Synthesis and Properties of UV-Curable Waterborne Unsaturated Polyester for Wood Coating

SOON-JOON JUNG,[1] SANG-JIN LEE,[2] WON-JEI CHO,[1] CHANG-SIK HA[1]

[1] Department of Polymer Science and Engineering, Pusan National University, Pusan 609-735, Korea

[2] Research Institute of Industrial Technology, Pusan National University, Pusan 609-735, Korea

ABSTRACT: UV-curable waterborne unsaturated polyesters for wood coatings were prepared. The effects of different polyols and acids on the properties of the UV-curable waterborne unsaturated polyesters were investigated. Several different unsaturated polyester prepolymers were prepared from three different polyols [ethylene glycol (EG), diethylene glycol (DEG), and propylene glycol (PG)] and three different acids [tetrahydrophthalic anhydride (THPAn), terephthalic acid (TPA), and trimellic anhydride (TMAn)]. UV-curable coating materials were formulated from the prepolymers and 2-hydroxy-2-methylphenyolpropane-1-one as a photoinitiator with distilled water as a diluent. Trimethylolpropane diallyl ether was used as an air inhibitor of cure. The dynamic mechanical studies showed the properties of those unsaturated polyesters were well correlated with their glass transition temperature behaviors. It was found that the unsaturated polyester prepared with 60/40 (mol %) TMAn/THPAn and the equimolar mixture of EG, DEG, and PG showed balanced coating properties such as good tensile properties and weatherability, as well as proper viscosity (ca. 2500 cps) when using distilled water as a diluent. © 1998 John Wiley & Sons, Inc. J Appl Polym Sci 69: 695–708, 1998

Key words: UV-curable coating; waterborne coating; unsaturated polyester; wood coating

INTRODUCTION

Unsaturated polyester has been widely applied as one of several polymeric coating materials in furniture and wood finishing, especially after radiation curing, because of its high gloss, fast cure characteristics, hardness, and impact resistance.[1] In general, the use of radiation coating, particularly a UV-curable coating, has attracted much interest because of its fast cure speed and energy saving characteristics, in spite of its relatively high expense over a thermal cured coating.[2–9] The UV-curable coating is particularly important in unsaturated polyesters because one of the major drawbacks of the unsaturated polyesters is that their polymerization is greatly inhibited by oxygen and the oxygen-reactive species.[10] The oxygen inhibition effect in polymerization is most pronounced in UV curing coatings owing to the high surface/volume ratio, which allows optimal oxygen diffusion into the coating film.[11]

Reactive monomers such as styrene are used as diluents to dictate the final properties in the formulation of the unsaturated polyester coating materials. There has been growing concern over the toxicity of the reactive monomers in the environment. Alternative monomers to solve the ecological problems, such as vinyl toluene, vinyl

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acetate, allyl ethers, and so on, have been attempted.[11] In some cases, solvents such as xylene have replaced styrene. However, such volatile organic compounds (VOCs) produce environmental problems intrinsically. Waterborne coatings have been increasingly used to reduce such airborne pollution from solvents and reactive monomers, along with other technologies such as high solids and powder coating, as well as radiation curing.[12]

In this work, UV-curable waterborne unsaturated polyesters for wood finishing were prepared. Several polyols and acids with different functionalities were tested to prepare the unsaturated polyesters and to investigate the properties of the prepolymers and final coating films after UV curing.

EXPERIMENTAL

Materials

Table I lists the materials and their chemical formulas used in this work. The materials were all commercially available grades and were used as received. Trimethylolpropane diallyl ether (TMPDAE, Perstorp Chem.) was used as the inhibitor of cure. The difunctional polyols used included diethylene glycol (DEG, Hyundai Petrochem.), ethylene glycol (EG, Hyundai Petrochem.), and propylene glycol (PG, Yukong Ltd.). For acids, difunctional fumaric acid (FA, Daenong Petrochem.), tetrahydrophthalic anhydride (THPAn, Daenong Petrochem.) as an unsaturated acid, and difunctional saturated acids terephthalic acid (TPA, Samsung Petrochem.) and trimellitic anhydride (TMAn, Tokyo Chem.) were tested. Hydroquinone (HQ, Aldrich) was used as an inhibitor of polymerization. 2-Hydroxy-2-methylphenyl propane-1-one (Darocur 1173, Ciba–Geigy) was used as a photoinitiator. Dibutyl tin oxide (Daenong Petrochem.) was used as a catalyst. Distilled water was used as a diluent. For waterborne coating, triethylene amine (TEA, Samsung Petrochem.) was used to neutralize the unreacted carboxylic acid.

Syntheses of Unsaturated Polyester Prepolymers

Two different preparation routes were applied to investigate the effects of acid kinds and contents. First, the polyesters using TMAn and THPAn with different mole ratios were synthesized by the type I route.

Initially, a given amount of solid bifunctional FA and THPAn was mixed with an excess of either of DEG, PG, EG or their equimolar ternary mixtures in the presence of 1 wt % HQ as an inhibitor at 80°C in 1 L of a five-necked flask. The mixture was heated to 195–200°C with a heating rate of 20°C/h to prevent the loss of polyols until the acid value of the product reached 60 mg KOH/g, followed by cooling product 1 to about 100°C. Then, the solid TMAn was added to product 1 and heated to 145–150°C. When the acid value reached 150–160 mg KOH/g, the reactant was cooled to 130°C. The water-insoluble unsaturated polyester, product 3, was obtained by adding TMPDAE to the viscous product 2. The structure of each product was identified by ^{1}H-NMR spectroscopy. Finally, product 3 was transformed to the waterborne coating material, product 4, by dropping TEA and water sequentially at 80°C.

The polyesters from TMAn and TPA were prepared by Type II procedures similar to type I, except that TPA was reacted with polyols with dibutyl tin oxide as a catalyst first and then fumaric acid was reacted with polyols because of the low reactivity of TPA. The reaction to obtain product 1 was performed at 230°C until the acid value reached about 1 mg KOH/g. The other procedure is just the same as type I. The type I and type II preparation routes are schematically illustrated in Figure 1.
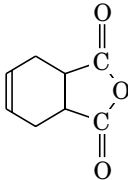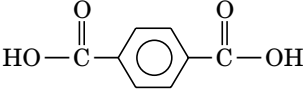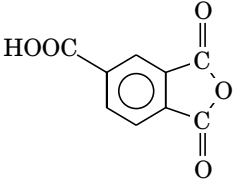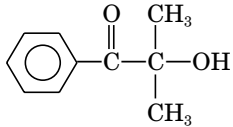
UV Curing

The final UV-cured unsaturated polyesters were prepared by casting the above formulated product onto a glass plate at room temperature, followed by drying the films under a vacuum at 60°C until reaching a constant weight. The dried films were cured using a medium pressure mercury lamp (80 W/cm, 6.3 Å). Radiation curing was carried out with a UV light of 365-nm wavelength. The thickness of the cast coating film was about 300 μm.

