

Properties of UV-Curable Polyurethane Acrylates Using Nonyellowing Polyisocyanate for Floor Coating

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SYNOPSIS

UV-curable polyurethane acrylates for poly(vinyl chloride) (PVC) floor coating were prepared using nonyellowing polyisocyanates. The effects of the chemical structure of the polyisocyanates and hydroxyacrylates, and the compositions of the prepolymer/diluent on the properties of the UV-curable polyurethane acrylates were investigated. Several different urethane acrylate prepolymers from four different polyisocyanates, isophorone diisocyanate (IPDI) adduct, hexamethylene diisocyanate (HDI) adduct, HDI biuret, and HDI isocyanurate, and two different hydroxyacrylates, hydroxypropyl acrylate (HPA), polycaprolactone modified hydroxyethylhexylacrylate (PCMHEA). UV-curable coating materials were formulated from the prepolymers and 1-hydroxycyclohexylphenyl ketone as a photoinitiator with polyethylene glycol diacrylate (PEGDA) as a diluent. The polyurethane acrylates prepared with HDI isocyanurate and the equimolar mixture of HPA and PCMHEA showed balanced coating properties such as tensile properties, hardness, weatherability, and good adhesion. The dynamic mechanical studies showed the properties of those polyurethane acrylates were well correlated with their glass transition temperature behaviors. It was also found that the adhesion was best as a PVC floor coating with the appropriate viscosity (below 150 P at 25°C) when 35% PEGDA as a diluent was used. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The use of a UV-curable coating for floor materials has attracted much interest since the first patent of Bayer in the late 1960s,¹⁻³ because of its fast cure speed and energy saving characteristics in spite of its relatively high expense over thermal cured coating. Usually, the UV-curable coating is formulated with the three basic components including prepolymer, diluent, and photoinitiator. The properties of the coating for floor materials such as hardness, viscosity, and weatherability are dependent on the type of prepolymer and diluent, the structure and the functionality of the diluent, and the overall composition of the formulation.^{4,5}

UV-curable coatings for poly(vinyl chloride) (PVC) floors has been widely used since the late 1980s. Unsaturated polyester, epoxy acrylate, polyester acrylate, and polyether acrylate have been used for UV-curable coatings.^{1,6} In this work we selected urethane acrylates as the prepolymer for UV-curable coatings because the oligomer is capable of imparting special properties, for example, high impact resistance at low temperature and high stability to hydrolysis, to the final UV-cured coating in which they are incorporated.^{7,8} The yellowing properties of the conventional urethane acrylates, however, have limited the more versatile properties for coating materials.

In this vein, therefore, we used four different antiyellowing polyisocyanates and two hydroxyacrylates to prepare urethane prepolymers. We investigated the effects of the polyisocyanate and the hydroxyacrylate types on the properties of the final

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coating film. Polycaprolactone diol (PCD) was selected as a polyol because of its hydrolysis resistance, low viscosity, and good heat resistance.⁹

The urethane oligomers are functionalized for UV-curable systems by reacting with 1-hydroxycyclohexylphenyl ketone as a photoinitiator. Formulation of the UV-curable coating was made with a diluent, polyethylene glycol diacrylate (PEGDA). In the present article, the effect of the overall composition of the prepolymer/diluent of the urethane acrylate coatings on the properties for PVC floor coating was also investigated.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI, Huls), hexamethylene diisocyanate (HD, Rhone-Poulenc), HDI biuret (Duranate 24A-100, Ashahi), and HDI isocyanurate (Duranate TPA-100, Ashahi) were used as received. IPDI adduct was prepared by the reaction of IPDI, HDI, and trimethyl propane (TMP, Youngwoo). TMP and polycaprolactone diol (PCD-0201, Union Carbide) were degassed at 80°C for 6 h under vacuum. The 2-hydroxypropyl acrylate (HPA, International Speciality) and polycaprolactone modified hydroxyethyl acrylate (PCMHEA, Tone M-100, Union Carbide) were kept dry with a 4-Å molecular sieve before use for 1 week. Stannous octoate (Yoshitomi) and 1-hydroxycyclohexyl phenyl ketone (HCPK, Irgacure 184, Ciba-Geigy) were used without further purification. PEGDA (PEG molecular weight 400, Kyoishia) were used as a diluent after purification. The structure of the four polyisocyanates is shown in Figure 1.

