

High Biobased Carbon Content Polyurethane Dispersions Synthesized from Fatty Acid-Based Isocyanate

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ABSTRACT: A series of high biobased carbon content polyurethane dispersions (PUD) was successfully synthesized from dimer fatty acid diisocyanate (DDI), castor oil (CO), alkoxysilane-modified castor oil (MCO), and dimethylolpropionic acid (DMIPA). This work focused on the improvement for the final performance of the renewable DDI-based PUD as well as the discussion of structure/property relationships. The chemical structure of MCO and Si–O–Si cross-link network structure on the dry-film of PUD were characterized by Fourier-transform infrared spectroscopy (FTIR) and solid-state ²⁹Si NMR. The effect of alkoxysilane and NCO/OH ratio on DDI-based PUD were investigated by differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), tensile tests, and electrochemical impedance spectroscopy (EIS). The glass transition temperature, Young's modulus, and tensile strength increased with the incorporation of alkoxysilane and increasing NCO/OH ratio. In the meanwhile, the initial degradation temperature and elongation at break were reduced with increasing content of alkoxysilane. Finally, the alkoxysilane-modified DDI-based PUD exhibited excellent corrosion resistance after the immersion in NaCl solution for 28 days. In general, the present research suggested that through appropriate modification the DDI-based PUD with high biobased carbon content could exhibit great mechanical properties and excellent anticorrosion properties.



INTRODUCTION

Polyurethane dispersions (PUD) belong to the polyurethane polymer systems which are dispersed in water. They are usually synthesized from polyols, isocyanates, and the dispersing-function monomers. PUD have received extensive attention from industry and academia once they were invented. After years of research and development, PUD have become one of the most important materials in the coatings and adhesives industry due to their nontoxicity and safety.¹ Nowadays, several novel types of PUD have been developed, such as 2K polyurethanes dispersions and nonisocyanate polyurethane dispersions.^{2–4} In the next few years, the usage of PUD coatings with water as a solvent is likely to rise rapidly as the concepts of environmentally friendly development become more popular. However, compared with conventional solvent-based polyurethane coatings, there is still a need for the enhancement of biobased PUD coatings properties, such as corrosion resistance and adhesion.

Over the years, biobased materials technology has been growing rapidly. Biobased materials, especially vegetable oil-based materials, are considered potential alternatives to conventional petroleum-based materials for the future.⁵ For example, the biobased materials, such as vegetable oil-derived polyols, have been widely applied in coatings, plastic films, lubricants, rubbers, and many other intermediate products.^{6–12} Multiple synthesis methods for vegetable oil-based polyols have been investigated including epoxidation and ring opening,

transesterification and amidation, ozonolysis and reduction, hydroformylation and reduction, and thiol–ene reaction.¹³ Although some of the petroleum-based products could be replaced by biobased materials, many important petroleum-based materials rarely have suitable alternatives for real application, such as isocyanates and amines. Therefore, for sustainable development it is significant to continuously study alternatives to petroleum-based materials.

In recent years, much attention has been drawn to the application of dimer fatty acid-derived isocyanate as a potential alternative to petroleum-based isocyanate.^{14–16} 2-Heptyl-3,4-bis(9-isocyanatononyl)-1-pentylcyclohexane (DDI) is a special aliphatic diisocyanate derived from dimer fatty acid with two branched long chains connected on the cyclic aliphatic unit. It exhibits excellent flexibility, low water sensitivity, outstanding water resistance, nonyellowing performance, low toxicity, and low viscosity. Calvo-Correas reported that the thermoplastic polyurethane synthesized from DDI showed a low glass transition temperature because the branched structure of DDI could reduce the degree of crystallization.¹⁷ Chaoen developed a biobased polyurethane elastomer from DDI and biobased macrodiols with 700% of elongation at break and 40 MPa of

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