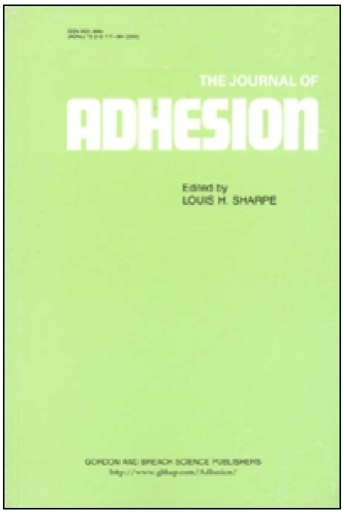

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Note

Imidazolidinone Diamine Modified Polyurethane Dispersions

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A cyanoalkylation and reduction process was used to synthesize novel imidazolidinone diamine monomers. The diamine monomers, characterized using wet methods and Nuclear Magnetic Resonance, were incorporated into anionic polyurethane/urea dispersion adhesives. Our studies have shown that small amounts of imidazolidinone monomer in anionic polymers can improve adhesion of polyvinyl chloride to itself three-fold, and the adhesion of acrylonitrile/butadiene/styrene copolymer to vinyl at high-temperatures in the presence of a polyfunctional isocyanate. Adhesion improvements are attributed to the polarity and hydrogen-bonding capabilities of the pendant imidazolidinone groups. Gloss improvements correlated well to levels of incorporated diamine.

Keywords: Monomer; Cyclic urea; Diamine; Imidazolidinones; Polyurethane; Dispersions; Adhesion

INTRODUCTION

For the last 40 years, cyclic urea derivatives have been utilized for a variety of applications, *e.g.*, corrosion inhibitors, textile modifiers, paper modifiers, lubricants, lubricant additives, and epoxy curing agents [1-3]. Often, the cyclic ureas of choice were imidazolidinones.

Imidazolidinone compounds can provide desirable properties. For example, when blended with aminoplast resins and emulsion polymers, imidazolidinones have been shown to enhance gloss-characterisitics

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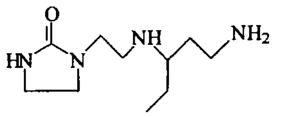
[4]. As comonomers, imidazolidinones have been useful in improving the wet-adhesion properties of latex paints [5–9]. These same property enhancements are often desirable in coatings and other adhesives as well.

Imidazolidinone functionality has been introduced into emulsion polymers through radical polymerization of ethylenically-unsaturated monomers. The structures of these monomers, however, are not conducive to other types of polymerization processes used in industry.

Water-based polyurethane emulsions for coatings and adhesives are systems we believed could be enhanced with imidazolidinone functionality. To do so, new diamine monomers had to be synthesized. By providing the imidazolidinone group on a chain-extending diamine monomer, the molecular weight of the resulting polymer would be increased and the imidazolidinone group distributed throughout the network, a distribution thought to be important for enhancing the properties of polyurethane adhesives and coatings.

A cyanoalkylation/reduction process was used to synthesize the novel diamines diagrammed below. The diamines were incorporated into anionic polyurethane dispersions (PUDs) at levels ranging from 0.5 to 7% by weight of the polymer.



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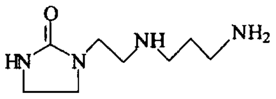

II.

This paper discusses adhesion and gloss improvements correlating to incorporated levels of I or II in anionic PUDs. Adhesive strengths of the modified PUDs were evaluated on polyvinyl chloride (PVC) and acrylonitrile–butadiene–styrene copolymer (ABS).