Syntheses of Urethane Acrylate Prepolymers

The acrylate terminated urethane oligomer was prepared by reacting 1 equiv HPA, PCMHEA, or their mixtures of various compositions with 1 equiv of polyisocyanate (either IPDI adduct, HDI adduct, HDI isocyanurate, or HDI biuret) at a temperature below 70°C. The reaction was continued until the theoretical isocyanate contents were reached as determined by the di-*n*-butylamine method. One equivalent of the urethane acrylate oligomer (or prepolymer) was mixed with the unreacted NCO equiv of dried polyol (PCD) and 0.01 wt % of stannous octoate under the rotation speed of 120 rpm using a high torque stirrer at 50°C for 2 h. Then the

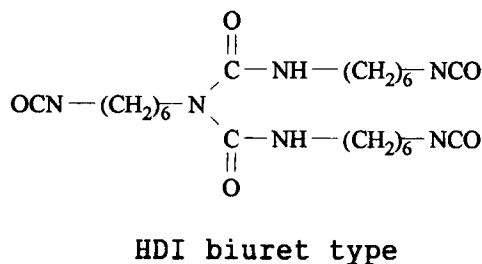
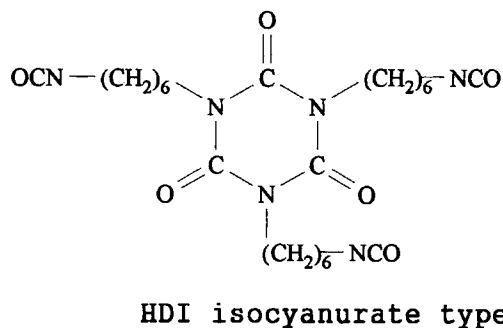
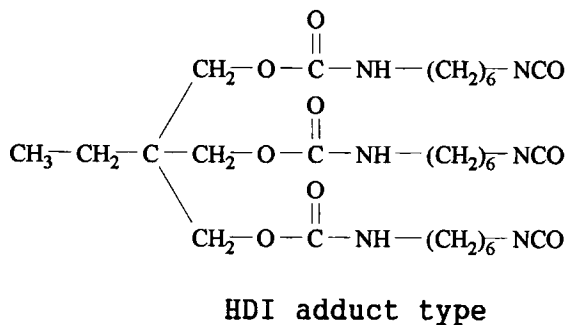
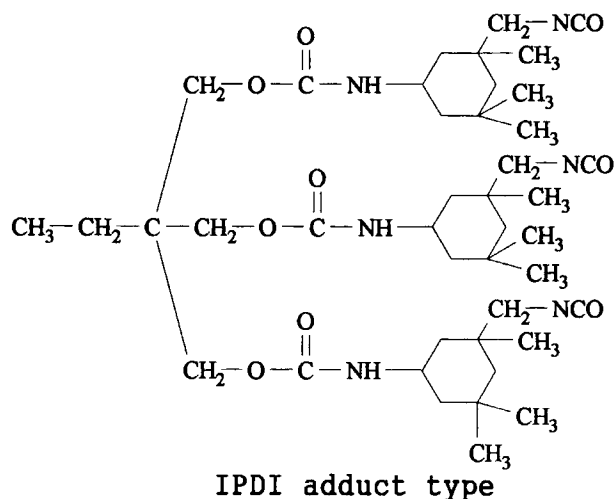


Figure 1 Structure of the four polyisocyanates.

