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

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High-solids polyesters were synthesized with two cycloaliphatic diacids, 1,4- cyclohexanedicarboxylic acid (1,4-CHDA) and 1,3-cyclohexanedicarboxylic acid (1,3-CHDA); and with five diols, 1,4-cyclohexanedimethanol (CHDM), neopentyl glycol (NPG), hydroxypivalyl hydroxypivalate (HPHP), 2-butyl-2-ethyl-1, 3-propanediol (BEPD), and 1,6-hexanediol (HD). The viscosity of the polyesters was dependent on the structures of diols. The viscosity of polyesters is lower with the diol HD, intermediate with BEPD and HPHP, and higher with the diols CHDM and NPG. The polyesters were crosslinked with hexamethylene diisocyanate isocyanurate (HDI isocyanurate) affording polyurethane coatings. The mechanical properties, tensile properties, fracture toughness, and viscoelastic properties were investigated for the polyurethane films with five different diols. The cyclohexyl structure of the CHDM provides the polyurethane with rigidity which is manifested in high tensile modulus, hardness, and fracture toughness. In contrast, the linear diol, 1,6-hexanediol provides polyurethane with very high flexibility, but these coatings suffer with respect to low hardness and tensile modulus.

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.[1,2] Radiation-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.[3] High solids typically are composed of a functionalized, low molecular weight polymer and a monomeric or oligomeric crosslinking agent dissolved in organic solvents.[4] High-solids coatings can be prepared using sophisticated methods for synthesizing low-viscosity oligomeric resins and crosslinkers.[2] 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.[5] 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.[6-14] The research on the

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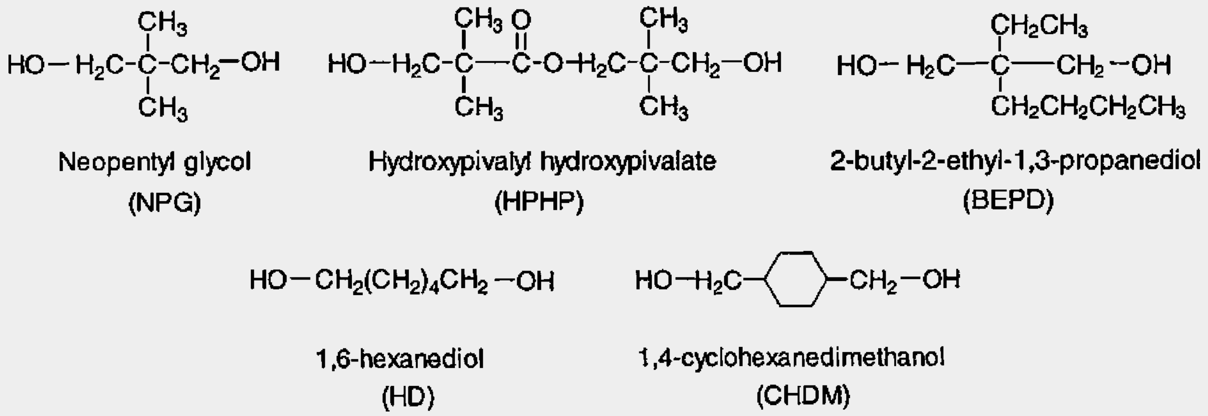


Scheme 1—The chemical structures of glycols.

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 disacids.[16] Another approach which was emphasized by Jones and co-workers[17] 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, hydropivalyl hydroxypivalate (HPHP), 2-butyl-2-ethyl-1,3-propanediol (BEPD) and 1,4-cyclohexanedimethanol (CHDM), have been reported.[6] The HPHP posseses 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.

Table 1—Formulations and Designations of Polyesters as a Function of Diols

		Diacids (mol)	
Polyester	Diol (mol)	1,4-CHDA	1,3-CHDA
CHDM(1,4; 1,3)	CHDM: 3	1	1
NPG(1,4; 1,3)	NPG: 2.85	1	1
BEPD(1,4; 1,3)	BEPD: 3.15	1	1
HPHP(1,4; 1,3)	HPHP: 3.50	1	1
HD(1,4; 1,3)	HD: 2.94	1	1
CHDM(1,4)	CHDM: 3	2	0
BEPD(1,4)	BEPD: 3.15	2	0
HPHP(1,4)	HPHP: 3.50	2	0

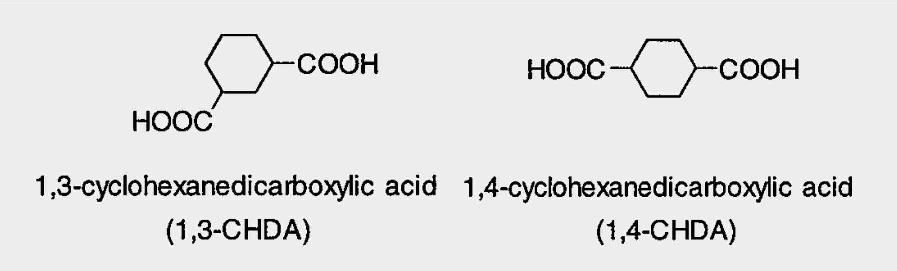
Three factors determine hydrolytic stability: (1) hydrophobicity, (2) T_g, and (3) steric factors. The steric factor is predicted by Newman's rule according to the substitutions.[19,20] The exception is CHDM which has a better hydrolysis-resistant property than predicted by Newman's rule.[21] Polyesters 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 T_g 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 T_g and was the most resistant to hydrolysis.[23]

