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ABSTRACT OF THE DISSERTATION

"Ferroelectric ceramic-polymer composites for electronic applications: design, fabrication and properties"

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This doctoral dissertation focuses on the development, synthesis, and characterization of ceramic-polymer composites based on barium-strontium titanate $Ba_{0.65}Sr_{0.35}TiO_3$ (BST) and specially designed water-borne polymer dispersions intended for use in microwave technologies, flexible electronics, and modern wireless communication systems. The primary objective of the work was to thoroughly investigate three key areas that determine the performance of dielectric composites: the structure and chemistry of the ceramic phase, the molecular architecture of the polymer matrix, and the processing technique. The relationships between these factors and the final functional properties of BST/polymer composites were then identified. The results provide new insight into the mechanisms governing composite behaviour and offer practical technological solutions enabling their use in future microwave devices, flexible electronic components, and additive manufacturing technologies.

The first stage involved the synthesis of BST powders via a solid-state reaction, with a focus on analysing how the polymorphic form of TiO_2 precursor (anatase or rutile) and the synthesis temperature influence the properties of the resulting ceramic phase. BET, XPS, SEM, and dielectric measurements enabled a detailed reconstruction of the links between precursor structure, reaction course, and microstructural features of the BST powders. It was found that synthesis from anatase leads to powders with a larger specific surface area, a higher density of surface defects – including Ti^{3+} centres – and a reduced band gap. Conversely, BST obtained from rutile exhibited fewer defect centres, more regular grain morphology, and improved dielectric stability. These relationships proved crucial for shaping interfacial polarization and dielectric stability in the later-prepared composites.

In parallel, a series of water-thinnable polymer dispersions was developed, differing in acrylate and methacrylate content, the presence of aromatic or branched alkyl groups, and glass-transition temperature. The analysis showed that the segmental mobility of the polymer chains is one of the most significant factors influencing the intensity of α and β dielectric relaxations, dielectric losses, and the stability of the dielectric response over a wide frequency range. Polymers with higher segmental flexibility enabled composites with increased permittivity, although at the expense of higher dielectric losses. Rigid polymers – containing aromatic or tert-butyl groups – displayed lower polarizability but offered enhanced thermal and frequency stability, along with reduced losses. Crucially, it was shown that the impact of polymer chemistry on composite performance is comparable to the influence of BST synthesis parameters, demonstrating the essential role of polymer-matrix design in the engineering of advanced dielectric materials.

In the next phase, composite dispersions were prepared for three distinct forming techniques. The first was classical tape casting, enabling the fabrication of thin and homogeneous films. The second was photo-tape casting, a photopolymerization-based approach in which particular attention was paid to

curing kinetics and polymerization shrinkage. The third technique – fused deposition modeling (FDM) – required the development of a process for producing a composite filament. Achieving a stable BST/polymer filament with reproducible rheology, sufficient mechanical strength, and structural stability was one of the major technological accomplishments of this work, enabling 3D printing of components with complex geometries. Very few studies describe BST-based composite filaments for FDM, and the results presented here open new opportunities for designing dielectric elements for additive manufacturing.

The fabricated composites were subjected to an extensive microstructural analysis, including density and porosity measurements, SEM observations, and detailed dielectric investigations. It was demonstrated that the wetting of BST grains by the polymer matrix and the uniformity of ceramic distribution depend strongly on polymer chemistry. Polymers containing aromatic and tert-butyl groups formed more compact and homogeneous structures around BST particles, resulting in reduced porosity and enhanced dielectric stability. In composites processed by the photo-tape casting method, interfacial cracking caused by polymerization shrinkage was observed, highlighting the need for further optimization of monomer composition and curing parameters.

Dielectric studies revealed a complex interplay between the structure of the ceramic phase, the polarizability and segmental mobility of the polymer matrix, and the microstructure resulting from the chosen processing method. Composites based on low-polarizability polymers exhibited the highest temperature and frequency stability, whereas those incorporating more flexible polymers showed increased permittivity but also higher losses. These findings confirm that achieving optimized dielectric performance requires coordinated and simultaneous control over the ceramic phase, polymer architecture, and processing conditions.

The final achievement of the dissertation was the development of three distinct forming techniques – tape casting for thin films, photo-tape casting for photopolymerizable structures, and FDM enabling additive manufacturing of three-dimensional components. This versatility allows BST/polymer composites to be tailored to a wide range of applications, from lightweight and flexible dielectrics, through UV-cured structures with precisely defined geometry, to 3D-printed components for microwave devices and antenna systems.

In summary, the research confirms that the properties of ceramic–polymer composites arise from the intricate interactions between the ceramic phase structure, the chemical characteristics of the polymer matrix, and the chosen forming technique. The comprehensive design strategy – integrating powder synthesis, polymer development, and processing optimization – provides a complete model for engineering BST/polymer composites with controlled permittivity, low dielectric losses, and high stability. The materials developed in this work meet the requirements of modern high-frequency technologies, and the results form a strong foundation for further advancements toward composites with improved dielectric performance and expanded functionality for electronic, telecommunication, and additive-manufacturing applications.

Keywords: ceramic-polymer composites, barium strontium titanate, colloidal processing, tape casting, 3D printing