Table I Composition, T_g , Viscosity, Tensile Properties, and Hardness of Coating Materials Prepared for PVC Floor

Composition of Prepolymer Polyisocyanate/Hydroxy Acrylate/Polyol	Diluent (wt %)	T_g (°C)	η (cps) at 25°C	Tensile			Hardness
				Strength (kg/cm ²)	Elongation at Break (%)	Modulus (kg/cm ²)	
HDI adduct/HPA/PCD	PEGDA (35)	53	7500	348.1	14.9	4325.1	77.4
HDI adduct/HPA/PCD	PEGDA (35)	30	3900	63.2	35.0	280.6	45.6
HDI biuret/HPA/PCD	PEGDA (35)	16	360	154.6	41.1	746.6	56.4
HDI isocyanurate/HPA/PCD	PEGDA (35)	29	298	165.0	29.9	2619.0	57.6
HDI isocyanurate/HPA (75%)/ PCMHEA (25%)/PCD	PEGDA (35)	9	188	99.0	34.4	238.1	48.2
HDI isocyanurate/HPA (50%)/ PCMHEA (50%)/PCD	PEGDA (35)	5	133	51.1	24.1	239.6	45.8
HDI isocyanurate/HPA (25%)/ PCMHEA (75%)/PCD	PEGDA (35)	2	118	30.3	19.9	163.7	41.4
HDI isocyanurate/HPA (0%)/ PCMHEA (100%)/PCD	PEGDA (35)	-4	98	30.2	19.1	99.6	37.8
HDI isocyanurate/HPA (50%)/ PCMHEA (50%)/PCD	PEGDA (20)	17	735	93.1	36.2	314.9	47.8
HDI isocyanurate/HPA (50%)/ PCMHEA (50%)/PCD	PEGDA (25)	15	324	142.2	57.4	251.9	47.2
HDI isocyanurate/HPA (50%)/ PCMHEA (50%)/PCD	PEGDA (35)	5	133	51.1	24.1	239.6	45.8
HDI isocyanurate/HPA (50%)/ PCMHEA (50%)/PCD	PEGDA (45)	2	38	35.3	16.7	207.5	42.8

coatings were formulated from the above viscous oligomers by adding the required amount of HCPK (4 wt %) and additional PEGDA. The air bubbles entrapped during mixing were removed by applying a vacuum at 30°C for 30 min and keeping them under vacuum at 60°C for 3 h.

UV Curing

The final UV-cured urethane acrylates were prepared by casting the above formulated product onto a glass plate at room temperature and cured using a medium pressure mercury lamp (80 W/cm, 6.3 Å). Radiation curing was carried out with a 365-nm wavelength UV light. The thickness of the cast coating film was about 300 μ m.

Measurements

IR Spectra

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

Gel Content

The 0.2-mm thick sample films cured under various curing times 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 with a Rheovibron DDV-II (Toyo Baldwin Co.) with a heating rate of 2°C/min over a temperature range of -80 to 80°C. Rectangular test specimens (0.3 × 1

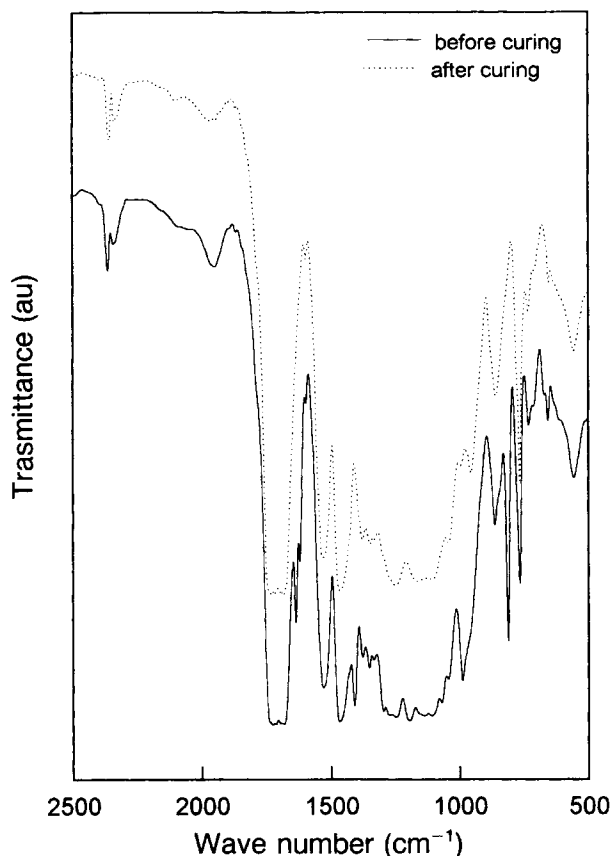


Figure 2 Infrared spectra of polymer (HDI isocyanurate/HPA/PCD) before and after UV curing.

