Oil Modified and Waterborne Polyurethane Resin

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Air-dried water-dispersed polyurethane resins were produced from poly(propylene-ethylene) copolymer triol, monoglyceride, toluene diisocyanate, and tartaric acid. Monoglyceride and poly(propylene-ethylene) copolymer triol were employed at different ratios, with the monoglyceride ranging between 50-70% of the total polyol used, and the isocyanate/hydroxyl ratio was kept at 1.82. Some surfaces showed heavy wrinkling when the monoglyceride was below 54.5% and above 60%, yet clear and unwrinkled surfaces occurred when the monoglyceride fell between 54.5-60%. The hardness values increased as the percentage of monoglyceride increased. Hardness, impact, adhesion, bending, and abrasion tests were applied and the samples passed each test. All exhibited very good flexibility and toughness.

INTRODUCTION

Ecological and economical pressures have stimulated interest in water-dispersed and waterborne paints. The increasing cost of solvents as well as restrictions on solvent emissions are forcing the paint industry to produce water-dispersed paints.[1,2]

The history of water-reducible resins is not new. Waterborne alkyds in solubilized and dispersed forms were introduced in the early 1950s. To impart solubility, the alkyd resin was produced at a high acidic number. The use of maleinized oils improved solubility but introduced a complex molecular structure that yielded poor control over the reaction.[3] The use of polyether polyol introduced hydrophilic groups on the backbone, but this makes the film water sensitive. The use of polyethylene and polybutylene glycol at appropriate ratios may help to balance the hydrophilic and hydrophobic properties at the desired level. The alkyd resins may also be made water-reducible by mixing a normally synthesized resin with a special alkyd that contains high acidic groups. This second alkyd can be prepared by reacting the resin with an anhydride of high functionality, such as trimellitic anhydride. The styrenated alkyd may be made water-reducible by using hydrophilic monomers such as acrylic acid or methacrylic acid as comonomers in the system.[3] Research on waterborne alkyds and polyesters has been an active subject in the paint industry and new patents demonstrate the use of different raw materials and techniques.[4-7] Water-dispersed acrylic resins and water-dispersed polyurethanes are two fundamental categories in the literature where most of the research has been done.

Although water-dispersed systems are not considered toxic, they do require careful selection of binders (e.g., resins) and additives such as biocides, cosolvents and coalescing agents, driers, neutralizing bases, etc., in order to avoid any toxicity caused by these components.[8] The main advantage of water-dispersed paints is to reduce the amount of volatile organic emissions. Although they display excellent performance in many areas of application, they lack tensile strength, abrasion resistance, chemical resistance, and general durability.[9] The research on waterborne paints covers a very wide range from the synthesis to characterization of resins produced from different raw materials.[10-13] During this research, polyurethanes were modified with monoglycerides to impart rigidity through air-drying. Polyurethanes are one of the most extensive and versatile classes of polymers. This is due to the rich choice and abundance of starting materials. Polyurethane paints are used primarily in the automotive industry and have undergone many research and development studies in the last few years with regard to dry paint quality and environmental aspects.

Water dispersion of polyurethanes is generally obtained by the insertion of ionic sites into the backbone of the prepolymer. Anionic dispersions result from inserting a carboxyl function, whereas cationic dispersions result from introducing tertiary amine groups into the backbone of the prepolymer. The carboxylic groups are usually neutralized by tertiary amines in anionic dispersions, while in cationic dispersions tertiary amines are neutralized with an acid or are quaternized with alkyl halides. The resulting prepolymer is then chain-extended with diamines to obtain higher molecular weight polymers.

The remarkable physical properties of most polyurethanes are based on the segmental primary structure that contains a "soft" segment, which is usually a polyester or polyether macrodiol, and a "hard" segment, which consists of an oligourethane unit or an (oligo-)urea unit built up from diisocyanates, and short chain diols or diamines or water. Thus, segmental polyurethane is built up of at least three components.