A series of polyesters based on cyclohexanedimethanol 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 chemical structures of 1,3-CHDA and 1,4-CHDA are shown in *Scheme* 2. The other three diols, BEPD, NPG, and HD were purchased from Aldrich Chemicals. The xylene (anhydrous) and methyl ethyl ketone (MEK) were obtained from Aldrich Chemicals; the crosslinker, HDI isocyanurate; and leveling agent (Additive 57) from Dow Corning. All the reactants were used as received.

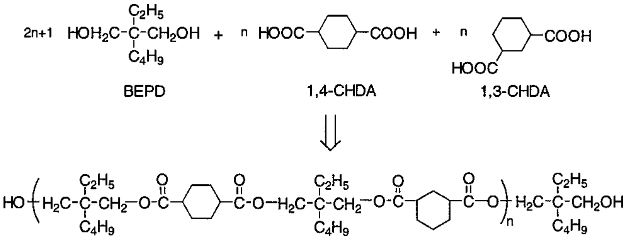


Scheme 2—The chemical structures of cycloaliphatic difunctional acids.

Synthesis of Polyesters

The formulations of syntheses of polyesters are listed in *Table* 1. The formulations in *Table* 1 are designed as a function of diols. A diacid mixture of 1,4-CHDA and 1,3-CHDA with mole ratio 1 to 1 was used for the first five polyesters. Single diacid 1,4-CHDA was used in the last three formulations. The numbers in the parentheses following diol were used to distinguish the isomeric diacid mixture and single diacid. The corresponding polyurethane films will also be designated as a function of diol.

An esterification reaction for the preparation of polyesters from the isomeric cycloaliphatic diacids of 1,4-CHDA and 1,3-CHDA is shown in equation (1).



(1)

A typical polycondensation technique was used to prepare polyester resin. The reactor (1000 mL) was equipped with mechanical stirrer and nitrogen purge, a modified Dean-Stark trap used for separating water and xylene. The reaction was under nitrogen purge and the maximum temperature at the post stage was kept at 210°C. The esterification reaction was monitored by the acid number and was controlled to an acid number between 3–6 mg KOH/g resin to keep the degree of reaction close for different formulations. The acid number and hydroxyl number polyesters were measured according to the ASTM standards D 1639-89 and D 4274-94, respectively.

Coating Formulation and Film Preparation

Polyesters (9.0 g) were diluted in methyl ethyl ketone (MEK, 1.0 g) and then mixed with the crosslinker, HDI isocyanurate (5.21g), MEK (0.58 g), and leveling agent, Additive 57 (0.071g, Dow Corning). The mole ratio of isocyanate group to hydroxyl group (from hydroxyl number) was kept constant at 1.1/1.0. The concentration of Additive 57 was 0.5 wt% overall nonvolatile composition.

Aluminum panels (alloy 3003 H14, Q-Panel Lab Products) were degreased with acetone; the films were cast on the aluminum panels with the thickness of 152.4 μm (6 mil) by a drawbar for the general mechanical test and on the glass plates with the thickness of 125.0 μm (5 mil) for the tensile and fracture toughness measurements. The polyesters were crosslinked with HDI isocyanurate at 120°C for one hour. The cured films were stored for three days under ambient atmospheric conditions before testing.

Instrumentation

Gel permeation chromatography (GPC) analysis was carried out using a five-column set of HR4, HT2, HR1, and HR0.5 Styragel, and 500Å Ultrastyragel columns (Waters Corporation). Tetrahydrofuran (THF) was applied as mobile phase and delivered at a rate of 1.0 mL/min. The calibration curve was generated using narrow polystyrene standards (Waters Corporation). Viscosity measure-

Table 2—Properties of Polyesters as a Function of Diols

Polyester	Acid Number (mgKOH/g)	Hydroxyl Number (mgKOH/g)	M_n (g/mol)	Viscosity (Pa·s)	Appearance of Oligomer in MEK	T_m (°C)
CHDM(1,4; 1,3)	3.5	152	891	8.3[b]	Transparent	—[e]
NPG(1,4; 1,3)	6.5	149	843	0.38[c]	Transparent	61
BEPD(1,4; 1,3)	5.7	150	865	1.3[b] /57.9[d]	Transparent	—
HPHP(1,4; 1,3)	5.2	153	839	0.71[b] /42.7[d]	Little hazy	—
HD(1,4; 1,3)	5.1	153	911	0.31[b] /2.18[d]	Transparent	—
CHDM(1, 4)	4.2	153	897	—	—	49
BEPD(1,4)	5.6	151	870	1.9[b] /91.5[d]	Transparent	—
HPHP(1,4)	5.6	154	836	1.5[b]	Hazy	—

(a) The mole ratio of diols/1,4-CHDA/1,3-CHDA.
(b) Diluted in 10 wt % MEK.
(c) Diluted in 20 wt % MEK.
(d) Neat polyesters.
(e) No melting point was observed.