× 3 cm) were prepared. The measured frequency range was 35 Hz.

Tensile Test

Tensile tests were performed on a tensile tester (Tinius Olsen 1000) at the cross-head speed of 5 mm/min according to the ASTM D-1822 method. The thickness of the samples was 300 μm .

Hardness

The hardness of the coating films with thickness of 2.5-mm was measured with a Shore durometer type D (Toyoseki) by the KS 3043 method.

Viscosity

The viscosity of the samples was measured with a Brookfield Viscometer (model BH) at 25°C.

Adhesion

The adhesion of the samples to the PVC floor was measured with a cross-cut tester (11 × 11 lines of

square with 1-mm width) according to the Korean Standards KS M5981 method. The thickness of the coating films on the PVC floor was 20 μm .

Weatherability

The weatherability (ASTM G53) was measured at 60°C, using a Q-Pannel Weathering Tester coupled with a UV lamp of 315–280 nm wavelength. The cross-sectional area of the films was 3 × 5 cm² and the thickness was 300 μm . The yellowing index (ΔYI) and color difference (ΔE) of the samples after exposure to UV for 2000 h were measured with Applied Color Systems (ACS-3300). To test the thermal resistance of the coating films, some of the films were placed in a dry oven at 180°C for 1 h before measuring ΔYI and ΔE values.

RESULTS AND DISCUSSION

Curing Evaluation

Several acrylate terminated urethane oligomers were synthesized. The composition and the properties of the prepolymers are summarized in Table I. Details of the result will be discussed in each proper section.

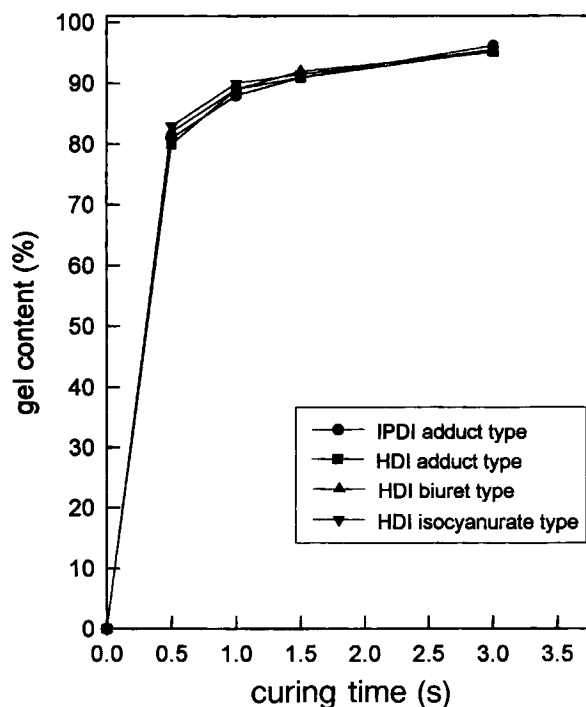


Figure 3 Gel content of dry films as a function of curing time for the polyurethane acrylate prepolymers of various isocyanate types.