Measurements

IR Spectra

IR spectra of unsaturated polyester prepolymers before and after UV irradiation were taken to compare the degree of cure with a Fourier transform infrared spectra (Bio-Rad FTS-165) using a KBr pellet.

Table 1 Chemical Formulas of Materials Used in This Work

	Materials	Chemical Structures
Acid	Fumaric Acid	HOOC—CH=CH—COOH
	Tetrahydrophthalic anhydride	
	Terephthalic acid	
	Trimellitic anhydride	
Alcohol	Ethylene glycol	HO—CH_2—CH_2—OH
	Diethylene glycol	HO—CH_2—CH_2—O—CH_2—CH_2—OH
	Propylene glycol	HO—CH_2—CH—OH $\quad$ CH_3
	Trimethylolpropane diallyl ether	
Neutralizer	Triethylene amine	
Photoinitiator	2-Hydroxy-2-methylphenylpropane-1-one	

Gel Content

The sample films of 0.2-mm thickness were cured under various curing times and were refluxed in toluene at room temperature for 24 h. When sorption reached equilibrium, the samples were rapidly removed from the solvent, wiped with filter paper to remove the surface droplets, and then weighed to the nearest 0.1 mg. The gel content of the samples was determined from the difference in weight before and after the extraction experiment as follows:

$$\text{gel content } (\%) = w/w_0 \times 100$$

where w_0 and w are sample weights before and after extraction, respectively. Several runs were made for each sample, and average values were taken.
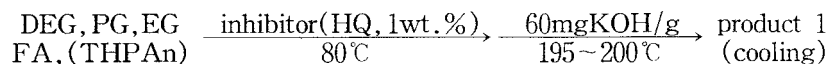
Dynamic Mechanical Properties

The dynamic mechanical properties were obtained on a Rheovibron DDV-II (Toyo Baldwin Co.) with a heating rate of 2°C/min over a temper-
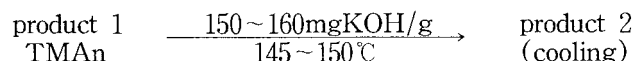
TYPE I.

	0.5mol / 0
TMAn/THPAn	0.4mol / 0.1mol
	0.3mol / 0.2mol
	0.2mol / 0.3mol

1st step.

$$\text{DEG, PG, EG} \atop \text{FA, (THPAn)} \xrightarrow[80\,℃]{\text{inhibitor(HQ, 1wt.%)}} \xrightarrow[195\sim200\,℃]{60\text{mgKOH/g}} {\text{product 1} \atop \text{(cooling)}}$$

2nd step.

$$\text{product 1} \atop \text{TMAn} \xrightarrow[145\sim150\,℃]{150\sim160\text{mgKOH/g}} {\text{product 2} \atop \text{(cooling)}}$$

3rd step.

$$\text{product 2} \atop \text{TMPDAE} \xrightarrow[180/190\,℃]{45\sim50\text{mgKOH/g}} {\text{product 3} \atop \text{(cooling)}}$$

4th step.

$$\text{product 3} \xrightarrow[\text{at } 80\,℃]{\text{TEA}} \xrightarrow{H_2O(50wt\%)} {\text{product 4} \atop \text{(work -up)}}$$
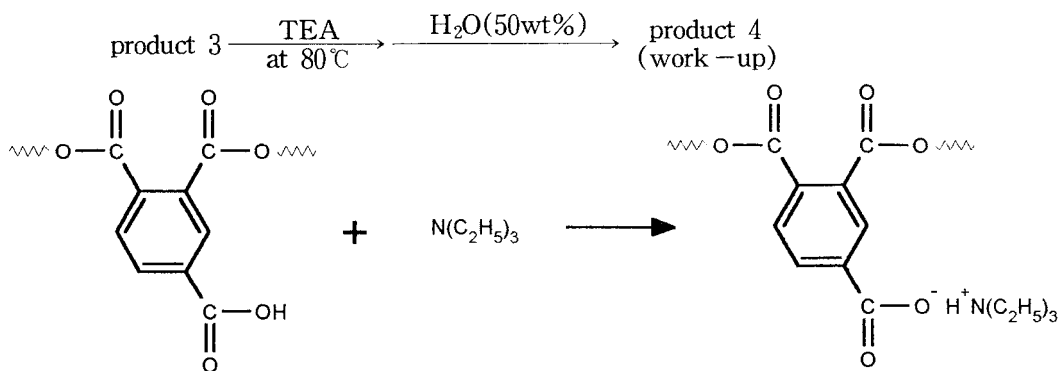

Neutralization of the polyester resin

Figure 1 The schematic illustration of type I and type II preparation routes of the UV-curable waterborne unsaturated polyesters.

ature range of $-60-100°C$. Rectangular test specimens (0.3 mm thick × 4 mm wide × 25 mm long) were prepared. The measured frequency range was 35 Hz.

Contact Angle

The static contact angle of water onto the surface of the coating film samples was measured by a Kyowa contact angle meter.

Tensile Test

Tensile tests were performed on a tensile tester (Instron 4204) at a crosshead speed of 2 mm/min according to the ASTM D-1822 method. The thickness of the samples was 300 μm.

Viscosity

The viscosity of the samples dispersed in water was measured with a Brookfield viscometer (model HAT) at 25°C.
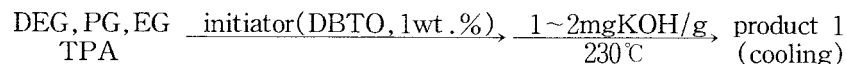
Weatherability

The accelerated weatherability was measured at 25°C by exposing sample films to UV radiation
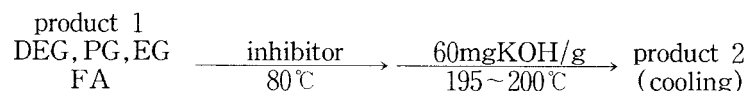
Type II.