Table 3—Coating Properties of Polyurethanes as a Function of Diols

Polyurethanes	Crosshatch Adhesion	Pull-off Adhesion ($lb_f/in.^2$)	Tukon Hardness (KHN)	Pencil Hardness	Reverse Impact (lb/in.)
CHDM(1,4; 1,3)	5B	305±19	8.2±0.4	F/H	> 80
NPG(1,4; 1,3)	5B	263±43	5.9±0.3	HB/F	> 80
BEPD(1,4; 1,3)	5B	241±37	2.8±0.2	B/HB	> 80
HPHP(1,4; 1,3)	5B	425±40	1.1±0.1	B/HB	> 80
HD(1,4; 1,3)	5B	211±26	0.76±0.13	3B/2B	> 80
CHDM(1,4)	5B	277±61	9.9±1.2	F/H	> 80
BEPD(1,4)	5B	287±40	2.7±0.1	B/HB	> 80
HPHP(1,4)	5B	378±48	1.2±0.1	B/HB	> 80

ments were performed on a Carri-Med CSL-100 rheometer with a parallel plate geometry. The thermal properties were measured by a differential scanning calorimeter (DSC, Perkin Elmer Model 7) with a heating rate of 10°C/min. Viscoelastic properties were obtained with a dynamical mechanical thermal analyzer (DMTA, Rheometric Scientific) with a frequency of 1 Hz and a heating rate of 3°C/min over a range of –50°C to 200°C. The gap distance was set up at 5 mm for rectangular test specimens (length 10 mm, width 9–11 mm, and thickness 0.05–0.1 mm).

Mechanical Properties

All mechanical tests were performed by standard procedures according to ASTM standards, including indentation hardness (Tukon hardness, ASTM D 1474-85), pencil hardness (ASTM D 3363-74), crosshatch adhesion (ASTM D 3359-87), pull-off adhesion (ASTM D 4541-85), reverse impact resistance (ASTM D 2794-84), and tensile properties (ASTM D 2370-82). The tensile property test was performed on an Instron Universal Tester Model 1000. The dimensions of films for tensile testing were 0.05-0.12 mm in thickness, 13-17 mm wide, and an initial length of 40 mm. A crosshead speed of 10 mm/min was applied to determine elongation-at-break, tensile modulus, and tensile strength. Eight samples were tested for each film. The data are reported as the mean of the data set, with an uncertainty based on the standard deviation.

Crosslink density was calculated using the elastic modulus on the rubbery plateau and corresponding temperature by the following equation:

$$E' = 3\,\nu_e RT \ (T >> T_g), \tag{2}$$

where ν_e is the number of moles of elastically effective network chains per cubic meter of film and E' is tensile storage modulus at corresponding temperature, T. This relationship is effective when $T >> T_g$, and for low crosslinking density elastomers.[25] For the highly crosslinked polyurethane system, it can only be used to evaluate the relative density of crosslinking.

Table 4—Fracture Toughness Properties of Polyurethanes

Polyurethanes	Fracture Toughness (K_c, MPa·$m^{1/2}$)	Tensile Modulus (E, MPa)	Energy Release (G_c, J/m^2) × 10^3	Deformation Zone
CHDM(1,4; 1,3)	1.81±0.15	569±60	5.8±0.9	craze
CHDM(1,4)	1.87±0.19	644±74	5.4±1.0	craze
NPG(1,4; 1,3)	0.609±0.053	516±67	0.72±0.13	n/o[a]
BEPD(1,4; 1,3)	0.186±0.012	177±31	0.20±0.04	n/o
BEPD(1,4)	0.211±0.020	170±18	0.26±0.04	n/o

(a) n/o:no deformation mechanism was observed.

Fracture Toughness

Plane-stress fracture toughness measurements were conducted on rectangular specimens with a single-edge-notch (SEN) geometry. The dimensions of films were 0.05–0.12 mm in thickness and 13–17 mm wide. Each film was cut with a razor blade to create the edge notch. This cutting procedure gave a crack which appeared sharp under a microscope. The length of the notch was less than 10% of the width of the sample. A fracture toughness tester which was mounted on a microscope stage and equipped with a 25 lb (111 N) load and a variable speed motor was used to deform the specimen in a tensile mode. The crosshead speed was 1.46 mm/min. The crack-tip region was observed at a magnification of 10 on the computer monitor, and the onset of crack propagation was noted and digitally marked on the load-displacement curve. The deformation zone near the crack tip could be observed continuously on the computer monitor during the measurement. The calculation of plane-stress fracture toughness (K_c, stress intensity factor at fracture) and the energy release rate per unit crack area at fracture (G_c) was described in our previous publication.[15] Six samples were tested for each film. The data are reported as the mean of the data set with the standard deviation.