Soft segments and hard segments differ in polarity, compatibility, and interchain interaction, which, in turn, affect hardness and flexibility. In a typical thermoplastic polyurethane elastomer, the soft segment is more than 50% by weight and forms a continuous matrix. The microdomains of hard segments

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Table 1—Formulations of Resins

Sample	MG (%)	MG (mole)	Polyol (mole)	TDI (mole)	TA (mole)	MEKO (mole)	TEA (mole)	EDA (mole)
1	50.00	0.700	0.700	5	1.000	3	2.000	1.5
2	53.33	0.800	0.700	5	0.900	3	1.800	1.5
3	54.50	0.876	0.876	5	0.386	3	0.772	1.5
4	56.25	0.700	0.700	5	0.800	3	1.600	1.5
5	57.00	0.670	0.670	5	0.855	3	1.710	1.5
6	60.00	0.700	0.700	5	0.650	3	1.300	1.5
7	62.50	0.630	0.630	5	0.775	3	1.550	1.5
8	63.50	0.680	0.680	5	0.580	3	1.060	1.5
9	70.00	0.600	0.600	5	0.450	3	0.900	1.5

have high cohesion. They represent physical crosslinking sites, which reversibly disappear at the melting temperature of the hard segment domains.[14]

Polyurethanes used in the paint industry must display sufficient rigidity after being spread on a surface. For this reason, most water-dispersed polyurethanes are made by using polyesters. Polyethers impart high flexibility but are preferably used when hydrolysis resistance is required. In this work, monoglycerides were inserted into the backbone to improve rigidity since double bonds of fatty acid residues form crosslinks by picking up oxygen from air. Fatty acid residues also impart superior alkyd resins properties to polyurethanes.

The second goal of this work was to use inexpensive raw materials available in the market. It was shown in an earlier work that tartaric acid, which is largely available in the market, could be used instead of dimethylol propionic acid. However, tartaric acid causes branching on the backbone.[15] The final polymer will have a network structure because it has fatty acid residues. Therefore, branching caused by tartaric acid is not a problem for the polymer synthesized. The excess rigidity caused in the final product by fatty acids can be compensated for by using a polyether-based polyol rather than a polyester-based polyol. Polyethers are more durable in hydrolysis than polyesters, and they show chemical resistance against hydrolysis in water-dispersed paints.

EXPERIMENTS

Preparation of Resin

Water susceptible materials were dehydrated. Poly(propylene-ethylene) triol (functionality=2.9, molecular weight=3066, source: AKSAN A.S.) used as the polyol was dehydrated at 120°C in an oven by passing nitrogen gas through it for 24 hr. Methyl ethyl ketone (MEK, source: Delta Kimya) and methyl ethyl ketoxime (MEKO, source: Volkan Boya) were each dehydrated over molecular sieves. L-tartaric acid (TA, source: Merck A.G.) was dehydrated in a heated oven at 120°C for two hours. Other materials were used as received. Toluene diisocyanate (TDI, source: ISBIR A.S.) was used as the diisocyanate to make polyurethane. Acid groups were neutralized by using triethyl amine (TEA, source: CBS A.S.), and the chain-extension was made using ethylene diamine (EDA, source: Merck A.G.).

Monoglyceride was obtained from the alcoholysis of sunflower oil. It was synthesized by mixing one mole of oil with two moles of glycerol and heating the mixture at 245-260°C under nitrogen atmosphere. Lithium hydroxide can be used as a catalyst at 0.02% of the total material. The reaction lasted about three hours, and the methanol test was used to determine the end of the reaction. A bright noncloudy solution is a sign of the end of the reaction. The transesterification reaction does not yield pure monoglyceride; the product may contain small amounts of diglycerides and unreacted glycerine. The small amounts of glycerine were removed with water, otherwise they would have caused gelation while forming polyurethane. The monoglyceride was then dried under a vacuum at 90°C for 24 hr to remove the water.

