxidations generally produce powders, while electrochemical synthesis leads to films deposited on the working electrode and enzymatic polymerization gives aqueous dispersions.[3] In order to produce PPy in nanoparticle form microemulsions are generally employed. S.Goel and A. Gupta have synthesized polypyrrole samples of different nanodimensions and morphologies by time dependent interfacial polymerization reaction.[4] Yang Liu and Ying Chu have reported synthesis of polypyrrole nanoparticles through microemulsion polymerization.[1] Hongxia Wang and Tong Lin have prepared polypyrrole nanoparticles by oxidation of pyrrole with ferric chloride solution during microemulsion polymerization process. Variation of particle size with variable surfactant concentration was reported.[5] The combination of conventional polymers with conductive polymers or fillers allows the creation of new polymeric materials with unique electrical properties.[2] Maria Omastova and Ivan Chodak have prepared conductive polypropylene/polypyrrole composites using the method of chemically initiated oxidative modification of polypropylene particles in suspension by pyrrole.[7] Eun Seong Lee and Jae Hyung Park have synthesized in situ formed procesable polypyrrole nanoparticle/amphiphilic elastomer composites.[8] Jürgen Pionteck and Maria Omastova have prepared an electrical-conducting polypropylene/polypyrrole (PP/PPy) composite by chemical oxidative modification reaction of pyrrole on the surface of PP particles in suspension.[2]

The aims of this study are synthesis of polypyrrole nanoparticles via microemulsion polymerization and preparation

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of PP/PPy nanocomposites in order to provide some level of processability to infusible and inprocessable PPy while inducing conductivity to insulating PP. The effect of dispersant on dispersion of PPy nanoparticles in PP matrix and its effect on mechanical and thermal properties were also investigated.

## Experimental Part

Pyrrole was supplied by Sigma Aldrich Chemie GmbH. Sodium dodecylsulphate (SDS), used as surfactant and dispersant, was purchased from Fluka BioChemika. All purifications were done by distilled water and methanol supplied by Fluka. The polymer matrix used is Polypropylene which was obtained from Petkim.

SDS (0,86 g) was dissolved in 30 ml distilled water by stirring for 30 minutes. Pyrrole (1 g) was added dropwise to the solution and an aqueous solution of the oxidant ($FeCl_3$ $6H_2O$, 9,25 g) in 5 ml distilled water was added dropwise to the mixture. The polymerization process was carried out for 3 hours at room temperature. The black polypyrrole precipitate was filtered off and washed with water and methanol several times. The black PPy powder was dried under vacuum at room temperature for 10 hours.

PP/PPy nanocomposites were prepared by melt mixing of pure PP with PPy at 75 rpm for 10 minutes at 210 °C using Brabender Plasti-Corder. The composition of nanocomposites varied between 1-20% PPy by weight. The identical procedure is employed with addition of 2% by weight dispersant (SDS) during mixing process of pure PP with PPy. The nanocomposites were processed by injection molding using Microinjector, Daca Instruments with barrel and mold temperatures of 210 °C and room temperature respectively.

FTIR analysis was carried out on a Nicolet 510 FTIR Spectrophotometer. The FTIR spectrum of polypyrrole was obtained by preparing a thin KBr pellet containing the sample. The thermal gravimetric analysis of samples were done using DTG-60 H Shimadzu thermal gravimetric analyzer. The samples were investigated at a heating rate of 10 °C/min under $N_2$ atmosphere. The tensile tests were performed according to ASTM D638, by using a Lloyd LR 30K Universal Testing machine at a test rate of 5 cm/min. The conductivity measurements of the samples were done using four probe measuring system using FPP 0602 Electrometer. The morphological studies of the samples were performed by FEI Quanta 400 F Scanning Electron Microscopy. The fracture surfaces of the samples were coated by a thin layer of gold before investigation.

## Results

The FTIR transmission spectrum of polypyrrole nanoparticles exhibited characteristic vibration bands at 1531 $cm^{-1}$, 1480 $cm^{-1}$, 1469 $cm^{-1}$ for pyrrole ring strecthing, 1458 $cm^{-1}$ for conjugated C-N strecthing and 781 $cm^{-1}$ for C-H wagging vibrations.[5,6] The vibration bands observed at 1300 $cm^{-1}$ and 1036 $cm^{-1}$ are due to C-H in-plane strecthing and C-H vibration of 2,5-substituted pyrrole.[9]

SEM micrographs of PPy nanoparticles are presented in Figure 1. The micrographs exhibited globular, nanometer-sized particles. The PPy nanoparticles are observed to have a distribution of dimensions between 50–150 nm.