RESULTS

The objective of this study is to evaluate the effects of diols on the properties of high solids cyclohexyl polyesters and polyurethane coatings. To obtain hydrolytic stability and ultraviolet resistance, the investigation of diacids focuses on cycloaliphatic diacids. Two sections were included in this study. The first series includes five polyesters which were synthesized using five different diols and the same isomeric cycloaliphatic diacids of 1,4-CHDA and 1,3-CHDA. The second series consists of three polyesters with three different diols and single cycloaliphatic diacid 1,4-CHDA.

For hydrolytic stability, diols used in polyurethane coatings such as NPG, HPHP, and BEPD, usually have two substitutents on the β-carbon, resulting in a high Newman's steric factor. Cyclohexyl diol CHDM was chosen since it was previously reported to afford higher T_g and better hydrolytic resistance than predicted by Newman's steric factors.[23] A linear HD was chosen for comparison. The tensile properties, fracture toughness, glass transition temperature and crosslink density of the polyurethanes were investigated as a function of polyol.

The study started with the first series of polyesters derived from mixed diacids of 1,4-CHDA and 1,3-CHDA. The polyester with NPG did not show potential for high solids. It is not included in the second series of polyesters. The linear diol HD is only used as a reference for comparison, and is not included in the second series of polyesters either. Thus, three of the five diols were chosen in the second series of study. If high solids could be achieved using one diacid 1,4-CHDA, it would simplify the formulation.

Properties of Polyesters

The properties of polyesters including acid number, hydroxyl number, number average molecular weight, and viscosity are listed in *Table* 2. Comparing the solubility in solvent MEK among the five polyesters based on isomeric mixed diacids, only polyesters containing CHDM, BEPD, and HD dissolved in 10 wt% MEK and formed a transparent solution. For three transparent diluents in 10 wt% MEK, CHDM(1,4; 1,3), BEPD(1,4; 1,3) and HD(1,4; 1,3), the viscosity is 8.3, 1.3, and 0.31 Pa·s, respectively. Polyester containing HPHP dissolved or partially dissolved in 10 wt% MEK, but the appearance was hazy. It has a viscosity of 0.71 Pa·s. However, the polyester with NPG in 10 wt% MEK is in solid state. By increasing the MEK to 20 wt%, the polyester NPG(1,4; 1,3) exhibited a transparent solution with a viscosity of 0.38 Pa·s.

Among the three transparent polyesters, CHDM(1,4; 1,3), BEPD(1,4; 1,3) and HD(1,4; 1,3), viscosity of neat CHDM(1,4; 1,3) was unmeasurable in the range of rheometer, neat BEPD(1,4; 1,3) has a viscosity of 57.9 Pa·s and neat HD(1,4; 1,3) has a viscosity of 2.18 Pa·s. The neat polyester HPHP(1,4; 1,3) is a little hazy and has the viscosity of 42.7 Pa·s. For three polyesters CHDM(1,4), BEPD(1,4) and HPHP(1,4) with single diacid, BEPD(1,4) had a measurable viscosity when neat and also was able to dissolve in 10 wt% MEK. When dissolved in 10 wt% MEK, the HPHP(1,4) polyester was hazy and had a viscosity of 1.5 Pa·s.

Mechanical Properties of Polyurethanes

The general mechanical properties of polyurethanes as a function of diol including crosshatch adhesion, pull-off adhesion, Tukon hardness, pencil hardness and reverse impact are shown in *Table* 3. Both Tukon hardness and pencil hardness showed that the polyurethanes behave from "hard" to "soft" with the rank from CHDM, NPG, BEPD, HPHP, to HD for the 1,4-CHDA and 1,3-CHDA mixed diacids series. The polyurethane derived from diol CHDM has highest hardness (Tukon 8.2 KHN; pencil F/H), and the polyurethane derived from linear diol had the lowest hardness (Tukon 0.76 KHN; pencil 3B/2B). The same trend in hardness was observed for the diol with the 1,4-CHDA based polyurethanes. All of the eight polyurethanes have highest grade crosshatch adhesion on aluminum substrate, 5B. The adhesion could be distinguished, however, by the pull-off adhesion. Typically, the polyurethanes containing the diol HPHP had 30–60% greater adhesion, 425 $lb_f/in.^2$ for the polyurethane HPHP(1,4; 1,3) and 378 $lb_f/in.^2$ for HPHP(1,4), than the polyurethanes derived from diols, CHDM, NPG, BEPD, and HD. All eight films have very high impact resistance (more than 80 lb/in.), which is out of the range of measurement.