EXPERIMENTAL

Materials

1-(2-aminoethyl)imidazolidinone (AEI) was supplied by the Synthelas S. A. (Elche, Spain). Acrylonitrile was obtained from Aldrich

Chemical Company (Milwaukee, WI), and the 2-pentenenitrile from Hooker S. A. (Barcelona, Spain). Reduction of the nitrile monoamines to the corresponding diamines was performed using RANEY^{TM} Cobalt 2724 catalyst or with RANEY^{TM} Nickel catalyst from W. R. Grace/Davidson (Chattanooga, TN). Benzene, 1,3-bis(1-isocyanato-1-methylethyl)-TMXDI was supplied by Cytec Industries Inc. (West Paterson, NJ), 1,6-hexanediol adipate polyester polyol Rucoflex^{TM} S-105-110 by Ruco Polymer Corporation (Hicksville, NY), and the polyfunctional isocyanate Desmodur DA by Bayer Corporation (Pittsburgh, PA). Standard commercial grade ABS and low phthalate content PVC were used. Vinyl was obtained from O'Sullivan Corporation (Winchestor, VA).

Synthesis

General Procedure for Diamine I Synthesis

The diamine I was prepared using a two-step cyanoalkylation/reduction process. 1-(2-aminoethyl)imidazolidinone was stirred in water (3.5 : 1) at room temperature under an atmosphere of nitrogen. 1.1 equivalents of 2-pentenenitrile were added as a steady stream to the reaction mixture that was heated to 85°C and stirred for 24 hours. The loss of the amine C^{13}-NMR carbon signal of the 1-(2-aminoethyl)imidazolidinone was used to monitor the conversion.

Once the conversion was complete, the material was transferred to an autoclave purged with nitrogen. Dry RANEY^{TM} Cobalt 2724 Catalyst (2% by weight of nitrile) was then added followed by nitrogen purges and the addition of 29% aqueous ammonia (13% by weight of nitrile). The mixture was agitated, appropriately purged, and then heated to 100°C under 800 psi (5.5 MPa) of hydrogen. The loss of the nitrile C^{13}-NMR signal was used to monitor the conversion. After 24 hours of 800 psi (5.5 MPa) pressure, the catalyst was filtered away. Short-path distillation was used to isolate and purify the diamine. After a forerun of *n*-propyl amine (90 mm Hg, evaporator 83–85°C, condenser 0°C) followed by water and 1-(2-aminoethyl)imidazolidinone (0.007 mm Hg, evaporator 130°C, condenser 70°C), the desired diamine I distilled as a water-white, odorless, semi-viscous liquid (0.006 mm Hg, evaporator 162–165°C, condenser 70°C).

General Procedure for Diamine II Synthesis

The diamine II was prepared using a two-step cyanoalkylation/ reduction process very similar to that used for the synthesis of diamine I with the following exceptions. The cyanoethylation of AEI was carried out in isopropanol (20% by weight) and the hydrogenation was carried out using RANEY^{TM} Nickel as the catalyst.

General Procedure for the Synthesis of Anionic-Polyurethane Dispersion

The anionic polyurethane dispersions were prepared using the prepolymer method. The prepolymer was obtained by stirring 1,6-hexanediol adipate polyester polyol (0.82 eq), diethylene glycol (0.38 eq), dimethylolpropionic acid (0.48 eq), 1,3-bis(1-isocyanato-1-methylethyl)benzene (2.46 eq), and triethyl amine (0.23 eq) at 85°C for 3 hours. Once the isocyanate content reached approximately 4.3% by titration, the prepolymer was added to water (1.7 × prepolymer wt.) and stirred for 0.5 hours to disperse. Hydrazine (0.083 – 0.022 eq) was added, followed by a specified amount of I or II (0 – 0.65 eq). Note: where specified, some of the dispersions were treated with Desmodur DA (5% by wt. of the dispersion) immediately prior to testing.

Analytical

T-Peel Test

Sheets of PVC (22 cm × 28 cm) coated with test dispersion (#40 Meyer Rod) were dried under ambient conditions and mated to uncoated PVC sheets using hand pressure. The samples were cut into strips (2.5 cm × 15 cm) and heat activated with a Sencorp Systems, Inc. Model 12ASL/1 heat sealer (80°C for 30 seconds, 50 psi (0.34 MPa)). *T*-peel measurements (2.5 cm prepeel, 7.6 cm peel) were made using a Thwing-Albert Model Intellect 500 tester (30.5 cm per minute).

