Iranian Polymer Journal (2020) 29:493–500
https://doi.org/10.1007/s13726-020-00813-9

ORIGINAL RESEARCH

Polyphosphazene nanotube and modified waterborne polyurethane prepared by in situ polymerization

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Received: 19 November 2019 / Accepted: 24 March 2020 / Published online: 9 April 2020

Abstract

Novel hybrid inorganic/organic poly[cyclotriphosphazene-*co*-(hexafluoroisopropylidene)] nanotubes (PZTs) were synthesized through nucleophilic substitution using one-step method. The surface of PZTs contains hydroxyl and fluorine groups with a ratio of approximately 1:3, which imparts many functional properties to the nanotubes. The introduction of the active hydroxyl groups increased the chemical bond crosslinking between the nanotubes and the matrix resin. The introduction of fluorine atom provided the hydrophobicity and abrasion resistance properties. The water contact angle of PZTs is 140.3°. Chemical reaction occurred between WPU and PZTs to form covalent bonds through in situ polymerization. The water contact angle and thermal stability of waterborne polyurethane (WPU)/PZTs increased with the increasing nanotube content. When the nanotube content was 1.0 wt%, the maximum tensile strength of the composites was 3.36 MPa and the maximum elongation-at-break was 446.8%. The nanotubes showed toughening and strengthening characteristics. When 1.0 wt% PZTs were incorporated, the friction coefficient and abrasion loss of the composites reached a minimum value. The addition of nanotubes could increase surface hardness and crosslinking degree, absorb the coating heat of friction, and reduce the adhesive wear of polymer and the wear amount. The introduction of fluorine atoms could form a chemical transfer membrane and reduce the friction coefficient. Polyphosphazene nanotubes showed excellent modification properties in the waterborne polyurethane system.

Keywords Waterborne polyurethane · Polyphosphazenes · In situ polymerization · Super-hydrophobic · Friction and wear

Introduction

Waterborne polyurethane (WPU) is a kind of polymer that has hydrophilic groups which can steadily dissolve or disperse in water. It is characterized by non-poisonous, non-ignitable, low VOC and adjustable chain segments. It is also called water dispersing polyurethane or water-based polyurethane [1]. There are two stages of prepolymerization and neutralization reaction in the compounding of WPU. During the prepolymerization reaction, WPU prepolymer is compounded by oligomeric diols, hydrophilic monomers, diisocyanates and chain extenders, which have large relative molecular masses. During the neutralization reaction, prepolymer is dispersed in water, which leads to low VOC of WPU. WPU has been used widely because of its environmental protection, such as adhesives, surface treatment agents and so on [2–4].

The preparation of lower VOC polyurethane matches the theme of 'Green Chemistry' and 'Four E' principles (Energy, Environment, Economy and Efficiency) [5, 6]. However, WPU owns weak mechanical property as same as thermal stability. Therefore, it is necessary to conduct modification studies. On account of nanoparticle surface effect, like macroscopical quantum tunnelling and quantum size, other matters compounding with it will perform special properties [7, 8].

In our previous work, polyphosphazene microspheres (PZMs) and nanofibers (PZFs) were synthesized by in situ polymerization, and prepared their waterborne polyurethane composites [9, 10]. The microstructures of WPU composites indicated that the polyphosphazene nanoparticles were

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