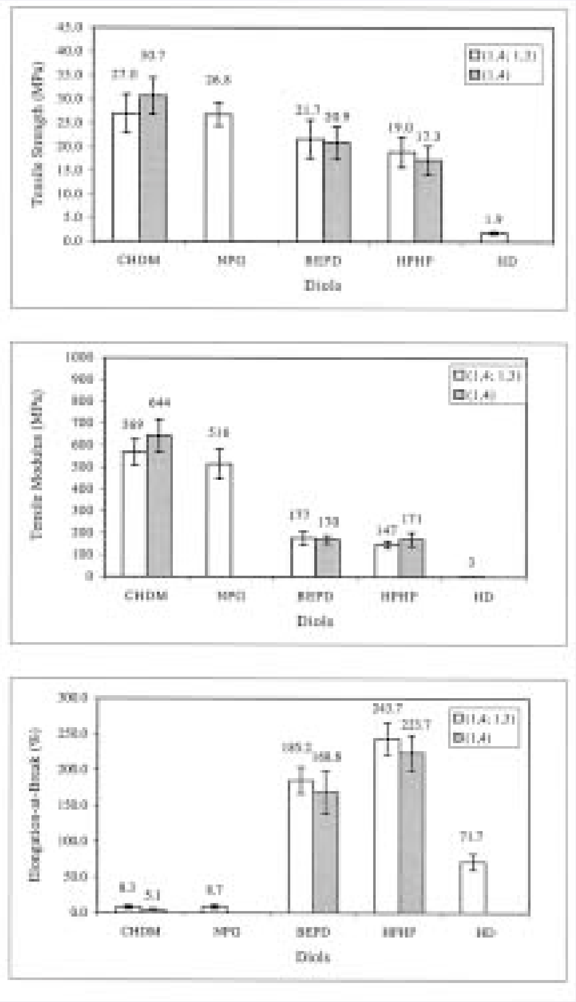


Figure 1—Tensile properties of polyurethane as the function of diols in polyesters.

Tensile Properties and Fracture Toughness

The tensile properties and fracture toughness of the polyurethanes are shown in *Figure* 1 and *Table* 4, respectively. Generally, the tensile properties were dependent on the structures of diols, which can be divided into three groups. The CHDM and NPG-based polyesters had a high tensile strength, low elongation-at-break, and high modulus. The BEPD and HPHP-based polyesters had an

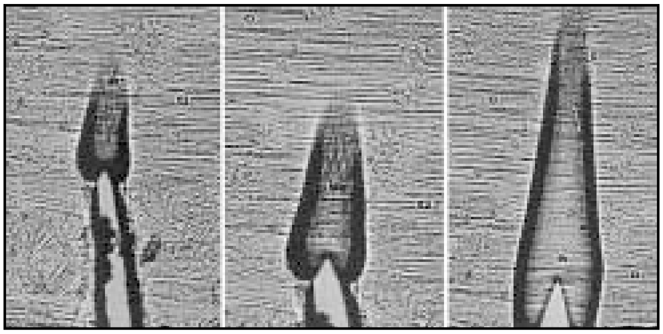


Figure 2—Crack-tip plastic deformation zone of the CHDM (1,4) polyurethane film under tension. The micrographs from left to right were taken at an increasing degree of deformation.

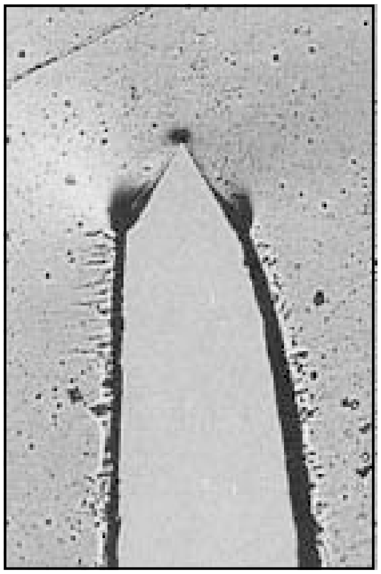


Figure 3—Crack-tip plastic deformation zone of the BEPD (1,4) polyurethane film under tension.

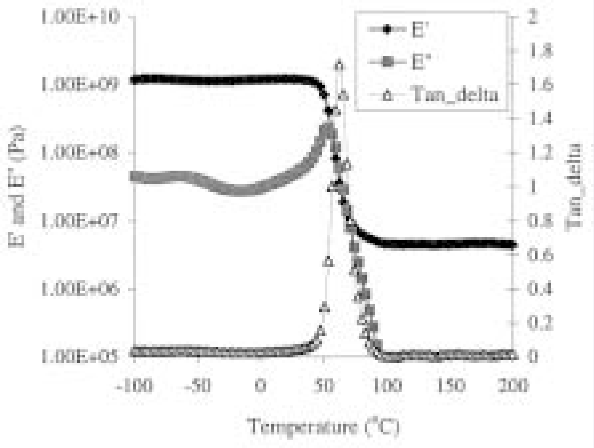


Figure 4—Dynamic mechanical properties of polyurethane BEPD (1,4). E', storage modulus, E"; loss modulus; and tan $\delta = E'/E''$.

intermediate range of tensile strength and modulus, and very high elongation-at-break (150-250%). Lastly, the HD based polyester had a middle range of elongation-at-break (71.7%) and very low tensile strength (1.9 MPa) and modulus (3 MPa).

