

Influence of microwave irradiation on various properties of nanopolythiophene and their anticorrosive nanocomposite coatings

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1. Optimization studies for the synthesis of mPTh using microwave technique:

For any synthesis to be made reproducible, optimization of the reaction conditions (in case of MW: Time of irradiation, MW power used, concentration of reactants) are necessary and thereafter, validating the procedure by synthesizing the same, by more than one time under similar conditions. In our case, we have first optimized the concentration of reactant to be used by taking 0.5 g, 1.0 g and 2.0 g in case of conventional emulsion polymerization of cPTh and found that with 1.0 g concentration of Th monomer, the maximum yield was achieved as compared to other concentrations. Hence, the same condition was taken for microwave synthesis with the time of irradiation at constant MW power (W) for obtaining the highest % yield, the obtained results are tabulated in Table S1. The best experimental conditions determined (one with the highest yield %) was then repeated three times to check the reproducibility and formation of the synthesized mPTh nanoparticles. The mPTh nanoparticle filler were synthesized in bulk (by repetitive experiments) for the formulation of mPTh-epoxy-PA anti-corrosive coatings, for physico-mechanical and electrochemical corrosion measurements. All syntheses were monitored by FT-IR studies to confirm their characteristic peaks (Fig.1, main manuscript) and it was observed that similar spectrum was obtained for every set of synthesis confirming the similar functionalities of PTh.

Table S 1: Optimization studies for synthesis of mPTh nanoparticles.

Synthesis No.	Time of MW irradiation (sec)	Power used (W)	Sample code	Millique water used (ml)	Nanoparticle yield (%)	
1.	60	360	mPTh1	30.0	62.1	
2.	120	360	mPTh2	30.0	67.9	
3.	180	360	mPTh3	30.0	63.5	
4.	240	360	mPTh4	30.0	61.8	
						Standard Deviation
5.	120	360	mPTh2	30.0	67.5	67.5±0.5
6.	120	360	mPTh2	30.0	68.0	
7.	120	360	mPTh2	30.0	67.0	

2. Solubility Test. The solubility of PTh nanoparticles (cPTh and mPTh) was investigated in various polar and non-polar solvents at room temperature (Table S2). In comparison to cPTh particles, mPTh particles had better solubility and were more easily dispersible in polar solvents as well as non-polar solvents. The better solubility of mPTh than that of cPTh can be attributed to the uniform non-agglomerated, smaller nano-size of mPTh (10 nm, Fig. 4(a)), which helped in uniform and easy dispersion of these particles in solvent, compared to the linked array of cPTh (30 nm, Fig. 4(a), main manuscript).

The observed higher solubility of both the PTh particles in polar solvents than non-polar solvent can be attributed to the formation of H-bonding in heterocyclic PTh nanoparticles having one sulphur atom, with the hydrogen of the solvent molecule.¹ The presence of lone pair electron in the orbital of the sulphur atoms in PTh projects into the space away from negatively charged nuclei, which produced a considerable charge separation. The lone pair imparts negative polarization on sulphur atom of thiophene, imparting ability to form the hydrogen bond in polar solvents.¹

Table S 2. Solubility studies of mPTh and cPTh in solvents of different polarity.

Solvent	Solubility	
	PTh	mPTh
Xylene	Insoluble	Insoluble
DMF	Soluble	Soluble
DMSO	Partly soluble	Soluble
Toluene	Insoluble	Partially soluble
CCl₄	Insoluble	Insoluble
THF	Insoluble	Insoluble
Acetone	Partially soluble	Partially soluble
Benzene	Insoluble	Insoluble
Ethyl methyl ketone	Soluble	Soluble
Ethanol	Insoluble	Soluble
Methanol	Soluble	Soluble
NMP	Insoluble	Soluble

3. Thermal gravimetric analysis. Thermal stability of cPTh and mPTh nanoparticles was investigated between 40 °C to 800 °C under nitrogen atmosphere. The corresponding thermograms were shown in Fig. S1 revealing three step decomposition in cPTh and mPTh samples. However, the % decomposition and temperature of subsequent (first, second and third step) degradation were found to be higher in case of mPTh, revealing the effect of synthesis technique. The initial 10 % weight loss in cPTh was started at 120 °C continued till 310 °C, however, in mPTh the first step degradation was started at 160 °C and continued till 335 °C. This degradation in wt can be attributed to the removal of trapped water in the polymer nanoparticles² and breaking of cross-linked bonds between thiophene rings (α - β and