The SEM results proves that the microemulsion polymerization system has provided similar dimensions of PPy nanoparticles with previous studies where 50-100 nm and 100-200 nm polypyrrole nanoparticles were reported.[5,6]

The mechanical properties of PP/PPy nanocomposites were investigated by tensile tests. The effect of loading different amounts of polypyrrole nanoparticles into thermoplastic polypropylene matrix and the changes in mechanical properties produced by incorporation of polypyrrole nanoparticles were examined. The Young's modulus, tensile strength and percentage

 

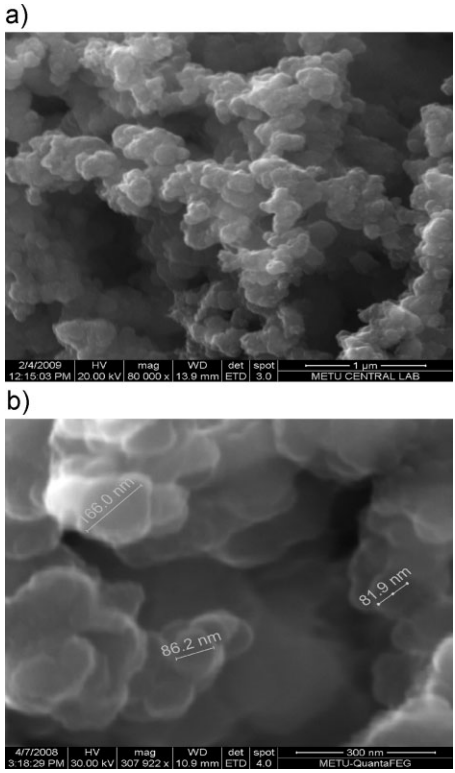


***Figure 1.***
SEM micrographs of PPy nanoparticles at magnifications of (a) 80000, (b) 300000.

strain at break values for PP/PPy nanocomposites are illustrated in Table 1.

The tensile test results of PP/PPy nanocomposites have shown that incorporation of PPy nanoparticles in PP improves the strength and the stiffness while limiting the elongation of PP. The Young's modulus, tensile strength and percentage strain at break values for nanocomposites prepared with dispersant are presented in Table 2.

The obtained results show that addition of PPy nanoparticles leads to a similar increase in tensile strength and Young's modulus of pure PP in both nanocomposite

***Table 1.***
Young's modulus, tensile strength, percentage strain values for PP, PP/PPy nanocomposites without dispersant.

| PPy content (w%) | Young's Modulus (MPa) | Tensile strength (MPa) | Percentage strain at break (%) |
|---|---|---|---|
| 0 | 430 ± 10 | 27,8 ± 0,5 | 424 ± 9 |
| 1 | 643 ± 53 | 34,0 ± 0,6 | 8,5 ± 0,7 |
| 5 | 703 ± 95 | 34,1 ± 1,2 | 8,4 ± 2,1 |
| 10 | 787 ± 63 | 34,0 ± 1,0 | 8,7 ± 2,0 |
| 20 | 801 ± 46 | 34,1 ± 0,2 | 8,9 ± 2,6 |

***Table 2.***
Young's modulus, tensile strength, percentage strain values for PP, PP/PPy nanocomposites with 2% dispersant by weight.

| PPy content (w%) | Young's Modulus (MPa) | Tensile strength (MPa) | Percentage strain at break (%) |
|---|---|---|---|
| 0 | 430 ± 10 | 27,8 ± 0,5 | 424 ± 9 |
| 1 | 583 ± 77 | 30,1 ± 0,4 | 14,4 ± 0,2 |
| 5 | 748 ± 53 | 32,8 ± 0,6 | 9,3 ± 0,9 |
| 10 | 786 ± 10 | 32,9 ± 0,4 | 8,0 ± 0,3 |
| 20 | 831 ± 31 | 33,2 ± 0,6 | 7,1 ± 0,2 |

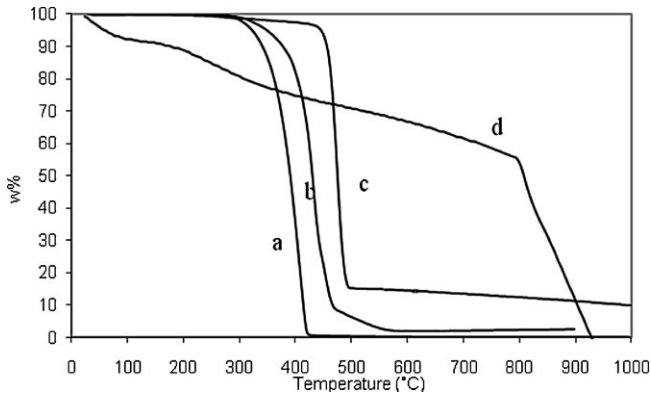


***Figure 2.***
TGA plots of (a) pure PP, (b) PP/10%PPy, (c) PP/20%PPy nanocomposites prepared without dispersant, (d) PPy.