Table 4 shows the plane-stress fracture toughness and the energy release rate of polyurethanes. The fracture toughness of polyurethanes CHDM(1,4; 1,3) and CHDM(1,4) is very high—1.81 and 1.87 MPa·m$^{1/2}$ respectively. In comparison, polyurethanes NPG(1,4; 1,3) and BEPD(1,4; 1,3) have fracture toughness of 0.609 and 0.186 MPa·m$^{1/2}$, respectively. This indicates that the diol CHDM gives the polyurethane better resistance to crack extension than NPG, even though the tensile properties of the two polyurethanes are experimentally indistinguishable. The diol BEPD reduced both the fracture toughness (from 1.81 to 0.186 MPa·m$^{1/2}$) and tensile modulus (from 569 to 177 MPa). The energy release rate was calculated from the fracture toughness and tensile modulus data in *Table* 4.[15] Generally, the trend in energy release rate as a function of diol is consistant with fracture toughness. The polyurethanes CHDM(1,4; 1,3) and CHDM(1,4) have the highest energy release rate among the five polyurethanes, 5.8×10^3 and 5.4×10^3 J/m^2, respectively.

Two types of deformation are shown in *Figures* 2 and 3 in crack propagating process. As shown in *Figure* 2, crazes were observed for the polyurethanes CHDM(1,4; 1,3) and CHDM(1,4) in the deformation region. However, no typical mechanism was observed for the three polyurethanes, NPG(1,4; 1,3), BEPD(1,4; 1,3), and BEPD(1,4) during the crack propagating process.

Viscoelastic Properties of Polyurethanes

The storage modulus (E′), loss modulus (E″), and tan δ of the polyurethane films were investigated using DMTA. A typical instance of dynamical mechanical properties is shown in *Figure* 4 for the polyurethane BEPD(1,4). The T_g of the polyurethanes was derived from the α-transition. The T_g for all the polyurethane coatings as a function of diols is listed in *Table* 5. The T_g was also measured by DSC, which is listed in *Table* 5 for comparison with the tan δ derived data. Among the five polyurethanes with the isomeric mixed diacids and different diols, the polyurethane CHDM(1,4; 1,3) has highest T_g, 81°C. In contrast, polyurethane HD(1,4; 1,3) with the linear diol HD has lowest T_g, 30°C. The polyurethanes NPG(1,4; 1,3), BEPD(1,4; 1,3) and HPHP(1,4; 1,3) have intermediate T_gs of 66, 60, and 56°C, respectively. The T_g determined by DSC shown in *Table* 5 is consistent with the trend in the T_g derived from DMTA.

The crosslink density of the polyurethanes is also listed in *Table* 5, which was derived from equation (2) using the E′ on rubbery plateau and the corresponding temperature. Of the five polyurethanes, CHDM(1,4; 1,3) has the highest crosslink density (449 mol/m^3), and HPHP(1,4; 1,3) has the lowest crosslink density (211 mol/m^3). The NPG(1,4; 1,3), BEPD(1,4; 1,3) and HD(1,3; 1,4) have the intermediate crosslink density. The other three polyurethanes with single diacid have a similar varying trend of crosslink density as a function of diols. The polyurethane CHDM(1,4) has the highest crosslink density (532 mol/

m^3), HPHP(1,4) the lowest (301 mol/m^3) and BEPD(1,4) intermediate (417 mol/m^3).

DISCUSSION

Properties of Polyesters

Both the viscosity and T_g of polyesters were dependent on the diol. The William-Landel-Ferry (WLF) equation was used to correlate the dependence of viscosity on the difference of measurement temperature and glass transition temperature.[17,26] According to the WLF equation, the viscosity increases with the T_g when the measurement temperature is constant. From the structural analysis of diols, the polyester CHDM(1,3; 1,4) containing rigid cyclic diol CHDM has the highest T_g among the five diols, therefore it has highest viscosity. The linear diol HD is very flexible and thus HD(1,4; 1,3) has the lowest T_g and viscosity. The three polyesters, NPG(1,4; 1,3), BEPD(1,4; 1,3) and HPHP(1,3; 1,4), have a similar structure with the substituting groups on the side chain. It is expected that the three polyesters have the T_g ranging between the polyester CHDM(1,3; 1,4) and HD(1,3; 1,4). The BEPD(1,4; 1,3) and HPHP(1,3; 1,4) have the intermediate viscosity as the prediction from T_g. However, the polyester NPG(1,4; 1,3) is a solid due to the proclivity toward a crystallized structure.

The intermolecular interaction is the other factor determining the viscosity of polyesters. Comparing the polyester BEPD(1,4; 1,3) with BEPD(1,4), the viscosity of BEPD(1,4; 1,3) neat and in MEK solution is lower than the polyester BEPD(1,4) neat and in MEK solution, respectively. It was found that all the polyesters with mixed isomeric diacid have lower viscosity than the corresponding polyesters with single diacid. As stated in our companion study,[15] the isomeric mixed diacids of 1,4-CHDA and 1,3-CHDA in polyesters reduced the intermolecular interaction and thus decreased the viscosity of polyesters comparing to single diacid.