β - β bonds).³ The second 20 weight % degradation in case of mPTh was recorded at higher temperatures in comparison to cPTh. It started from 330 °C and ended at 425 °C, while the same decomposition in cPTh was observed within the temperature range of 310 °C to 410 °C. This decomposition involved the breaking of polymer chain and evolution of acetylene or ammonia gases.² The third weight loss (*ca.* 30 %) for both cPTh and mPTh lasted upto 680 °C, which can be corroborated to the degradation of residual polymer.^{4, 5} Thus, the thermal analysis from 40 °C to 800 °C inferred higher thermal stability for mPTh particles due to well ordered (semi-crystalline) and compact dense structure of mPTh particles.

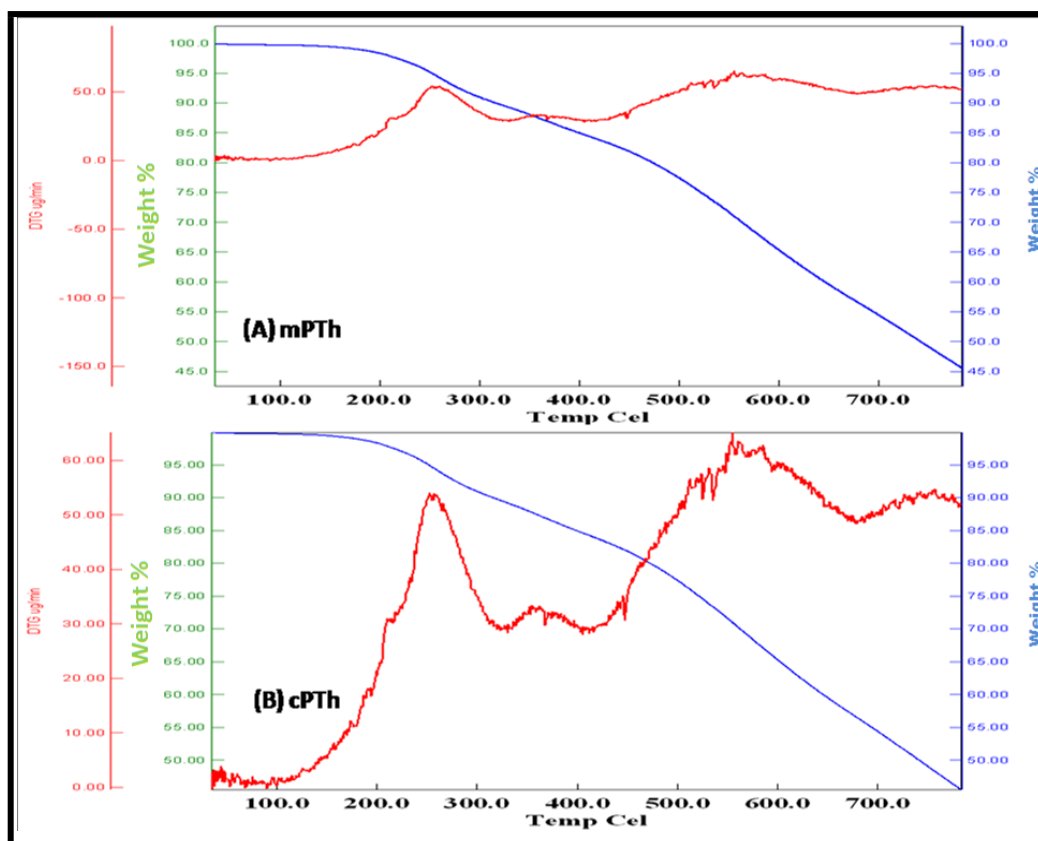


Figure S1 Thermogravimetric analysis of (A) mPTh and (B) cPTh nanoparticles

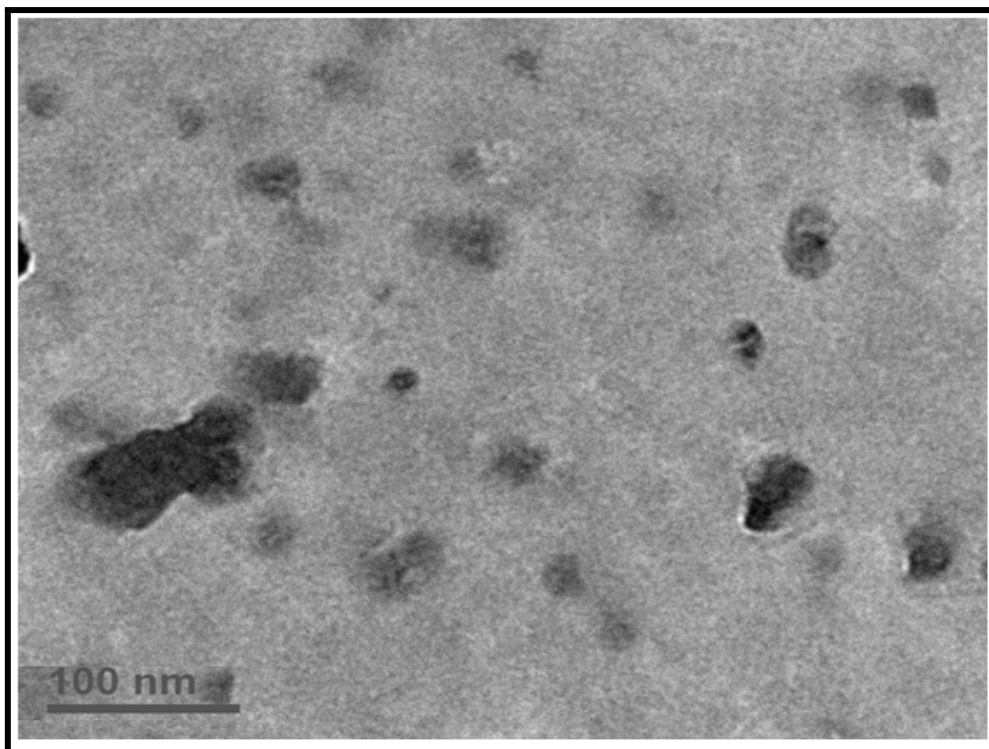


Figure S2 TEM micrograph of well dispersed mPTh nanoparticle in epoxy matrix

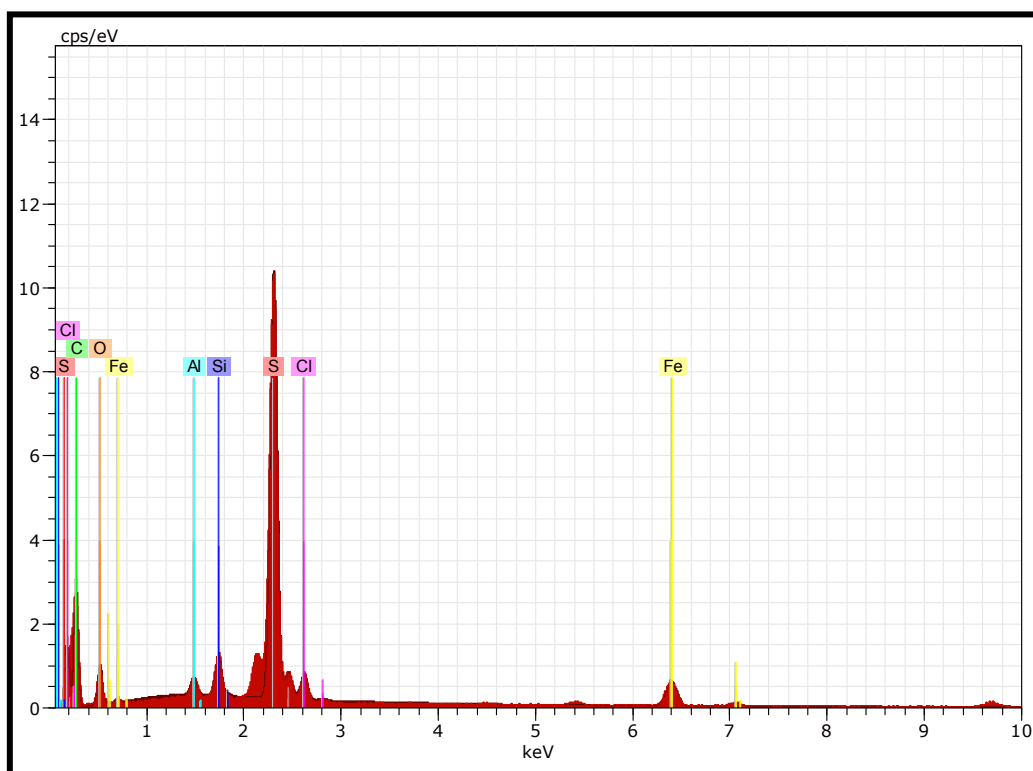


Figure S3 EDAX of Polythiophene (mPTh) nanoparticle.