 

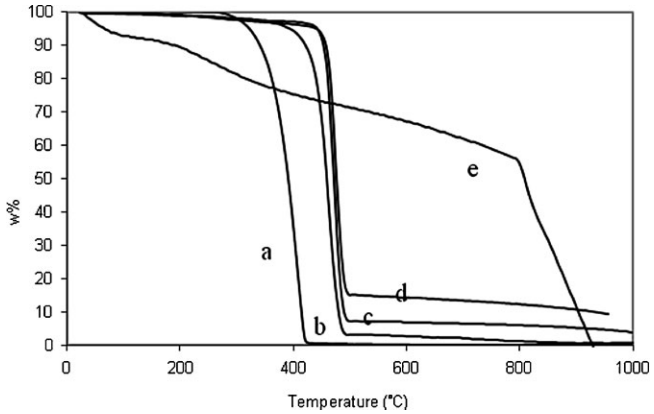


***Figure 3.***
TGA plots of (a) pure PP, (b) PP/5%PPy, (c) PP/10%PPy (d) PP/20%PPy nanocomposites prepared with dispersant, (e) PPy.

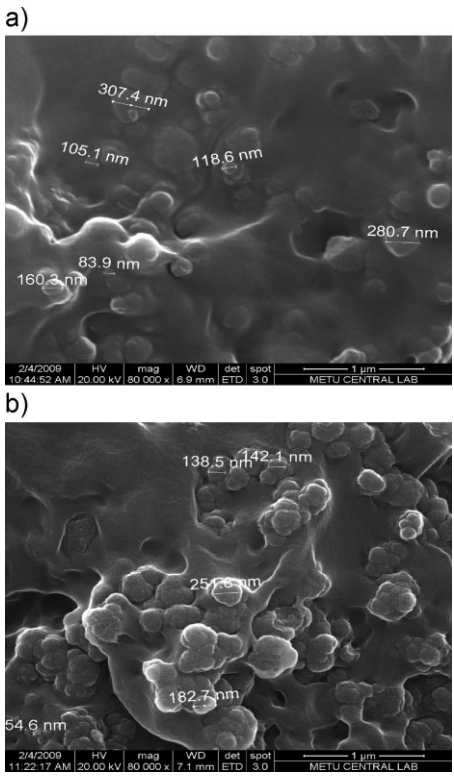


***Figure 4.***
Fracture surfaces of PP/1%PPy nanocomposites prepared (a)without, (b) with dispersant at magnification of 80000.

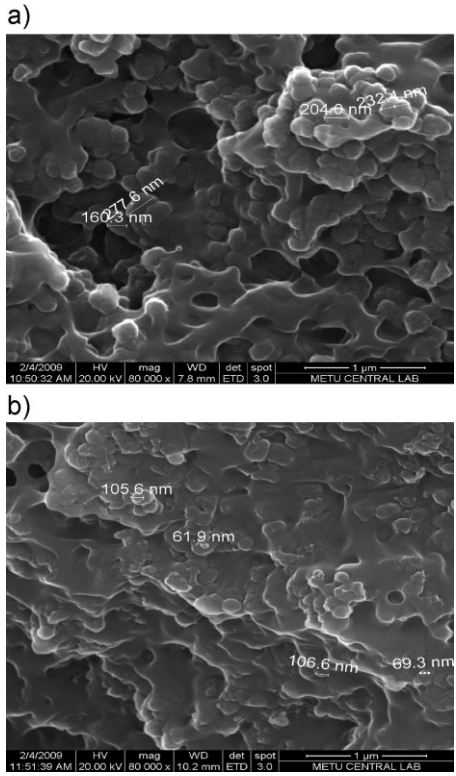


***Figure 5.***
Fracture surfaces of PP/5%PPy nanocomposites prepared (a)without, (b) with dispersant at magnification of 80000.

 

***Table 3.***
Electrical conductivities of PP/PPy nanocomposites

| w% PPy | PP/PPy without dispersant Conductivity ($Scm^{-1}$) | PP/PPy with dispersant Conductivity ($Scm^{-1}$) |
|---|---|---|
| 0 | $1{,}0.10^{-16}$ | $1{,}0.10^{-16}$ |
| 1 | $5{,}60.10^{-5}$ | $9{,}5.10^{-5}$ |
| 5 | $1{,}24.10^{-4}$ | $1{,}35.10^{-4}$ |
| 10 | $1{,}32.10^{-4}$ | $1{,}43.10^{-4}$ |
| 20 | $2{,}25.10^{-4}$ | $2{,}40.10^{-4}$ |
| 100 | $5{,}2.10^{-2}$ | $5{,}2.10^{-2}$ |

sets. The nanocomposites prepared using dispersant exhibited a regular decrease in percentage strain at break while a sudden decrease was observed for nanocomposites prepared without dispersant. The higher decrease in nanocomposite prepared without dispersant can be explained by considering weaker interaction of polypyrrole with polypropylene.

