Structure–Property Relationships of Waterborne Polyurethane–Anisotropic Titanate Nanotube Nanocomposites

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This study investigates the structure–property relationships of waterborne polyurethane (WPUD) systems in aqueous formulations, with emphasis on the role of anisotropic one-dimensional (1D) nanofillers. Inspired by assembled nanowire materials, where anisotropy governs macroscopic properties, anisotropic titanate nanotubes (TiNTs) were incorporated into WPUDs synthesized from a polycarbonate-based macro-diol, providing a model system to study the interplay between polymer architecture and nanoscale filler geometry.

Although WPUDs are environmentally (and health-) friendly due to low volatile organic compound (VOC) content, their mechanical and thermal performance is often limited. These limitations are closely related to the internal structure formed in aqueous environments, including phase separation and interparticle interactions. Introducing anisotropic nanofillers provides a pathway to tailor the morphology and the internal cohesion (structure–property relationships).

TiNTs, characterized by high aspect ratio and surface hydroxyl functionality, enable strong and directional interactions within the polymer matrix. A novel strategy was employed to incorporate unmodified TiNTs directly from aqueous dispersions into WPUDs without freeze-drying, preserving their fine 1D morphology and minimizing aggregation.

Nanocomposites containing 1–5 wt% TiNTs were prepared and characterized. Transmission electron microscopy confirmed uniform dispersion, while ash analysis confirmed the filler content. The structure of the nanocomposites was further investigated using solid-state NMR, X-ray diffraction (XRD), small- and wide-angle X-ray scattering (SAXS/WAXS), providing insight into filler–matrix interactions and micro-phase organization. Rheological measurements were performed to probe viscoelastic behavior and structural evolution in the aqueous state.

The incorporation of TiNTs influenced the microphase organization of the polyurethane matrix, promoting enhanced intermolecular interactions, particularly hydrogen bonding, and improved stress transfer. As a result, the nanocomposites exhibited increased mechanical performance and storage modulus. These findings highlight the critical role of anisotropic 1D nanofillers in controlling structure–property relationships in WPU systems and support the design of advanced, nature-friendly and bio-mimetic polyurethane nanocomposites.

Keywords:
Nanocomposite, waterborne polyurethane dispersions, titanate nanotube

References:

Mares Barbosa, S. et al. ACS Applied Polymer Materials, 2025, 7 (8), 4858-4875.
Serkis-Rodzeń, M. et al. Prog. Org. Coat. 2017, 106, 119–127.
Sardon, H. et al. Prog. Org. Coat. 2014, 77, 1436–1442.
Kasuga, T. et al. Langmuir 1998, 14, 3160–3163.
Beneš, H. et al. Macromolecules 2018, 51 (15), 5989–6002.

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