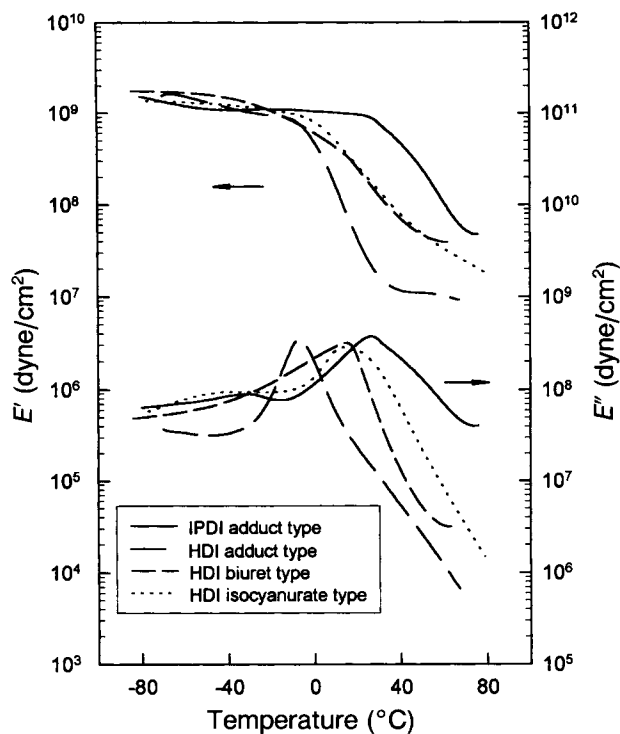


Figure 4 Moduli (storage modulus and loss modulus) as a function of temperature for polyurethane acrylates with various isocyanate types.

The curing of the urethane acrylate prepolymers as analyzed by FTIR. Figure 2 shows a typical IR spectrum of HDI isocyanurate/HPA/PCD urethane prepolymer before and after UV irradiation for 3 s. The urethane acrylate prepolymer was identified by the characteristic peaks around 2270 cm^{-1} (N—C—O) and 1720 cm^{-1} (C—O). The N—C—O stretching band near 2270 cm^{-1} was used to monitor the extent of the reaction between the isocyanate and the hydroxy group. The urethane acrylate has C—C absorption bands at 810 and 1635 cm^{-1} before UV irradiation, but the band was no longer detectable after irradiation. The characteristic C—C absorption of urethane acrylate at 810 and 1635 cm^{-1} was used to determine the extent of photopolymerization. The result in Figure 2 indicates that radiation curing and the polyisocyanate reaction had been performed.

The degree of cure of the urethane acrylate prepolymers prepared from HPA and PCD and either of four different polyisocyanates after exposure to UV was measured in terms of gel content. The results are shown in Figure 3. Figure 3 illustrates the change in gel content as a function of curing time for four urethane acrylates consisting of different

polyisocyanates. It is seen that there are dramatic increases in gel content up to 90% within 0.5 s. But thereafter there are very small gains in gel contents with further increasing time, and the gel content reached about 90% regardless of the polyisocyanate types used. It is generally accepted that a gel content of 90–96% indicates a complete cure of the coatings on the floor.

Dynamic Mechanical Behavior and General Properties

Effect of Polyisocyanate Structure

The dynamic mechanical behaviors of the urethane acrylate prepolymers of four different polyisocyanates with HPA, PCD, and 35 wt % PEGDA are shown in Figures 4 and 5. Figure 4 is the storage modulus (E') change with temperature. The storage moduli of the IPDI adduct based urethane prepolymer above room temperature showed higher values than any other polyisocyanate based urethane prepolymers. The storage moduli of the urethane prepolymers consisting of different polyisocyanates at room temperature were higher in the order IPDI adduct > HDI isocyanurate > HDI biuret > HDI adduct.