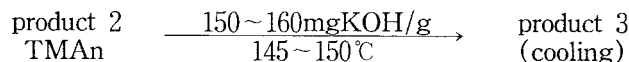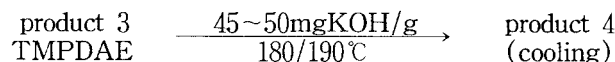| TMAn/TPA | 0.5mol / 0 |
	0.4mol / 0.1mol
	0.3mol / 0.2mol
	0.2mol / 0.3mol

1st step.

$$\text{DEG,PG,EG} \atop \text{TPA} \xrightarrow{\text{initiator(DBTO,1wt.\%)}} \xrightarrow[230°C]{1\sim 2\text{mgKOH/g}} \text{product 1} \atop \text{(cooling)}$$

2nd step.

$$\text{product 1} \atop \text{DEG,PG,EG} \atop \text{FA} \xrightarrow[80°C]{\text{inhibitor}} \xrightarrow[195\sim 200°C]{60\text{mgKOH/g}} \text{product 2} \atop \text{(cooling)}$$

3rd step.

$$\text{product 2} \atop \text{TMAn} \xrightarrow[145\sim 150°C]{150\sim 160\text{mgKOH/g}} \text{product 3} \atop \text{(cooling)}$$

4th step.

$$\text{product 3} \atop \text{TMPDAE} \xrightarrow[180/190°C]{45\sim 50\text{mgKOH/g}} \text{product 4} \atop \text{(cooling)}$$

5th step.

$$\text{product 4} \xrightarrow[\text{at } 80°C]{\text{TEA}} \xrightarrow{\text{H}_2\text{O(50wt\%)}} \text{product 5} \atop \text{(work -up)}$$
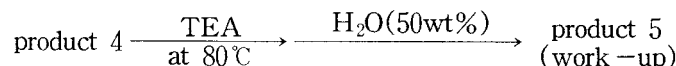
Figure 1 *(Continued from the previous page)*

(80 W/cm × 2 lamps × 5 m/min) for a given time from 0 to 100 s. Details of the measurement are described elsewhere.[8] The films were 300 μm thick. The color differences (ΔE) of the samples after exposing them to UV for a given time were measured with an Applied Color Systems ACS-3300.

RESULTS AND DISCUSSION

Curing Evaluation

Several unsaturated polyester oligomers were synthesized. The composition and properties of the prepolymers are summarized in Tables II and III. Details of the result will be discussed in the proper section.

The curing of the unsaturated polyester prepolymers was analyzed by FTIR. Figure 2 shows a typical IR spectrum of unsaturated polyester prepolymer before and after UV irradiation for 3 to 9 s. The unsaturated polyester prepolymer was identified by the characteristic peaks around 1720 cm^{-1} (C=O) and 810 and 1636 cm^{-1} (C=C). The unsaturated polyester had C=C absorption bands at 810 and 1636 cm^{-1} before UV irradiation, but the band disappeared with time and was no longer detectable after irradiation for 9 s. The characteristic C=C absorption of unsaturated polyester at 810 and 1636 cm^{-1} was used to determine the extent of photopolymerization. The re-

Table II   Composition, Viscosity, Contact Angle, and T_g of Unsaturated Polyesters with Different Polyols

Composition	H_2O (wt %)	η (cps) at 25°C	Contact Angle (θ)	T_g (°C)
DEG (33%)/PG (33%)/EG (33%)	0	175000	—	—
DEG (33%)/PG (33%)/EG (33%)	10	62600	—	—
DEG (33%)/PG (33%)/EG (33%)	20	28500	—	—
DEG (33%)/PG (33%)/EG (33%)	30	13800	—	—
DEG (33%)/PG (33%)/EG (33%)	40	7700	—	—
DEG (33%)/PG (33%)/EG (33%)	50	4000	81.5	46
DEG (100%)/PG (0%)/EG (0%)	50	960	74	26
DEG (0%)/PG (100%)/EG (0%)	50	28640	84	47
DEG (0%)/PG (0%)/EG (100%)	50	5840	82.5	56
DEG (33%)/PG (33%)/EG (33%)	50	4000	81.5	46

TMAn (100%) was used as the acid, and water was used as the diluent.

sult in Figure 2 indicates that radiation curing had been completed after 9 s.

The degree of cure of the unsaturated polyester prepolymers after exposure to UV was also measured in terms of gel content. It was found that there were dramatic increases in gel content up to 85% within 3.0 s, but thereafter there were very small gains in gel contents with further increasing time. The gel content could reach about 90% after 12 s, regardless of the types and contents of the polyols or the acids used in this work. It is generally accepted that a gel content of 90–95% indicates a complete cure of the coatings on the wood or floor.[1]

Dynamic Mechanical Behavior and General Properties

Effect of Polyols

The viscosity change with rotation speed for the unsaturated polyester prepolymers of three differ-

Table III   Composition, Viscosity, Contact Angle, and T_g of Unsaturated Polyesters with Acids TMAn/THPAn and TMAn/TPA

Composition	H_2O (wt %)	η (cps) at 25°C	Contact Angle (θ)	T_g (°C)
TMAn (60%)/THPAn (40%)	0	132,800	—	—
TMAn (60%)/THPAn (40%)	10	43,000	—	—
TMAn (60%)/THPAn (40%)	20	19,500	—	—
TMAn (60%)/THPAn (40%)	30	10,000	—	—
TMAn (60%)/THPAn (40%)	40	6,040	—	—
TMAn (60%)/THPAn (40%)	50	2,520	73	41
TMAn (60%)/TPA (40%)	0	444,800	—	—
TMAn (60%)/TPA (40%)	10	143,900	—	—
TMAn (60%)/TPA (40%)	20	65,500	—	—
TMAn (60%)/TPA (40%)	30	43,700	—	—
TMAn (60%)/TPA (40%)	40	23,750	—	—
TMAn (60%)/TPA (40%)	50	13,300	79	79
TMAn (100%)/THPAn (0%)	50	4,000	81.5	46
TMAn (80%)/THPAn (20%)	50	3,300	79	43
TMAn (60%)/THPAn (40%)	50	2,500	73	41
TMAn (40%)/THPAn (60%)	50	1,850	70	37
TMAn (100%)/TPA (0%)	50	4,000	81.5	46
TMAn (80%)/TPA (20%)	50	8,500	81.5	60
TMAn (60%)/TPA (40%)	50	13,300	79	79
TMAn (40%)/TPA (60%)	50	24,000	77.5	90

