Cycloaliphatic Polyester Based High Solids Polyurethane Coatings: I. The Effect of Difunctional Alcohols

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INTRODUCTION

Traditionally, polyurethane coatings have been formulated mainly in organic solvent, however, the organic solvents have become the subject to strict regulation. Volatile organic compounds (VOC) have been a driving force to develop alternative coating technologies: (1) high solids, (2) radiation-curable, (3) powder, and (4) waterborne. Radi-curable, powder, and waterborne technologies have different advantages with respect to the applications and performances. However, there are some limitations for each technology. For instance, zero VOC can be approached using powder coatings, but large or heat-sensitive substrates are difficult to coat using powder. High solids typically are composed of a functionalized, low molecular weight polymer and a monomeric or oligomeric crosslinking agent dissolved in organic solvents. High-solids coatings can be prepared using sophisticated methods for synthesizing low-viscosity oligomeric resins and crosslinkers. In addition, compared with the other three technologies, the application is easier for any substrate.

Generally, solventborne polyurethane coating formulations comprise approximately 70% by weight polyol, the other component being the crosslinker, a polyisocyanate. Polyisocyanates usually have low viscosity; therefore, the polyol controls the viscosity. Low viscosity is essential for achieving a low VOC. Hydroxy-terminated polyester and hydroxy-functional acrylic resins are the most common polyols, followed by polyethers which are seldom used in the coating industries due to the limited properties. Generally, polyesters can achieve higher solids, greater solvent resistance, and better adhesion to metals compared with acrylic resins. In contrast, acrylic resins have much higher average molecule weight, and thus are more difficult to achieve high solids.

Typical low-solids formulations of polyesters are prepared from aromatic diacids such as phthalic anhydride (PA) and isophthalic acid (IPA), and an aliphatic diacid such as adipic acid. However, the phenyl ring of aromatic diacids can cause yellowing of the cured enamel and the aliphatic diacids have poor hydrolytic stability. To overcome this detrimental effect, cycloaliphatic diacids are used instead of the combination of aromatic diacids and aliphatic diacids.* The research on the
The chemical structures of glycols.

Scheme 1—The chemical structures of glycols.

cycloaliphatic polyesters was reviewed and also reported in our previous paper.15

The approaches to obtain low VOC for polyesters include (1) controlling molecular weight and molecular weight distribution, (2) using hydrogen-bond acceptor solvents, and (3) reducing the ratio of aromatic/aliphatic diacids.16 Another approach which was emphasized by Jones and co-workers17 was lowering VOC using mixtures of diacids. The mixture of diacids can disorder uniform structure and thus reduce the intermolecular interaction. A mixture of three linear diacids was used instead of one diacid to suppress the melting point of oligoester below room temperature. The crystallinity of single diacid was avoided and very low viscosity was achieved. A mixed cycloaliphatic diacid was also used in our previous work to reduce the viscosity.15

The diol is particularly important for achieving high solids. Typical diols for high solids are linear glycol including ethylene glycol, 1,4-butanediol, and 1,6-hexanediol and branched glycol, neopentyl glycol (NPG).18 For comparison, chemical structures of these glycols are in Scheme 1. The viscosity and glass transition temperature of polyesters are affected by the diol structure; for the linear glycols, the longer diol chain, the lower the viscosity and softer the resultant polyurethane film. The branched NPG has two-methyl group substitution on the backbone, and is used to formulate the rigid polyurethane film. Several other diols, hydroxypivalyl hydroxypivalate (HPHP), 2-butyl-2-ethyl-1,3-propanediol (BEPD) and 1,4-cyclohexanediol (HD), 1,4-cyclohexanediol (CHDM), have been reported.6 The HPHP possesses the advantage of an internal ester which can result in reduction of aromatic acid in the polyester. The BEPD has greater hydrophobicity compared to NPG.

Three factors determine hydrolytic stability: (1) hydrophobicity, (2) Tg, and (3) steric factors. The steric factor is predicted by Newman’s rule according to the substituents.19,20 The exception is CHDM which has a better hydrolysis-resistant property than predicted by Newman’s rule.21 Polyesters of three glycols—BEPD, HPHP, and NPG—of similar structure and steric hindrance (Newman’s rule) were compared.14,22 The diol with the most hydrophobic character, BEPD, resulted in polyester with the best hydrolytic stability. Another study with diols focused on the effect of Tg on hydrolytic stability. The NPG, 2,2,4-trimethyl-1,3-pentanediol (TMPD), and CHDM were compared; the polyester based on CHDM had both the highest Tg and was the most resistant to hydrolysis.23

A series of polyesters based on cyclohexanediol with aromatic, cyclic and acyclic diacids was crosslinked with hexamethylene diisocyanate (HDI) isocyanurate in a companion study.15 As a continuation, high solids polyesters based on cycloaliphatic diacids (1,4-CHDA and 1,3-CHDA) were investigated as a function of diol structure. Similar to the previous study, the polyesters were designed to have a low molecular weight 800-1000 (g/mole) to achieve a low viscosity for high-solids coating.24 The polyesters will be crosslinked by the crosslinker HDI isocyanurate producing polyurethanes. The high-solids potential of the polyesters was evaluated with respect to solubility and viscosity. The general coatings and thermomechanical properties were evaluated in the polyurethanes.

### EXPERIMENTAL

#### General Information

The diacids, 1,3-CHDA and 1,4-CHDA, and diols, CHDM and HPHP were obtained from Eastman Chemicals. The