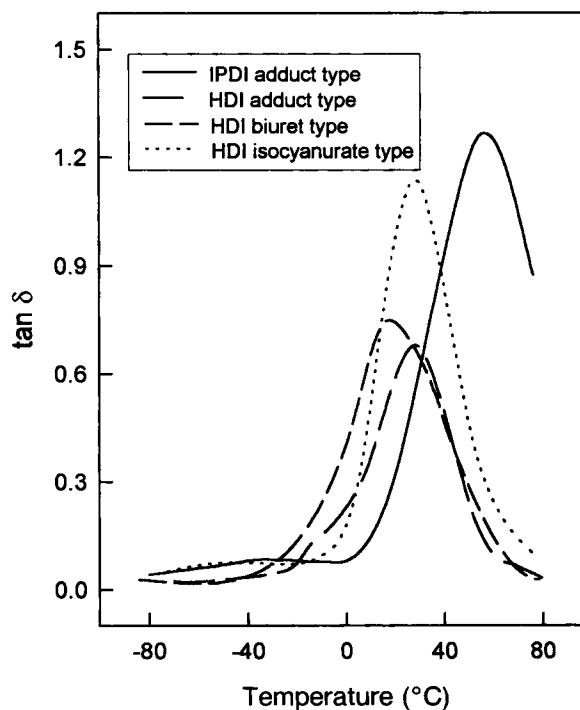


Figure 5 $\tan \delta$ as a function of temperature for polyurethane acrylates with various isocyanate types.

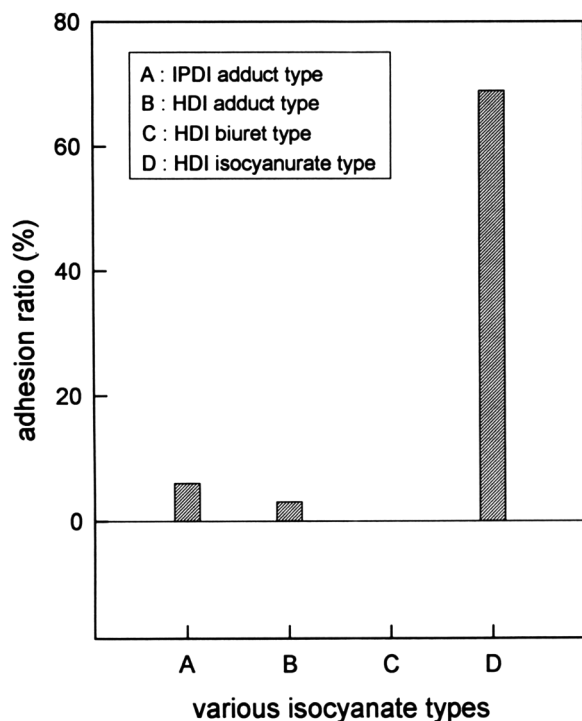


Figure 6 Adhesion ratio of the cross-cut film of the coating for the polyurethane acrylate prepolymers of various isocyanate types.

Figure 4 also shows the loss modulus (E'') change with temperature; but one of more significance is shown in Figure 5, which illustrates the $\tan \delta$ change with temperature. The peak position related to the glass transition temperature (T_g) was higher in the order IPDI adduct > HDI adduct > HDI isocyanurate > HDI biuret. The higher T_g for IPDI adduct based urethane prepolymer was interpreted as being due to the effect of the more difficult microBrownian motion of the stiffer chains rather than any other polyisocyanate chains. The T_g values estimated from the maximum peak of $\tan \delta$ are given as 53, 30, 29, and 16°C for the urethane prepolymer from IPDI adduct, HDI adduct, HDI isocyanurate, and HDI biuret, respectively. The hardness and tensile properties, as summarized in Table I, also show the same trend with the E' behavior. The highest mechanical strengths such as tensile strength, tensile modulus, and hardness of the urethane acrylates prepared from IPDI adduct are related to its highest T_g .

Table I also shows the viscosities of the urethane acrylate prepolymers with different polyisocyanates. The viscosities of the urethane acrylate prepolymers were much higher when IPDI adduct or HDI adduct was used as a polyisocyanate than when HDI isocyanurate or HDI biuret was used. The urethane

acrylate prepolymer with IPDI adduct is too viscous not to be processable for coating, in spite of its superior mechanical strengths such as tensile strength and hardness, to other polyisocyanate types. Table I also shows that the HDI adduct is not a good polyisocyanate for the urethane acrylate coating formulation because it has the poorest mechanical properties among the four polyisocyanate based urethane acrylate prepolymers as well as its high viscosity. The urethane acrylate prepolymers from the other two polyisocyanates, HDI isocyanurate and HDI biuret, exhibited comparable tensile properties and hardness and viscosity for coating. Careful inspection of the mechanical property data in Table I, however, shows clearly that the HDI isocyanurate is a better candidate for urethane acrylate prepolymers for this work than the HDI biuret.