Table S3 Electrochemical parameters obtained from PDP studies for uncoated and coated CS with cPTh/epoxy-PA and mPTh/epoxy-PA in different media of varying pH=1,3,5,7,9,12 and 14 at room temperature.

Code	Immersion period (hour)	E_{corr} (V)	I_{corr} (Acm⁻²)	Corrosion Rate (mpy)
(pH 1)				
CS	6	-0.61385	8.91E-04	10.39805
Epoxy	6	-0.51424	9.82E-05	1.145126
cPTh/Epoxy	6	-0.40889	7.90E-06	0.092176
mPTh/Epoxy	6	-0.38903	9.51E-07	0.011096
(pH 3)				
CS	6	-0.59614	2.5101E-04	2.928291
Epoxy	6	-0.49886	5.1362E-05	0.599191
cPTh/Epoxy	6	-0.36051	1.3862E-06	0.016171
mPTh/Epoxy	6	-0.35641	2.074E-07	0.00242
(pH 5)				
CS	6	-0.57141	8.51E-05	0.993048
Epoxy	6	-0.47324	2.10E-06	0.024533
cPTh/Epoxy	6	-0.34303	6.79E-07	0.007917
mPTh/Epoxy	6	-0.32458	2.52E-08	0.000294
(pH 7)				
CS	6	-0.51073	2.1312E-05	0.248627
Epoxy	6	-0.45505	9.3862E-07	0.01095
cPTh/Epoxy	6	-0.32138	1.1003E-08	0.000128
mPTh/Epoxy	6	-0.30301	3.1587E-09	3.68E-05
(pH 9)				
CS	6	-0.53147	4.98E-05	0.58133
Epoxy	6	-0.4663	7.91E-06	0.092317
cPTh/Epoxy	6	-0.33951	1.22E-07	0.001425
mPTh/Epoxy	6	-0.3133	9.15E-09	0.000107
(pH 12)				
CS	6	-0.5691	9.20E-05	1.073322
Epoxy	6	-0.48475	1.11E-05	0.129796
cPTh/Epoxy	6	-0.34119	5.92E-07	0.006904
mPTh/Epoxy	6	-0.33923	3.12E-08	0.000364
(pH 14)				
CS	6	-0.58102	1.95E-04	2.269627
Epoxy	6	-0.49625	6.39E-05	0.745016
cPTh/Epoxy	6	-0.37202	9.82E-07	0.011461
mPTh/Epoxy	6	-0.35789	4.39E-08	0.000512

Table S4 Comparative analysis of present study with other reported corrosion protective conducting polymer systems

S.No	Sample	Method of synthesis	Medium	E _{corr} (V)	I _{corr} (Acm ⁻²)	Reference
1.	mPTh-epoxy-PA	Microwave	5M NaCl solution of pH =1	-0.38903	9.51E-07	Present study
			3	-0.35641	2.074E-07	
			5	-0.32458	2.52E-08	
			7	-0.30301	3.1587E-09	
			9	-0.3133	9.15E-09	
			12	-0.33923	3.12E-08	
			14	-0.35789	4.39E-08	
2	cPTh-epoxy-PA	Conventional	pH = 1	-0.40889	7.90E-06	Present study
			3	-0.36051	1.3862E-06	
			5	-0.34303	6.79E-07	
			7	-0.32138	1.1003E-08	
			9	-0.33951	1.22E-07	
			12	-0.34119	5.92E-07	
			14	-0.37202	9.82E-07	
3	(polypyrrole-co-bithiophene) copolymer	Electropolymerization	3.5 % NaCl	35.97	-0.026	⁶
4	PPY/PTh	Electropolymerization	3.5 % NaCl	0.043	-0.520	⁷
5	PTh	Electropolymerization	3.5 % NaCl	0.0005	-0.450	⁸
6	CNT/PU nanocomposite	Conventional	3.0 % NaCl	7.63 x 10 ⁻⁶	-0.0436	⁹

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