PÔSTER - RESUMO - MATERIAIS E BIOMATERIAIS

ULTRASOUND-DRIVEN STRUCTURAL REORGANIZATION AND CHARGE TRANSPORT ENHANCEMENT IN POST-SYNTHESIZED POLYANILINE EMERALDINE-SALT FORM

Jamilton Silva Boaes (jsilvaboaes@gmail.com)

Adriano De Souza Carolino (adriano.asc.fis@gmail.com)

Yvonne Primerano Mascarenhas (yvonne@ifsc.usp.br)

Célio Matias Airone Macalia (cemacalia@gmail.com)

Querem Hapuque Felix Rebelo (aquerem@gmail.com)

Edgar Aparecido Sanches (esanches@ufscar.br)

A scalable, green, and chemically non-invasive post-synthesis strategy based on ultrasound-assisted processing [1] was employed to enhance charge transport in powdered polyaniline emeraldine salt form (PAni-ES) [2-3] dispersed in different media (distilled water and 1 M HCl). Experimental results from structural, spectroscopic, thermal, and electrical analyses were rigorously correlated with density functional theory (DFT) calculations. The dispersion medium and ultrasonic power (300, 450 and 600 W) emerged as decisive parameters governing macromolecular organization and, consequently, the electrical conductivity of PAni-ES. XRD analysis revealed that increasing ultrasonic power in distilled water progressively reduced crystallinity (from 49% to 33%), as evidenced by peak broadening and diminished p–p stacking coherence. In contrast, ultrasonication in 1 M HCl induced a power-dependent

increase in crystallinity (up to 63%), reflecting cooperative structural reorganization and protonation-stabilized densification. ATR–FTIR analysis confirmed that ultrasonication under acidic conditions promoted effective molecular reorganization and enhanced structural ordering, whereas neutral conditions induced only modest conformational changes. In 1M HCl, Q/B ratios approached unity and crosslinking indices increased significantly (˜57–72%), evidencing strengthened interchain stabilization. Accordingly, ultrasonication in 1 M HCl reduced the optical band gap (down to ˜1.83 eV) and systematically decreased the Urbach energy (˜10^4 meV at 600 W), indicating enhanced electronic delocalization, improved doping efficiency, and a significant reduction in tail-state disorder. Electrochemical impedance spectroscopy revealed that samples ultrasonicated in distilled water exhibited low conductivity (10-6 – 10-4 (O·m)-¹) and pronounced frequency dependence, indicating localized hopping transport consistent with structural disorder and limited doping. In contrast, ultrasonication in 1 M HCl increased conductivity by several orders of magnitude (10-² – 10-¹ (O·m)-¹) and yielded nearly frequency-independent spectra, characteristic of well-established percolative charge transport pathways. Finally, DFT simulations demonstrated that dopant incorporation and ultrasound-induced interchain coupling promoted backbone planarization, reduced torsional disorder, and significant HOMO–LUMO gap narrowing, while the calculated FTIR spectra reproduced key C–N vibrational features associated with interchain interactions. These findings demonstrate that controlled ultrasonication constitutes an effective non-thermal and non-chemical strategy for enhancing electrical conductivity in PAni-ES, highlighting a sustainable and scalable pathway for tailoring structure–property relationships in conducting polymers. References: [1] 10.3390/molecules27154905; [2] 10.1016/j.molstruc.2012.12.025; [3] 10.3303/CET1972071. Acknowledgments: The authors gratefully acknowledge the support of INEO and the funding agencies FAPESP (Grant No. 2025/27044-5) and CNPq (Grant No. 408449/2024-1).

Palavras-chave: conducting polymers; band gap modulation; percolative transport; ultrasonication.