Figure 6 shows the adhesion ratios of the cross-cut films of the coating for the urethane acrylate prepolymers from four different polyisocyanates. HDI isocyanurate based urethane acrylate prepolymers exhibit the best adhesion to the PVC floor among the four different prepolymers. It is also seen that the HDI biuret based urethane acrylate showed no adhesion to the PVC floor, although it showed generally good properties as shown in Table I. Thus the HDI biuret should not be used in the polyure-

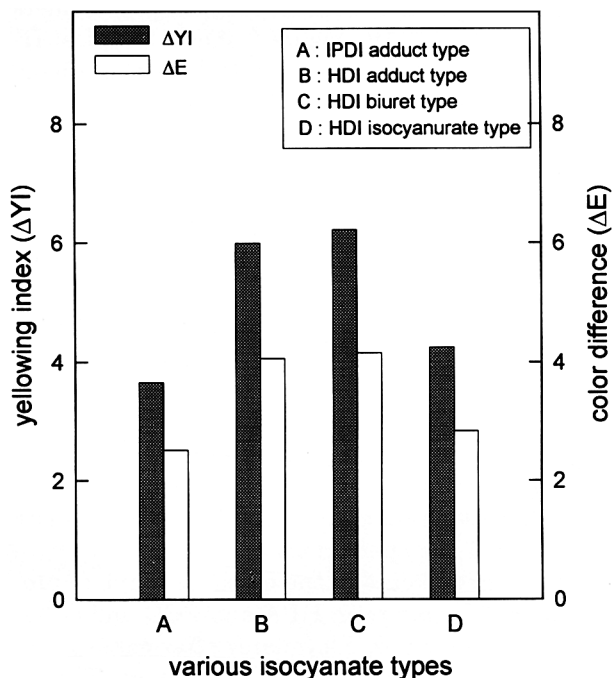


Figure 7 Accelerated weatherability (yellowing index and color difference) of polyurethane acrylate prepolymers of various isocyanate types.

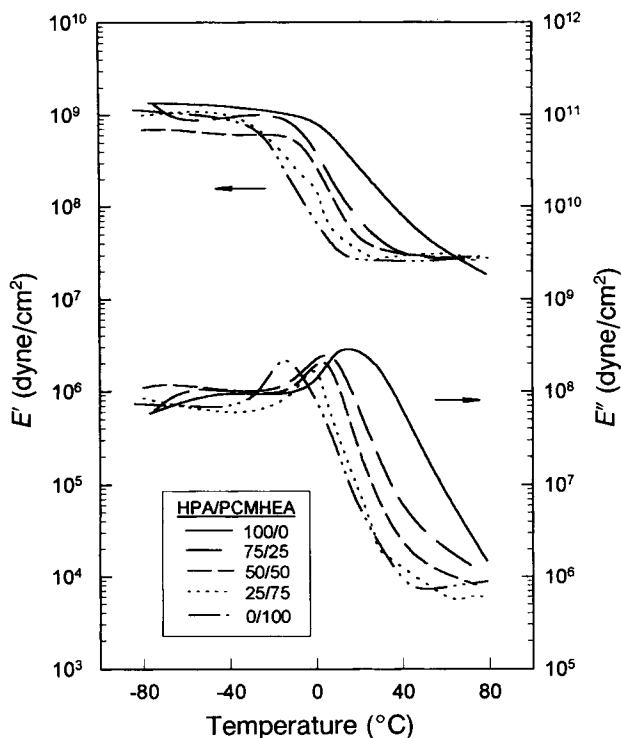


Figure 8 Moduli (storage modulus and loss modulus) as a function of temperature for polyurethane acrylates of HDI isocyanurate type with different mole ratios of HPA/PCMHEA.

thane acrylate for coating a PVC floor. It is of no use if the coating formulations do not have enough adhesion to a coated material (PVC floor in this work); however, they do have good mechanical properties.