Among the eight polyesters, CHDM(1,4; 1,3) has the highest viscosity and CHDM(1,4) is solid state. It is more difficult to achieve a high-solids formulation with CHDM than with the other four diols.[23] At 10 wt% MEK, the polyester NPG(1,4; 1,3) does not yield a high solids formulation. However, it has a very low viscosity in 20 wt% MEK solution. Both BEPD(1,4; 1,3) and BEPD (1,4) have very low viscosity in 10 wt% MEK, which is lower than the viscosity of crosslinker HDI isocyanurate (~3 Pa·s). Similar to the polyesters with diol BEPD, both polyester HPHP(1,4; 1,3) and HPHP(1,4) achieved high solids; however the neat and 10 wt% solutions in MEK of the two polyesters were slightly hazy. Although the HD-based polyester can achieve a solventless system, the resultant polyester and polyurethane have unacceptable hydrolytic stability.

Properties of Polyurethanes

Clearly, the thermomechanical properties of the polyurethane coating depended on the structure of the diol. The effect of the diol on hardness, tensile properties, and fracture toughness reflects the importance of diol selection upon the soft segment properties of the polyurethane coating. The T_g decreased for polyurethanes in order with the corresponding diols, CHDM, NPG, BEPD, HPHP, and HD (*Table* 5). The least flexible cyclic diol (CHDM) had the highest T_g, and linear diol (HD) had the lowest T_g. The Tukon hardness (*Table* 3) and glass transition temperature, T_g, followed the same trend. The higher hardness was correlated to the rigid cyclohexane structure and the high T_g.

Table 5—Glass Transition Temperature of Polyurethanes as a Function of Diols in Polyesters

Polyurethanes	T_g (°C DMTA)	Crosslink Density (mol/m^3)	T_g (°C DSC)
CHDM(1,4; 1,3)	81	449±13	56
NPG(1,4; 1,3)	66	359±55	43
BEPD(1,4; 1,3)	60	295±27	32
HPHP(1,4; 1,3)	55	211±38	28
HD(1,4; 1,3)	30	309±24	6
CHDM(1,4)	84	532±20	60
BEPD(1,4)	62	417±24	36
HPHP(1,4)	53	301±24	27

Not surprisingly, the tensile modulus and fracture toughness follow the T_g of the polyurethanes. The polyurethane CHDM(1,4; 1,3) has 300% higher fracture toughness than NPG(1,4; 1,3) and 800% higher than BEPD(1,4; 1,3) (*Table* 4). Similar trends were observed when CHDM(1,4) was compared with BEPD(1,4). Therefore, the fracture toughness within the series of polyurethanes reported in this study was predominately dependent on diol. Unfortunately, there are not a lot of examples of fracture toughness of polyurethane with which to compare.[27] The study of fracture toughness for the polyurethane coating as a function of cycloaliphatic diacids provided an important reference. The three diols, NPG, BEPD, and HPHP have similar propanediol structure. However, there are slight differences in chemical structure between the three diols which are manifested in the polyurethane coatings. The BEPD(1,4; 1,3) polyurethane has lower T_g, hardness, and tensile modulus than polyurethane based on NPG. By increasing the length of the aliphatic side chain, chain packing is disturbed, providing more free volume. Additional degrees of freedom afforded by bond rotation, interruptions of main chain symmetry, or spacing side chains all result in the creation of free volume. This manifests itself in the properties associated with soft segment behavior including fracture toughness. It is anticipated that the dissipation of energy within a hard and soft segment polyurethane coating will be predominately controlled by the ability of the soft segment to absorb and diffuse that energy. It would be interesting to compare the fracture toughness of the polyurethane films as a function of temperature, thus removing the T_g effect. However, we presently do not have a cooling unit for our fracture toughness instrument. It was found that the mechanical energy required to propagate the crack should be directly related to the types of potential failure for the automotive clearcoat/basecoat systems.[28] We plan to relate the fracture toughness to marring and scratching resistance for the coatings in real applications in future studies.

CONCLUSIONS

High solids (~90 wt% or more) were achieved using the diols, CHDM, BEPD, HPHP, and HD, with a mixture of isomeric cyclohexyl diacids(1,3 and 1,4), and only two of the diols (BEPD and HPHP) could achieve >90 wt% with a single diacid(1,4-CHDA). Of the cyclohexyl diacids polyesters, BEPD had the best combination of solubility in MEK, and lowest viscosity, and steric hindrance which affords hydrolytic stability. Polyurethanes with CHDM-based polyesters were in the plastic region at room temperature and polyurethanes with high HD-based polyester were in the rubbery plateau. Polyurethanes based on BEPD and HPHP polyesters were in the transition at ambient temperature between the plastic and rubbery states. The diol CHDM provides the polyurethanes with high T_g, tensile modulus, fracture toughness, and hardness. Both BEPD and HPHP gave the polyurethane coatings very high elongation-at-break, affording a broader range of flexibility.

