

Fast and Convenient Synthesis of Cross-Linked Poly(urethane-isocyanurate) in the Presence of Tetrabutylammonium Phthalimide-*N*-oxyl or Tetraethylammonium 2-(Carbamoyl)benzoate as Efficient Metal-free Cyclotrimerization Catalysts

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Poly(urethane-isocyanurate) networks were prepared from toluene diisocyanate and poly(propylene glycol) via prepolymer method in the presence of tetrabutylammonium phthalimide-*N*-oxyl (TBAPINO) or tetraethylammonium 2-(carbamoyl)benzoate (TEACB) as effective and metal-free cyclotrimerization catalysts. The effect of various NCO/OH stoichiometric ratios on the structure and mechanical properties of the synthesized elastomers was investigated against different catalyst loadings of TBAPINO. The chemical structures of the synthesized poly(urethane-isocyanurate) networks were characterized by FTIR spectroscopy. The results of thermogravimetric analysis experiments showed that the thermal stability of the polymer networks is enhanced in appropriate NCO-free contents of the prepolymers using 1 mol% of TBAPINO or TEACB.

Keywords Isocyanurate cross-linking units; Metal-free catalyst; Poly(urethane-isocyanurate) networks; Tetrabutylammonium phthalimide-*N*-oxyl; Tetraethylammonium 2-(carbamoyl)benzoate

INTRODUCTION

The polyurethanes (PUs) are a special group of engineering materials which are used almost in both industry and human life. PUs are widely used in manufacturing of coatings, adhesives, foams, thermoplastic elastomers and resins^[1–5]. PUs are characterized by the urethane linkage which is formed by the reaction of an isocyanate group with a hydroxyl group. PUs are multiblock copolymers which consist of hard and soft segments. The soft segment is derived from polyether or polyester diols while the hard segment is obtained from the reactive isocyanates with a chain extender^[6–9].

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PUs demonstrate excellent mechanical properties, but they have low thermal stability due to the thermal instability of the urethane group. To overcome this problem, chemical modification of PU structures by introducing the thermally stable heterocycles such as isocyanurate, oxazolidine, imide and triazine has been well documented^[10–14]. The resulting polymer networks exhibit higher thermal stability, greater fire resistance, and improved dimensional stability as a consequence of cross-linking between polymer chains. Among different cross-linking structures, the isocyanurate (hexahydro-1,3,5-triazine-2,4,6-trione) ring show highest thermal stability. When an excess of isocyanate functional group exists, isocyanurate structure can be formed in the presence of an appropriate cyclotrimerization catalyst^[15–18].

The high reactivity of the isocyanate functional group and diversity in the resulting products is well known. Products such as trimer, dimer, carbodiimide, urethane or allophanate have been characterized depending on the reaction conditions^[15]. Therefore, the exploitation of selective catalysts to form isocyanurate structure, as cross-linking agent, is a crucial factor to fabricate PU networks with suitable chemical and physical properties. Different catalysts have been introduced for cyclotrimerization of monofunctional isocyanates^[19,20].

In general, the cyclotrimerisation catalysts can be classified as: organometallics mainly with Lewis acidic character, anionic or neutral catalysts having Lewis basic character, and combined catalysts. For instance, organometallics and complexes consisting of Sn, Pd, Pr, Yb, Eu, Sm, Nd, Nb, Y, Ge, and Zr and Lewis basic catalysts such as alkali metals or tetraalkylammonium salts of dibenzylamide, 2-(carbamoyl)benzoate, fluoride, sulfite, and sulfate or proazaphosphatranes have been introduced recently^[21–26].