Peel Test (180-Degree)

Sheets of ABS (10 cm × 15 cm) were coated with test dispersion (#40 Meyer Rod) and dried under ambient conditions for ~1 hour. The

ABS sheets were mated to the uncoated vinyl sheets and heat activated at 50°C for 20 seconds at 50 psi (0.34 MPa) using Sencorp Systems, Inc. Model 80811 heat sealer. The vinyl layers of the bonded samples were scored into strips (2.5 cm × 15 cm). Samples were heated to 90°C or conditioned at ambient temperature for 24 hours. Peel measurements were made using an IMASS Inc. Model SP-101B slip/peel tester (5.0 cm per minute for 1 minute).

Gloss Measurements

The aqueous dispersions were drawn down on Gardner Form 7B paint cards using a 40-mil (1 mm) Baker Bar and dried under ambient room conditions for 24 hours. The gloss properties were evaluated using a BYK Chemie Tri Gloss Meter at a 20-degree angle.

RESULTS AND DISCUSSION

The cyanoalkylation/reduction process used produced 87% by weight of the colorless diamine I. C^{13}-NMR analysis indicated that the material was very pure. Purity was 98% by amine-number titration.

Physical property measurements were performed and the values are listed in Table I. Diamine I has negligible vapor pressure and offers to be an environmentally-friendly replacement for the common chain-extender ethylene diamine.

The cyanoalkylation/reduction process produced 53% by weight of the colorless diamine II. Purification of this diamine proved to be more difficult. C^{13}-NMR analysis revealed that the diamine contained

TABLE I Typical physical property values of diamine I

Physical property	*Value*
Viscosity	800 cps
Water Solubility	Complete
pkb(s)	3.8, 6.5
pH 1% solution	10.25
Flash Point (ASTM D-93)	> 450°F (232°C)
Boiling Point at 0.05 torr	160°C
Vapor Pressure at 25°C	0.000004 torr

Note: Diamine I purity > 98%.

approximately 18% of the starting monoamine, *i.e.*, AEI. The presence of the monoamine was taken into account during PUD synthesis.

Diamine I chain extender was incorporated into anionic PUDs at levels of 0.5, 1.0, 3.0, 5.0 and 7.0% by weight of the polymer. The total amount of chain extender added to each PUD was equivalent through appropriate additions of a second chain extender, *i.e.*, hydrazine. The chain extenders consumed 90% of the prepolymer isocyanate functionality in each case. PUDs prepared in this manner had similar number-average molecular weight distributions enabling the adhesion effects of I to be studied. Peel strength of the resulting PUDs were tested on PVC to PVC. Figure 1 shows the effect the incorporated diamine I on the adhesion of a typical anionic PUD.

As demonstrated, 1% or more by weight of the diamine produced a 2-3-fold increase in adhesion. At 5.0 and 7.0% by weight diamine, the corresponding PUDs produced substrate failure in 3 of 5 samples tested. The reported values in Figure 1 at these levels, therefore, are a minimum. The improvements in adhesion were offset somewhat by increases in viscosity. Viscosities for polymers with 1, 3, 5 and 7% by weight diamine I were 1,000 cps, 1,000 cps, 2,600 cps and 3,500 cps (Brookfield Viscometer Model RVT, #4 Spindle @ 10 rpm).

