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Mapping Nanoscale Viscoelastic Changes in Thermally Aged Polymeric Coatings

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Extended Abstract

Abstract

Polymeric coatings exhibit complex, time-dependent degradation mechanisms driven by thermal and moisture-related stresses. These processes often initiate at the nanoscale, which remains inaccessible to conventional bulk characterization techniques. Consequently, nanoscale investigation is essential to gain deeper insight into early-stage degradation phenomena. In this study, Atomic Force Microscopy (AFM)-based nanomechanical testing was employed to analyze nanoscale viscoelastic property changes in a waterborne acrylate latex coating subjected to controlled thermal aging and freeze–thaw cycling. The aim was to elucidate degradation mechanisms by correlating localized mechanical responses with surface topography. Coating samples were exposed either to cyclic thermal loading between −20 °C and 50 °C or to repeated immersion–freeze cycles consisting of 24 h of water immersion followed by 24 h of freezing. Nanomechanical measurements were conducted using the Nanosurf ViscoElastic Analyzer (VEA), an AFM-based technique designed to replicate conventional Dynamic Mechanical Analysis (DMA) at the nanoscale. A sinusoidal excitation applied to an AFM probe in contact with the coating enabled quantitative determination of the storage modulus, loss modulus, and loss tangent (tan δ) with high spatial resolution. This approach allows assessment of local viscoelastic behavior and mechanical heterogeneity in thin polymer films. The reference state of the coating exhibits a relatively homogeneous surface morphology and a narrow distribution of nanoscale mechanical properties. In contrast, environmental exposure led to pronounced changes in both morphology and viscoelastic response. Both thermal aging and freeze–thaw exposure results in increased nanoscale storage modulus, consistent with bulk mechanical measurements. Freeze–thaw cycling produced the most significant effects, including a marked increase in spatial heterogeneity. AFM revealed the formation of distinct rod-like nanoscale surface features associated with locally elevated storage modulus values, indicating the presence of mechanically reinforced regions within a softer polymer matrix. Overall, this study demonstrates the effectiveness of AFM-based viscoelastic nanomechanical testing for probing environmentally driven degradation in polymeric coatings and underscores its relevance for improving coating durability and accelerating material development.

Keywords:

Atomic force microscopy Viscoelastic nanomechanics Polymeric coatings