The conductivity values of PP/PPy nanocomposites prepared without and with dispersant are shown in Table 3.

Addition of even the smallest amount of PPy results in a considerable increase in electrical conductivity of insulating PP matrix. Increasing amount of PPy nanoparticles increases the conductivity of the nanocomposite up to $2{,}4.10^{-4}$ S $cm^{-1}$.

Increasing amount of PPy supports formation of a stronger network. As the network gets stiffer and solid by addition of PPy, the elongation of the PP fibers is restricted and decreases gradually by increasing amount of PPy.

The percolation threshold for PP/PPy nanocomposites prepared without and with dispersant are found to be 2,0% w

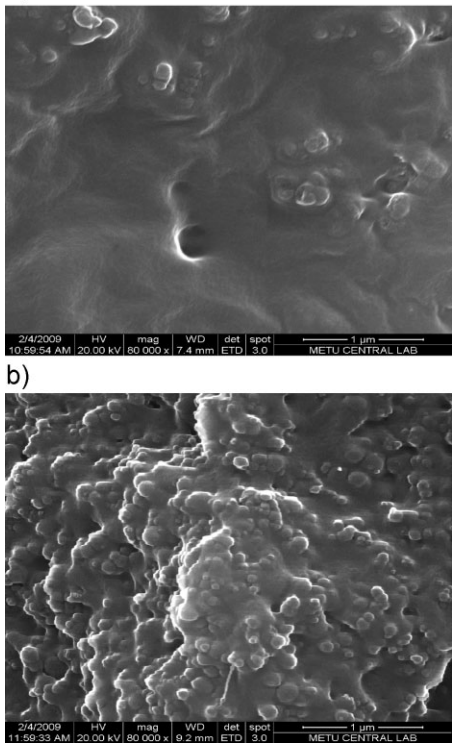


***Figure 6.***
Fracture surfaces of PP/10%PPy nanocomposites prepared (a)without, (b) with dispersant at magnification of 80000.

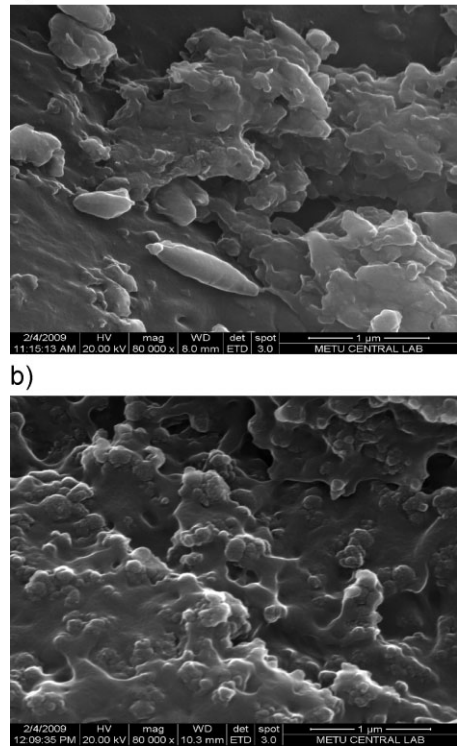


***Figure 7.***
Fracture surfaces of PP/20%PPy nanocomposites prepared (a)without, (b) with dispersant at magnification of 80000.

 

and 2,4% w PPy respectively. The order of magnitude, the trend in conductivity and elongation with increasing PPy content are similar for nanocomposites prepared with and without dispersant.

The thermal stability of nanocomposites was studied by Thermal Gravimetric Analysis.

The obtained results for both sets have shown that presence of PPy nanoparticles leads to enhancement in thermal stability of pure PP as expected from previous studies.[10] The greater shifts observed for maximum decomposition temperature of nanocomposites prepared with dispresant confirms greater enhancement in thermal stability of pure PP indicating the improvement in dispersion of PPy nanoparticles in PP matrix.

The SEM results have shown that low PPy content nanocomposites prepared with dispersant involve smaller dimension nanoparticles compared to ones prepared without dispersant.

## Conclusion

The morphology of PPy prepared by microemulsion polymerization is globular, nanometer-sized particles having dimensions between 50–150 nm with electrical conductivity in the order of $10^{-2}$ $Scm^{-1}$. The tensile tests have revealed that addition of PPy has increased the strength and stiffness while limiting the elongation of PP. Incorporation of PPy have increased the conductivity and the thermal stability of pure PP considerably. SEM micrographs have shown the improvement in dispersion of PPy nanoparticles in PP matrix which has positive effect on mechanical and thermal properties.

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