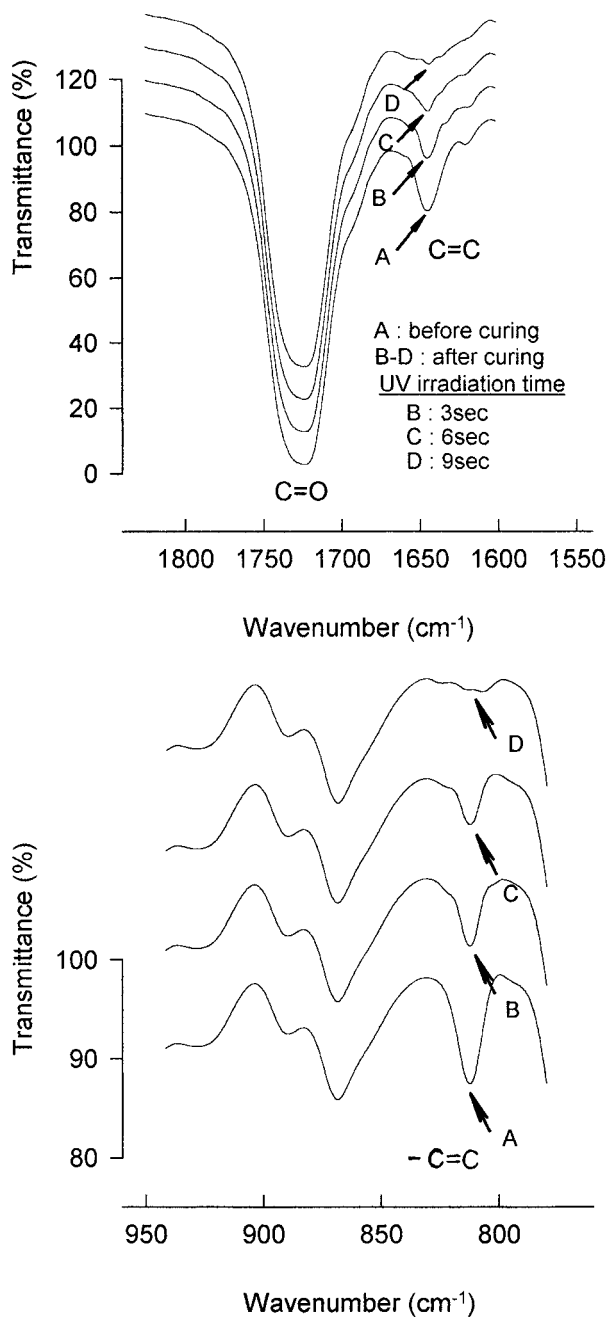DEG (33%)/PG (33%)/EG (33%) was used for the polyol and water was used as the diluent.

ure 4, prove that the DEG-based system is more hydrophilic than the EG- or PG-based system. The viscosity of the unsaturated polyester prepolymers consisting of different polyols at room temperature was higher in the order PG > EG > DEG. Figure 3 also shows the viscosity change of the DEG/PG/EG equimolar mixture based unsaturated polyester coating system dispersed in water as a function of rotation speed.

In general, the processability of the coating was better but the stable coating film-forming properties, as well as the mechanical strength of the films, was worse because the viscosity of the diluted coating system was lower. The PG-based unsaturated polyester showed too high viscosity, the DEG-based one exhibited too low viscosity, and the EG-based one or the DEG/PG/EG equimolar ternary mixture based one exhibited proper viscosity values for coatings. However, the lifetime of the final coating system using EG as a polyol was the worst due to its stronger structural stability than DEG and PG. Because no single polyol satisfied the viscosity, the film-forming property, and the lifetime, several mixtures were
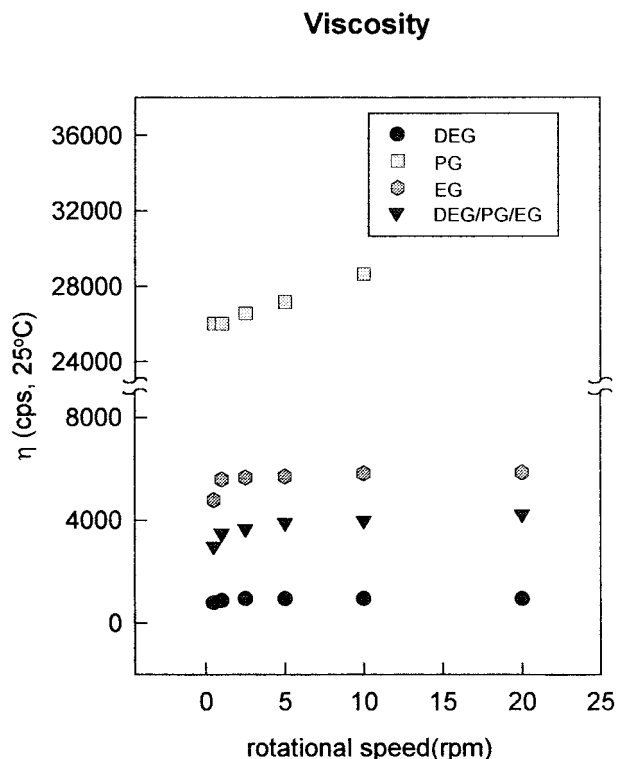

Figure 2 Infrared spectra of unsaturated polyester before and after UV curing.

ent polyols with 50 wt % water as a diluent are shown in Figure 3 (see also Table II). TMAn was used as the acid to investigate the effect of polyols on the properties of the unsaturated polyesters, unless otherwise specified. The DEG-based unsaturated polyester showed the lowest viscosity of any of the polyol-based unsaturated polyester prepolymers. The contact angle results, shown in Fig-

Viscosity

Figure 3 Viscosity change at 25°C as a function of rotational speed in a Brookfield viscometer for unsaturated polyesters with different polyols. Water was used as the diluent.
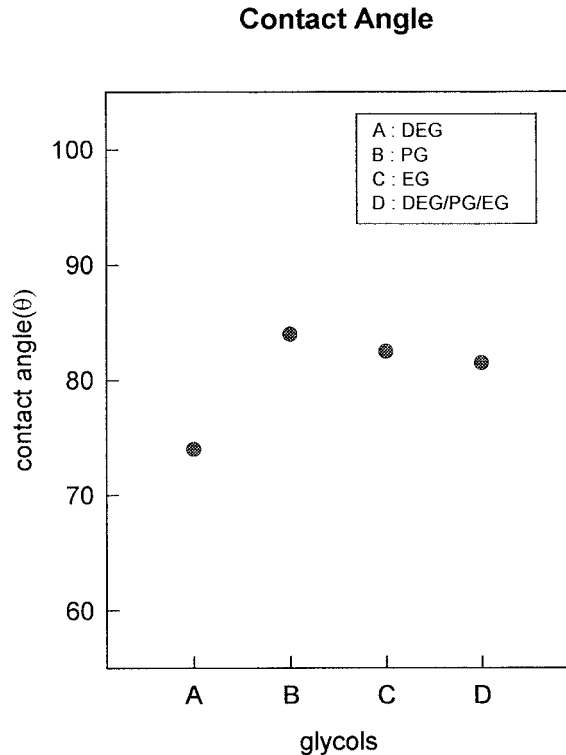
Contact Angle

Figure 4 Contact angles of final UV-cured coating films of unsaturated polyesters with different polyols. TMAn (100%) was used as an acid.

tested. As a result, our previous analyses showed that the unsaturated polyester formulated with an equimolar mixture of DEG, PG, and EG exhibited balanced properties and processability.