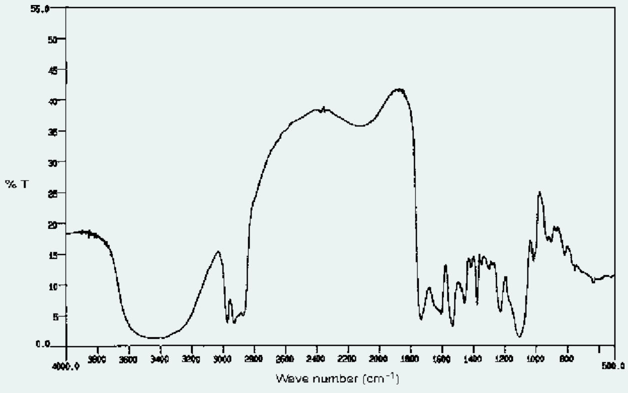

Figure 1—IR spectrum of resin (57% MG)

The experiments were carried out in a five-neck glass flask of 500 ml volume equipped with a mechanical stirrer, condenser, thermometer, and an inlet and outlet for dry nitrogen gas. The reaction was carried out in a constant temperature water bath. The basic formulations of the feed are given in *Table* 1.

The following procedure was carried out for the production of waterborne polyurethane paints.

(1) The polyol, the monoglyceride (MG), and the tartaric acid were dispersed in MEK and were used as a cosolvent (50/50 w/w) by stirring at 70°C under N_2 atmosphere for 30 min to obtain a homogeneous mixture, which is important for the equal distribution of the hydrophilic monomer (i.e., tartaric acid) on the polymer backbone. Tartaric acid was dispersed in MEK. After the addition of MG and polyol all materials dissolved in MEK.

(2) TDI was added to the homogenized mixture and the reaction was allowed to proceed for three hours at 70°C. In the meantime, the reactor was mechanically stirred. The duration of the reaction was determined by the di-butylamine back titration method in which the unreacted NCO groups were observed. Isocyanate/hydroxyl molar ratio was kept at 1.82.

(3) After the completion of the previously mentioned reaction the prepolymer was cooled to 50°C, and the free isocyanate (NCO) groups, if there were any, were blocked with MEKO for approximately two hours.

(4) To neutralize the carboxyl (COOH) groups, TEA was added to the solution for 30 min at 50°C.

(5) Water was added to the solution in an amount equal to 50% of the total

mass from a stopcock burette. The water was added one drop at a time every two or three seconds under agitation of the mixture to get a water-dispersed resin.

(6) EDA was added at room temperature as a chain-extender at half mole of unreacted NCO group just before the application of the resin on a surface.

(7) Metallic driers were added at an amount of 0.4% of the fatty acid residues present in the resin.

Tests

For the stability test, the resins were kept at room temperature for two months. No significant thickening took place during this period. The preliminary experiments showed that the resins synthesized from monoglyceride, which contains small amounts of glycerine, caused delayed gelation.

The IR analysis was made using a Perkin-Elmer (Model: 19PC) FTIR spectrophotometer.

Test panels used for physical and mechanical tests were coated with 50 μm wet film. They were air-dried for one day, and then heated at 125°C in an oven for three hours. Air-drying provided crosslinking between fatty acid residues. In oven heating, MEKO is removed first, and the free isocyanate groups thus generated cause crosslinking reactions, possibly with –NH– groups on the backbone.

RESULTS AND DISCUSSIONS

Preliminary Experiments

The initial goal of this research was to produce water-dispersed, air-dried polyurethane resins using toluene diisocyanate and monoglyceride. However, several attempts to achieve such a resin failed. The polymer gelated easily, possibly due to the abundance of unsaturated fatty acid chains which were polymerizing at close proximity. So, monoglyceride was diluted with a reactive polyol. Resins with monoglyceride (MG) percentages above 70% in an MG plus polyol mixture were very viscous and sticky. Therefore, lower percentages of MG were used.

Infrared Analysis

The IR spectra of MG, polyol, tartaric acid, TDI, and the product were examined to determine the extent of reaction. The IR spectrum of sample 6 given in *Table* 1 is shown in *Figure* 1.

Figure 1 shows that the sample has low OH which might be due in part to the water that was absorbed. The cyanate group of TDI has a characteristic peak at 2250 cm^{-1}. It does not appear in *Figure* 1, indicating that no free isocyanate groups were left in the polymer.