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References

(1) Jones, F.N., "Targets for Resin Development in the New Millennium," Journal of Coatings Technology, *72*, No. 909, 153 (2000).
(2) Jones, F.N., *Proc. FSCT 78th Annual Meeting Technical Program,* Chicago, IL, p. 241, October 2000.
(3) Wicks, Z.W. Jr., Jones, F.N., and Pappas, S.P., "Powder Coatings; IV," Journal of Coatings Technology, *71*, No. 895, 67 (1999).
(4) Sherwin, M.A., Koleske, J.V., and Taller, R.A., "Solution Properties of High Solids Intermediates," Journal of Coatings Technology, *53*, No. 683, 35 (1981).
(5) Charrière-Perroud, E., in *Waterborne & Solvent Based Surface Coating Resins and their Applications, Volume III Polyurethanes,* Thomas, P. (Ed.), John Wiley and Sons, New York, Chapt. 5, 1998.
(6) Johnson, L.K. and Sade, W.T., "New Monomers for Polyester Powder Coating Resins," Journal of Coatings Technology, *65*, No. 826, 19 (1993).
(7) Heidt, P.C. and Elliott, M.L. "Aliphatic Dibasic Acid-Modified Polyesters Thermoset Industrial Coatings," Waterborne, High-Solids, and Power Coatings Symposium, New Orleans, LA, February 1995.
(8) Eastman Publication N-341A, "1,4-CHDA Cycloaliphatic Intermediate for High-Performance Polyester Resins," (October 1994).
(9) Eastman Publication N-327A, "Improved Coil Coating Performance with Eastman 1,4-CHDA," (February 1995).
(10) Eastman Publication N-342, "Improved Hydrolytic Stability of Waterborne Polyester Resins with 1,4-CHDA and BEPD," (September 1994).
(11) Eastman Publication N-335A, "Eastman 1,4-CHDA vs. IPA, AD, and HHPA In a High-Solids Resin System Based on TMPD Glycol," (April 1996).
(12) Ni, H., Skaja, A.D., Thiltgen, P.R., Soucek, M.D., Simonsick, W.J. Jr., and Zhong, W., *Polym. Prepr.,* Am. Chem. Soc., Div. Polym. Chem., 40(1), 615 (1999).
(13) Heidt, P.C., "Cycloaliphatic-Based Thermoset Industrial Coatings," Waterborne, High-Solids, and Powder Coatings Symposium, New Orleans, LA, February 1994.
(14) Jones, T.E. and McCarthy, J.M., "A Statistical Study of Hydrolytic Stability in Amine Neutralized Waterborne Polyester Resins as a Function of Monomer Composition," Waterborne, High-Solids, and Power Coatings Symposium, New Orleans, LA, February 1995.
(15) Ni, H., Daum, J.L., Thiltgen, P.R., Soucek, M.D., Simonsick, W.J. Jr., and Zhong, W., "Cycloaliphatic Polyester-Based High Solids Polyurethane Coatings: II. The Effect of Difunctional Acid," Submitted to *Prog. Org. Coat.*, 2001.
(16) Wicks, Z.W., Jones, F.N., and Pappas, S.P. *Organic Coatings Science and Technology, Volume I: Film Formation, Components, and Appearance,* John Wiley and Sons, New York, Chapt. 8, 1992.
(17) Jones, F.N., "Toward Solventless Liquid Coatings," Journal of Coatings Technology, *68*, No. 852, 25 (1996).
(18) Huber, H.F. and Stoye, D., in *Coatings Technology Handbook*, Satas, D. (Ed.), Marcel Dekker, New York, Chapt. 39, 1991.
(19) Turpin, E.T., "Hydrolysis of Water Dispersible Resins," Journal of Paint Technology, *47*, No. 602, 40 (1975).
(20) Sullivan, C.J., Dehm, D.C., Reich, E.E., and Dillon, M.E., "Polyester Resins Based Upon 2-Methyl-1,3 Propanediol," Journal of Coatings Technology, *62*, No. 791, 37 (1990).
(21) Golob, D.J., Odom, T.A. Jr., and Whitson, R.W., *Polym. Mater. Sci. Eng., 63*, 826 (1990).
(22) Jones, T.E., "Statistical Study of Hydrolytic Stability in Amine-Neutralized Waterborne Polyester Resins as a Function of Monomer Composition," Journal of Coatings Technology, *67*, No. 844, 57 (1995).
(23) Eastman Publication N-329C, "Triangle Glycol Study," (June 1998).
(24) Belote, S.N. and Blount, W.W., "Optimizing Resins for Low VOC," Journal of Coatings Technology, *53*, No. 681, 33 (1981).
(25) Hill, L.W. and Kozlowski, K., "Crosslink Density of High Solids MF-Cured Coatings," Journal of Coatings Technology, *59*, No. 751, 63 (1987).
(26) Hill, L.W., Kozlowski, K., and Sholes, R.L., "Theory and Practice of Viscosity Reduction in High Solids Systems," Journal of Coatings Technology, *54*, No. 692, 67 (1982).
(27) Ballard, R.L., Sailer, R.A., Larson, B., and Soucek, M.D., "Fracture Toughness of Inorganic-Organic Hybrid Coatings," Journal of Coatings Technology, *73*, No. 913,107 (2001).
(28) Nichols, M.E., Gerlock, J.L., Smith, C.A., and Darr, C.A., *Prog. Org. Coat., 35*, 153 (1999).