Figure 5 shows the tensile properties of the crosscut films of the coating for the unsaturated polyester prepolymers from different polyols. DEG-based unsaturated polyester prepolymers exhibited the lowest tensile strength and modulus among the three different polyol prepolymers, which may be expected from the lower viscosity than any other polyol-based unsaturated polyester prepolymers (Fig. 3). The lowest elongation at break for the DEG-based system was also due to the poor structural stability coming from the low bond energy and high chain scission of DEG by water during storage because of its strong hydrophilicity. It was also seen that the PG-based unsaturated polyester showed the highest tensile
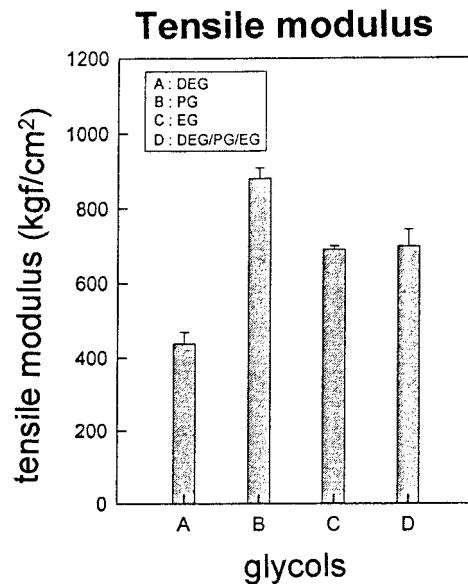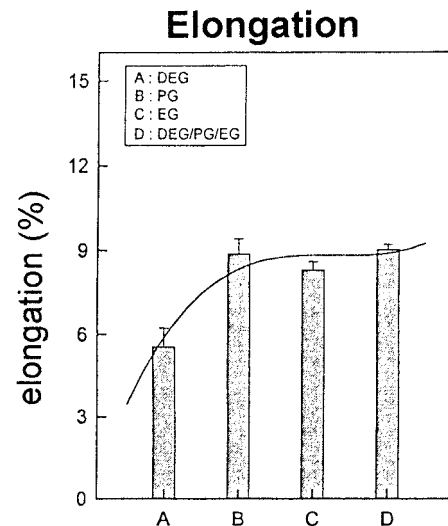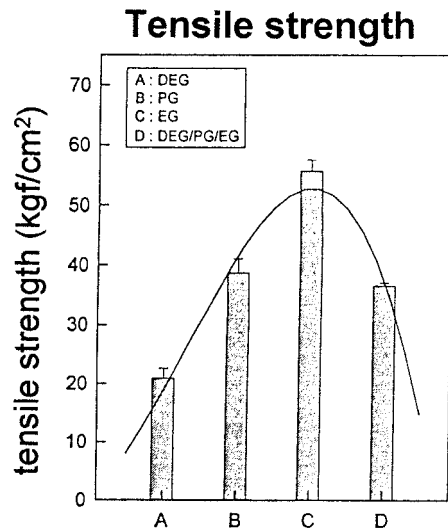
Figure 5 Tensile properties (strength, elongation, and modulus) of the crosscut film of UV-cured coating films of unsaturated polyesters with different polyols. TMAn (100%) was used as an acid.
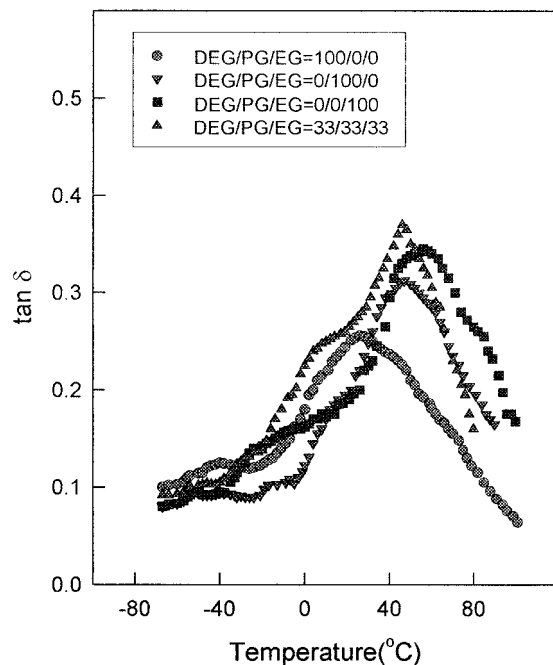
Tensile strength

Elongation

Tensile modulus

Figure 6 Tan δ behaviors of final UV-coating films of unsaturated polyesters with different polyols. TMAn (100%) was used as an acid.

modulus and the EG-based one showed the highest tensile strength. The equimolar DEG/EG/PG ternary polyol system exhibited a little lower tensile properties than EG- or PG-based systems. It should be noted, however, that the tensile properties of the unsaturated polyester of the equimolar ternary polyol mixtures was still much lower for a coating material when TMAn was used exclusively as the acid, which will be discussed later.

Figure 6 shows the tan δ change with temperature. The peak position of tan δ related to the glass transition temperature (T_g) had the order EG > PG > DEG. The higher T_g for the EG-based unsaturated polyester prepolymer was interpreted as being due to the effect of the more difficult micro-Brownian motion of the stronger structurally stable chains rather than DEG or PG. The T_g values estimated from the maximum peak of tan δ is given as 56, 47, 26, and 46°C for the unsaturated polyester prepolymer from EG, PG, DEG, and their equimolar ternary mixture, respectively (see also Table II). The tensile strength, as seen in Figure 5, also showed the same trend as the T_g behavior. The higher mechanical strengths such as tensile strength and tensile modulus of the unsaturated polyesters prepared from EG or PG may be related to their high T_g, even though no definite explanation could be made.

There is no doubt that coating for wood should have good weatherability, suitable viscosity, and good mechanical properties such as tensile properties. Figure 7 compares the accelerated weatherability for the polyunsaturated polyesters with various polyol types in terms of color difference (ΔE). The ΔE has been widely used as a semiquantitative expression of a measure of the weatherability (i.e., the smaller ΔE mean, the better weatherability).[13–15] The prepolymers from PG and EG exhibited good weatherability but that from DEG showed poor weatherability. The prepolymers with an equimolar mixture of DEG/EG/PG showed weatherabilty intermediate between that from PG or EG and DEG. In this work, however, the equimolar mixture of polyols could be a candidate as a suitable polyol for the formulation for wood coating, because the unsaturated polyester prepolymers prepared from the equimolar ternary polyol mixtures showed generally good properties to meet the general requirements for coating materials.