Surface Appearance

The cured film was yellowish and transparent. Although MEK and EDA can react and yield a dark colored film, there was no indication of such a reaction. In fact, blocking the resin with MEKO and adding EDA at the last minute minimizes the possibility of such a reaction.

The surface appearance of the coated panels was interesting. Some samples showed heavy wrinkling. This wrinkling is sometimes a desired property and the polymer chain must be specially designed to exhibit this property. In industrial coatings, the short alkyd–phenol formaldehyde resins are specially formulated to achieve wrinkled surfaces. In this work, the nonwrinkling range was quite narrow, between 54.5–60% MG. *Table* 2 shows the wrinkling properties of samples.

The physical aspects and the theoretical investigation of the wrinkling mechanism for the polymers produced needs to be investigated in a future work.

Here, film drying took place via two mechanisms: (1) physical, and (2) chemical. Most waterborne paints or resins studied in the past dry through physical processes. In physical drying, the particles get closer to each other, and they coalesce and form paint films after the evaporation of water.

This physical mechanism also took place in this work. In addition, there also was chemical drying. The metallic driers cause the formation of a network structure between fatty acid residues. The metallic naphthanates accelerate the reaction between atmospheric oxygen and unsaturated bonds of fatty acid residues. The resins produced in this work were dried with and without driers. The metallic driers caused much faster drying, as was expected.

Hardness

The hardness of the wrinkled surfaces could not be measured by the pendulum hardness test, which is based on the swing of a pendulum. Hardness in Persoz vs. percentage MG for clear and unwrinkled surfaces is shown in *Figure* 2. Hardness increases as the percentage of MG increases. The maximum hardness was obtained at 69 Persoz and 57% MG. The hardness then declined as the amount of MG increased further. We concluded that after a certain MG percentage, the properties started to decline. This must be due to the increase of wrinkling after about 60% MG. There was no visual wrinkling on the 60% MG sample; the pendulum probably detected the start of wrinkling.

Other Tests

All samples were tested for their impact strengths according to ASTM D 2794. No cracks were observed on the film surfaces and they all showed an impact resistance above 20 J, which is the maximum limit of the impact device. The resin surface exhibited very good toughness.

All samples passed the mandrel bending test conducted according to ASTM D 522. No cracks after bending were observed on the coated test panels.

Samples tested for their abrasion resistance showed no significant loss of film thickness. The test was done according to ASTM D 968, and the loss was only 1.20%.

The adhesion test was carried out by using a cross-hatch cutter, and was performed as described in ASTM D 3359. All samples met the maximum adhesion number.

CONCLUSIONS

(1) A mixture of monoglyceride and poly(propylene-ethylene) copolymer triol with a monoglyceride percentage ranging between 50 and 70, when reacted with toluene diisocyanate and tartaric acid, produced a waterborne resin that can be air-dried.

(2) The IR spectrum in *Figure* 1 shows that there are no excess isocyanate groups in the mixture.

Table 2—Surface Appearance of the Coated Panels

Sample Number	MG %	Wrinkling	No Wrinkling	Semi-Wrinkling
1	50.00	X	—	—
2	53.33	X	—	—
3	54.50	—	X	—
4	56.25	—	X	—
5	57.00	—	X	—
6	60.00	—	X	—
7	62.50	—	—	X
8	65.00	X	—	—
9	70.00	X	—	—

(3) Clear and unwrinkled surfaces could be achieved when 54.5–60% monoglyceride was used in the total polyols (MG plus poly(propylene-ethylene) copolymer triol). Wrinkled surfaces appeared both below and above these percentages.

(4) Of the clear and unwrinkled surfaces, the resin with 57% MG showed the highest hardness value.

(5) Samples tested for impact resistance rated above 20 J. In mandrel bending there were no cracks observed on the surfaces of the samples tested. The abrasion loss was 1.20%. All samples met the highest adhesion number.

(6) When considering all the properties, the mixture containing 57% MG in the total polyols produces the best resin.

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