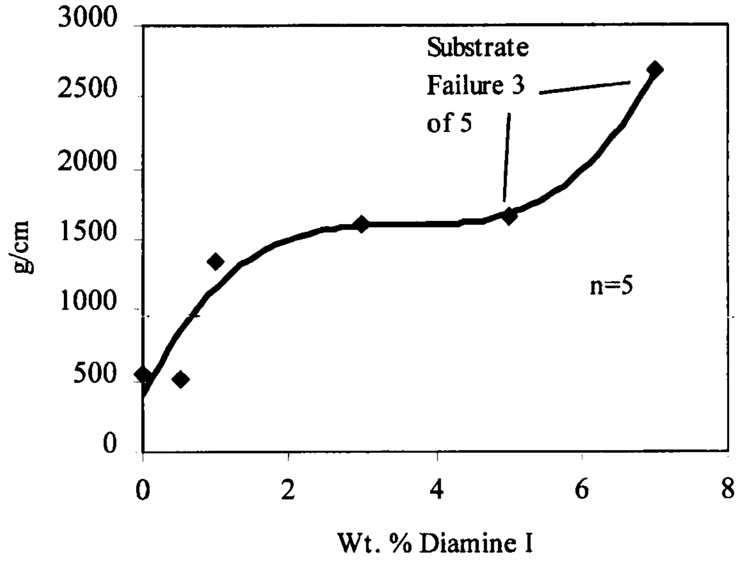

FIGURE 1 Effect of incorporated diamine I on adhesive strength.

To study the effect of imidazolidinones on adhesion heat-resistance, diamine II was incorporated into an anionic PUD polymer at 4% by weight and tested on ABS/vinyl in the presence of Desmodur DA (5% by wt. of dispersion). The data illustrated in Table II shows that the diamine II was able to improve adhesion five-fold at an elevated temperature of 90°C.

The effects of the incorporated diamine I on % gloss were studied for coating applications. Figure 2 is the % gloss of anionic PUDs as a function of the weight % of incorporated diamine I.

A parabolic correlation is apparent and a maximum four-fold % gloss increase was observed around 6% by weight incorporated diamine I.

TABLE II Effect of incorporated diamine II on adhesion at elevated temperatures

Sample	*Substrates*	*Temp.*	*Average 180° Peel strength (g/cm)*
Anionic PUD (Control)	ABS/Vinyl	Ambient	Substrate Failure
Anionic PUD (4% of II by wt.)	ABS/Vinyl	Ambient	Substrate Failure
Anionic PUD (Control)	ABS/Vinyl	90°C	35
Anionic PUD (4% of II by wt.)	ABS/Vinyl	90°C	188

Note: 5% Desmodur DA polyfunctional crosslinker added to each. Heat activation temperature of 50°C for 20 sec @50 psi (0.34 MPa). Bonded samples were conditioned for 24 hrs.

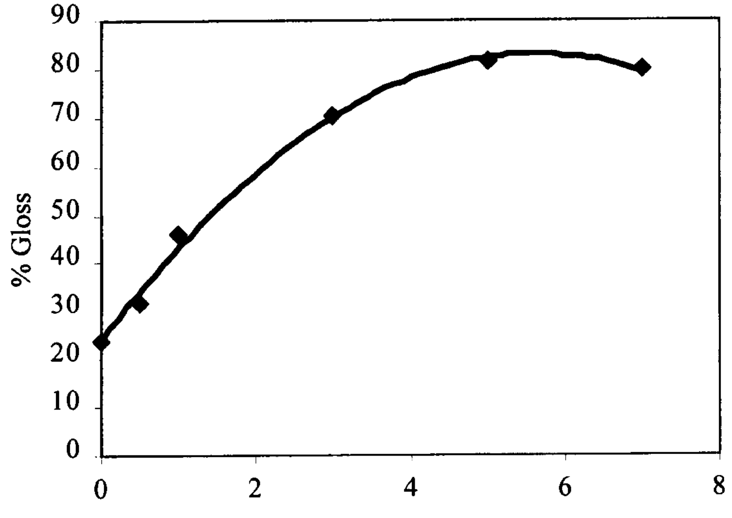

FIGURE 2 % Gloss as a function of incorporated diamine I.

CONCLUSIONS

Imidazolidinone diamines incorporated into anionic polyurethane polymers of aqueous dispersions at levels of 1 – 4% increased PVC to PVC adhesion approximately three-fold. Imidazolidinone functionality can dramatically improve adhesion of ABS to vinyl at elevated temperatures in the presence of the polyfunctional isocyanate as well. The ureido hydrogen of the imidazolidinone group is readily available for hydrogen bonding. The ability of the imidazolidinone group to interact with the substrate, the polymeric network of the cured polyfunctional isocyanate, and the adhesive base polymer through hydrogen bonding as well as dipole – dipole attractions seems responsible for the improved adhesion. Gloss improvements of polyurethane coatings correlate well to levels of incorporated diamine.

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