Effects of Acid Kinds and Compositions

The effect of different acid kinds and contents on the tan δ behavior of the unsaturated polyester
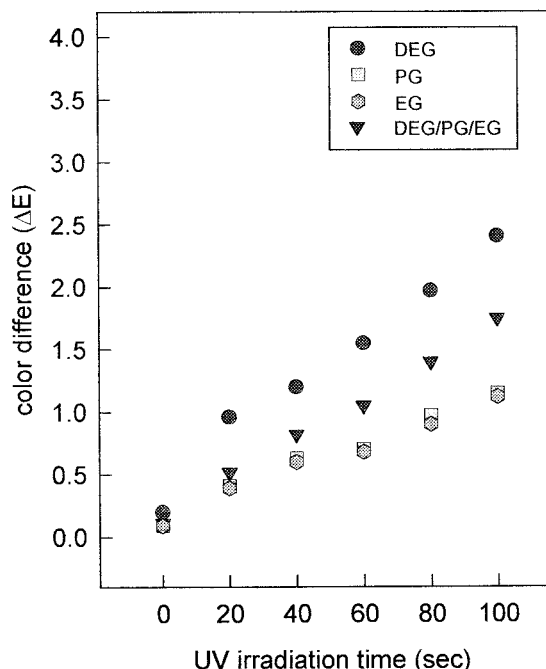
Accelerated weather resistance

Figure 7 Accelerated weather resistance of final UV-cured coating films of unsaturated polyesters with different polyols. TMAn (100%) was used as an acid.
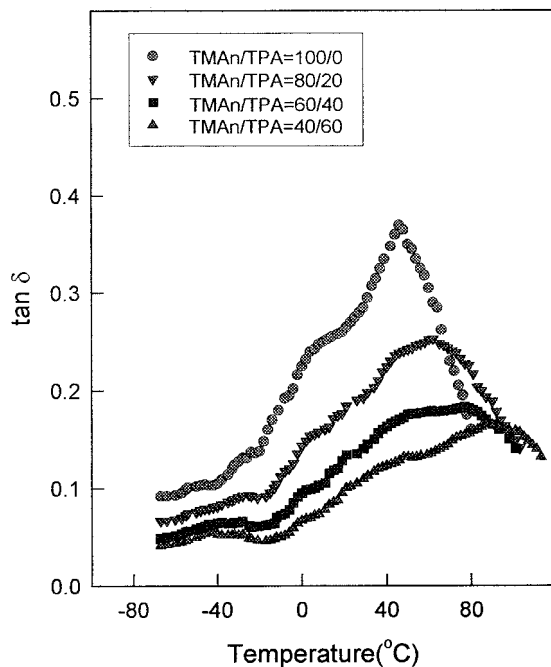
Figure 8   Tan δ behaviors of final UV-coating films of unsaturated polyesters with different acids (TMAn/TPA). DEG (33%)/PG (33%)/EG (33%) was used for the polyol.

prepolymers is shown in Figures 8 and 9. In this case, an equimolar mixture of DEG, PG, and EG as the polyol and 50 wt % of distilled water as a diluent were used. In Figure 8, the T_g determined from the peak position of tan δ shifted toward a higher temperature as the ratio of TPA was increased in the mixed TMAn/TPA acid. The T_g values estimated from the maximum peak of tan δ are given as 46, 60, 79, and 90°C for the prepolymers having TMAn with a TPA composition of 0, 20, 40, and 60 wt %, respectively (see also Table III). The higher shift of T_g for TPA richer unsaturated polyester prepolymer may be ascribed to the rigid chain characteristics of TPA as compared with that of TMAn chains. The result leads to higher mechanical properties such as tensile strength and tensile modulus as the composition of TPA is increased in the prepolymer using the mixtures.

In the case of a TMAn/THPAn mixture, however, the T_g was slightly decreased in the order $46 > 43 > 41 > 37$°C as the THPAn composition increased from 0, 20, and 40 to 60 wt %, respectively (see Fig. 9, Table III). The difference in T_g is, however, not significant when compared to that of the TMAn/TPA mixture.

Figure 10 shows the tensile properties of the

crosscut films of coatings of unsaturated polyesters. The tensile strength and tensile modulus were increased with increasing TPA or THPAn compositions when the TMAn/TPA or TMAn/THPAn mixtures were used as acids. The elongation at break, however, was increased with THPAn contents while decreased with TPA contents. The elongation at break is one of the very important coating film properties in the sense of film flexibility. Thus, the unsaturated polyesters prepared from the TMAn/THPAn mixture can be said to be better coating materials than those from the TMAn/TPA mixture, even though the tensile strength and tensile modulus of the TMAn/THPAn mixture based polyesters were lower than those of the TMAn/TPA mixture based ones. Note, however, that the tensile strength and the tensile modulus of the unsaturated polyesters prepared from the TMAn/THPAn mixed acids are much higher than those prepared from 100% TMAn only.

Figure 11 shows the effect of THPAn and TPA contents on the contact angles of the UV-cured coating film. The contact angle decreased as the THPAn or TPA contents increased, meaning that the hydrophilicity increased or the easiness of the waterborne coating formulation increased. It is
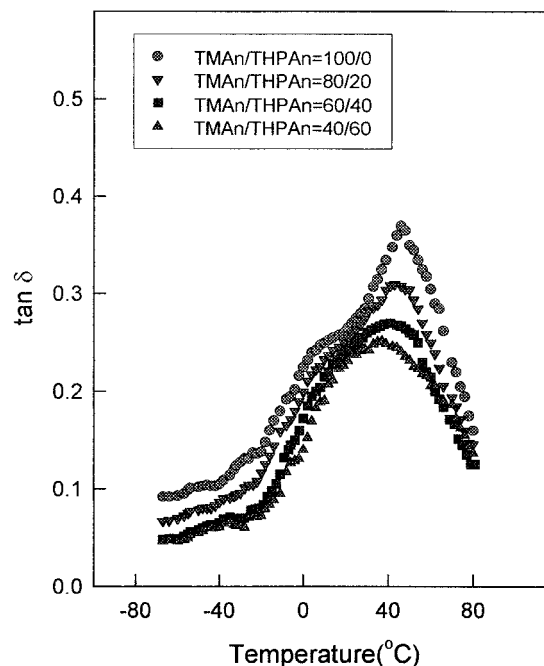

Figure 9   Tan δ behaviors of final UV-coating films of unsaturated polyesters with different acids (TMAn/THPAn). DEG (33%)/PG (33%)/EG (33%) was used for the polyol.
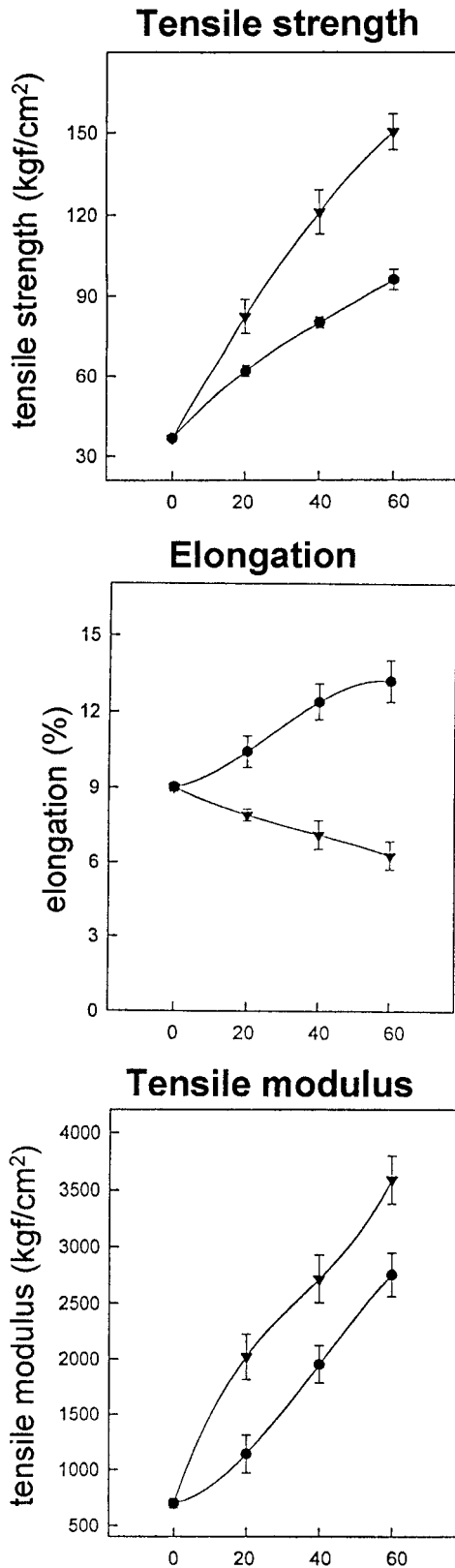
Tensile strength

Elongation

Tensile modulus

Figure 10 Tensile properties (strength, elongation, and modulus) of the crosscut film of UV-cured coating
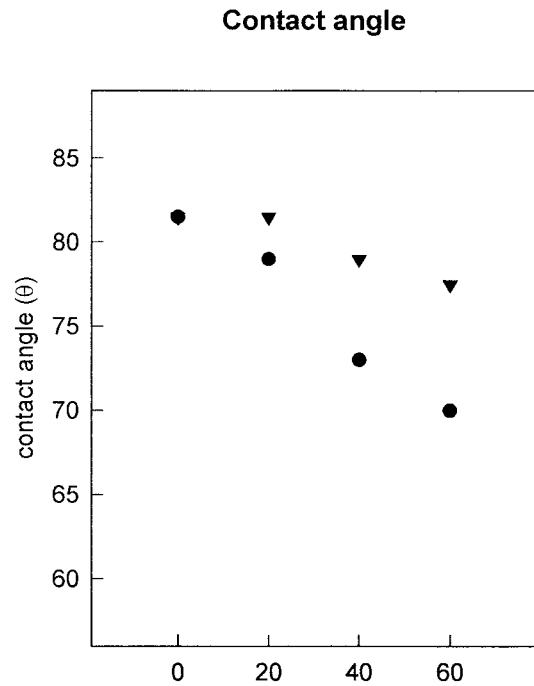
Contact angle

Figure 11 Contact angles of final UV-cured coating films of unsaturated polyesters with different acids (mol %): (●) THPAn and (▼) TPA. DEG (33%)/PG (33%)/EG (33%) was used for the polyol.

also seen that the decrease of the contact angle was much larger when THPAn was used with TMAn than when TPA was used with TMAn. The unsaturated acid, THPAn, may be more hydrophilic than the saturated acid, TPA, due to the more unstable character of the maleic anhydride group against water by the easy ring cleavage of the group in the presence of water than the carboxyl group of TPA. Figures 12 and 13 show the effects of TPA or THPAn compositions on the accelerated weatherability of the unsaturated polyesters in terms of ΔE. The results show that the weatherability of the unsaturated polyesters became better as the TPA or THPAn contents increased. The results of tensile properties and weatherability, as well as the contact angle data, explain why TPA or THPAn was used together with TMAn in the formulation of the UV-curable waterborne unsaturated polyesters, which was used exclusively in the previous section to investigate the effect of polyols on the properties of the final unsaturated polyester coating films. Careful

films of unsaturated polyesters with different acids (mol %): (●) THPAn and (▼) TPA. DEG (33%)/PG (33%)/EG (33%) was used for the polyol.

inspection of Figures 12 and 13 indicate that the weatherability of TMAn-based unsaturated polyester coating film was improved more when THPAn was mixed with TMAn than when TPA was mixed with TMAn. The result may be due to the presence of the remaining C=O group in TPA, which is vulnerable to UV radiation, when TPA is dehydroxylated after exposure to UV light, but THPAn possesses ester linkage when the ring cleavage in THPAn takes place after exposure to UV light. The results of tensile properties, contact angle, and weatherability may lead to the conclusion that the use of THPAn in the mixed acid is better than that of TPA for the formulation of coating materials.

Effect of Diluent Content

Diluents are used in UV-curable systems to provide mainly viscosity control of the formulation. They are very important in determining the speed of cure, crosslink density, and final surface properties of the cured coating films. For the waterborne coating, water was used as a diluent (50 wt
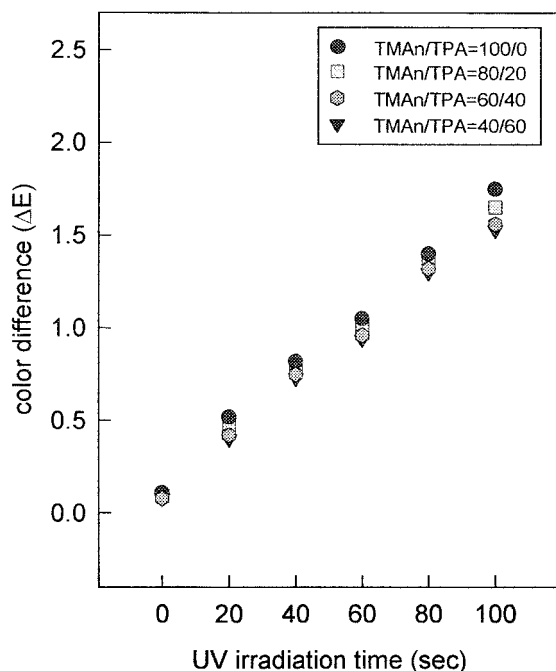
Accelerated weather resistance

Figure 12 Accelerated weather resistance of final UV-cured coating films of unsaturated polyesters with different acids (TMAn/TPA). DEG (33%)/PG (33%)/ EG (33%) was used for the polyol.
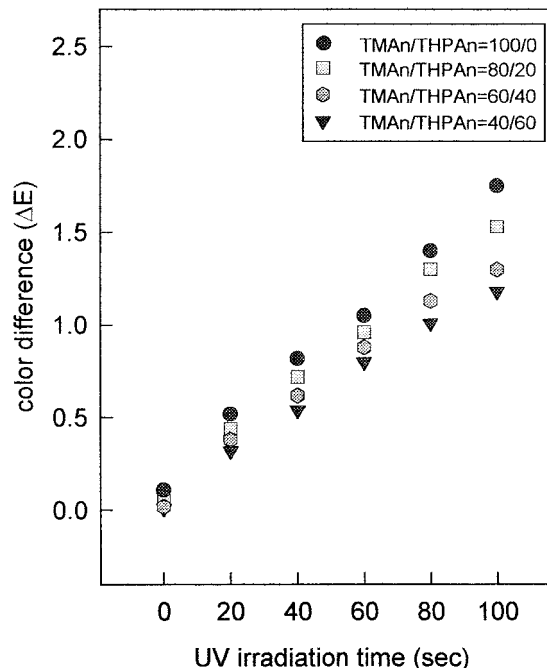
Accelerated weather resistance

Figure 13 Accelerated weather resistance of final UV-cured coating films of unsaturated polyesters with different acids (TMAn/THPAn). DEG (33%)/PG (33%)/EG (33%) was used for the polyol.

%). Figure 14 shows the effect of the THPAn or TPA contents on the viscosity of the prepolymers. Here the coating films were formulated from a equimolar ternary mixture of DEG, EG, and PG. As the TPA contents increased, the viscosity increased; the viscosity decreased slightly with increasing THPAn. As explained in Figure 11, the unsaturated acid, THPAn, is more hydrophilic than the saturated acid, TPA, due to the more unstable character of the maleic anhydride group against water, by the easy ring cleavage of the group in the presence of water, than the carboxyl group of TPA. The slightly decreasing viscosity with increasing THPAn contents may be due to the more structurally unstable character of THPAn, while the increasing viscosity with rising TPA contents may be due to the higher structural stability of TPA than THPAn. In the case of TPA-rich prepolymers, the viscosity was too high for application as a coating material.

The effects of diluent content on the viscosity is also clearly seen from Tables II and III. In general, the viscosity for all the formulated prepolymers was decreased with increasing water con-
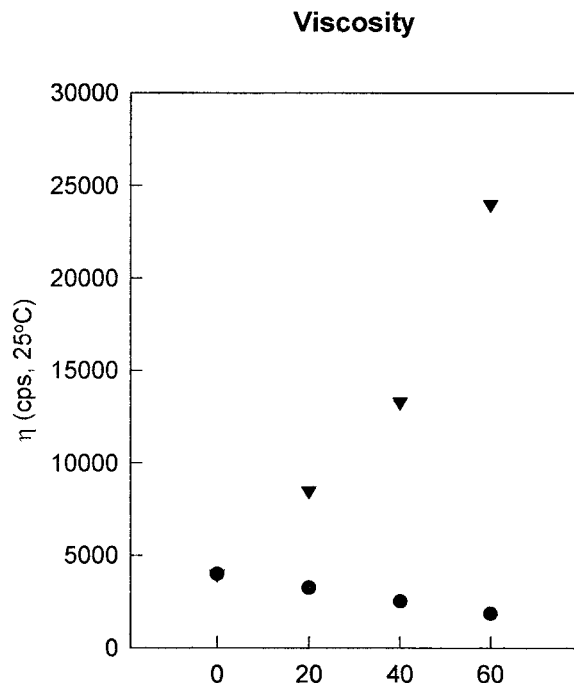
Viscosity

Figure 14 Viscosity as a function of (●) THPAn or (▼) TPA contents (mol %) for the polyunsaturated polyesters of different acids. DEG (33%)/PG (33%)/EG (33%) was used for the polyol and water was used as the diluent.

tents. It has been reported that for the UV-cured polymers low viscosity (ca. 2000–5000 cps) is required for use in wood coating. The viscosity of the prepolymer without diluent is given above 100,000 cps. The result implies that the use of diluent is very essential for coating and only 50% water can be used for the final formulation. The viscosity for the unsaturated polyester prepolymer formulation below 2000 cps is a little bit low to be applied as a coating. Tables II and III summarize the results. Even though the unsaturated polyester coating film prepared from TMAn/THPAn mixed acids showed better tensile properties, hydrophilicity, and weatherability when the THPAn compositions were higher, the viscosity of the unsaturated polyester in 50 wt % of water, formulated with THPAn of more than 40 mol %, was less than 2000 cps, which is a slightly low for coatings. It is concluded, therefore, that the optimum water composition for a coating formulation is 50 wt % and the composition of TMAn/THPAn is 60/40 mol % for coating applications.

Finally, the viscosity of the systems dispersed in water was measured in this work. The coating properties of the films, however, were measured after the water had been removed from the sys-

tems by drying. No clear side effect after drying, such as the shrinkage effect of dried films, was observed. Even though all the films used in this work were dried under a vacuum at 60°C until they reached a constant weight before UV curing and property measurements, there is no doubt that those films might be subjected to the effect of moisture in high humidity conditions because the oligomers in this work were hydrophilic enough to be waterborne. Thus, we will investigate the drying kinetics of a waterborne coating in the near future.

CONCLUSIONS

The UV-curable unsaturated polyesters for wood coating were formulated from unsaturated polyester prepolymer, three different polyols (PG, EG, and DEG), and three different acids (TMAn, THPAn, and TPA). 2-Hydroxy-2-methylphenyl-propane-1-one was used as the photoinitiator. Water was used as the diluent. The properties of the unsaturated polyester coating (contact angle, tensile properties, weatherability, and viscosity) were dependent on the type of unsaturated polyester prepolymer and the overall composition of the acids and the prepolymer/diluent.

The gel content of the UV-curable unsaturated polyesters reached about 85% within 3 s. The dynamic mechanical studies showed the properties of those unsaturated polyesters with various polyols and acids were well correlated with their T_g behaviors. It was found that the unsaturated polyester containing an equimolar ternary mixture of DEG, PG, and EG as a polyol showed better tensile properties, hydrophilicity, and weatherability properties than that containing only one of the three polyols. The tensile strength and tensile modulus of the unsaturated polyester formulated with TMAn/THPAn or TMAn/TPA mixed acids with equimolar DEG/PG/EG polyol mixtures were increased with increasing THPAn or TPA compositions in the mixed acids. The elongation at break, however, was increased with THPAn contents while decreased with TPA contents.

It was observed that the unsaturated polyesters prepared with an equimolar mixture of polyols and 60/40 mol % TMAn/THPAn showed balanced coating properties, hydrophilicity, and weatherability, as well as good tensile properties. The viscosity was acceptable for coating (ca. 2500 cps at 25°C) as a wood coating when 50% water was used as the diluent.

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