Figure 7 compares the weatherability for the polyurethane acrylates with various isocyanate types in terms of yellowing index (ΔYI) and color difference (ΔE). The ΔYI and ΔE had been widely used as semiquantitative expressions of a measure of the weatherability; that is, the smaller ΔYI and ΔE mean better weatherability.¹⁰⁻¹² The result in Figure 7 well shows that the polyurethane acrylates with HDI isocyanurate have the best weatherability among the four different polyisocyanate types.

It is of no doubt that the coating for floor should have good adhesion and weatherability as well as suitable viscosity and good mechanical properties such as tensile properties and hardness. In this work, therefore, only HDI isocyanurate could be a candidate as the suitable anti-yellowing polyisocyanates for the formulation for PVC floor coating, since the urethane prepolymers prepared from the polyiso-

cyanates showed generally good properties to meet the general requirements.

Effect of Hydroxyacrylate Compositions

The effect of different hydroxyacrylates on the dynamic mechanical behavior of the urethane prepolymers is shown in Figures 8 and 9. In this case, a mixture of HPA and PCMHEA with a different composition and 35 wt % PEGDA was used as a diluent. In Figure 8 the HPA prepolymer showed higher E' over the temperature range of -80 to 80°C than the PCMHEA prepolymer. A similar trend is shown in Figure 9 in the $\tan \delta$ change as a function of temperature. The T_g determined from the peak position shifted toward the lower temperature as the ratio of PCMHEA was increased in the mixed hydroxyacrylates. The T_g values estimated from the maximum peak of $\tan \delta$ are given as 29, 9, 5, 2, and -4°C of HPA, HPA75/PCMHEA25, HPA50/PCMHEA50, HPA25/PCMHEA75, and PCMHEA based urethane prepolymer, respectively. The lower shift of T_g for PCMHEA richer urethane prepolymer may be ascribed to the flexible longer chain characteristics of PCMHEA rather than that of the HPA chains. The result leads to lower mechanical properties such as tensile strength, tensile modulus,

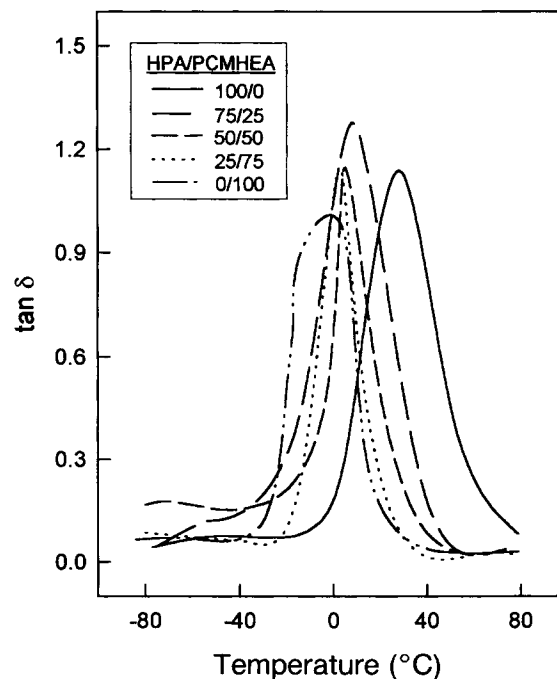


Figure 9 $\tan \delta$ as a function of temperature for polyurethane acrylates of the HDI isocyanurate type with different mole ratios of HPA/PCMHEA.

hardness, and lower viscosity as the composition of PCMHEA is increased in the mixed hydroxyacrylate prepolymer. Table I shows the result. Figure 10 shows the effect of hydroxyacrylate composition on the weatherability of the urethane acrylates in terms of ΔYI and ΔE . The result also shows that the HPA rich urethane acrylates have better weatherability than the PCMHEA rich ones. This result means that HPA is a good hydroxyacrylate for the urethane acrylate coating material. This is the reason why we used the HPA as a hydroxyacrylate to investigate the effect of polyisocyanates for the formulation of the urethane acrylates. It is again noteworthy, however, that the adhesion property is the most important requirement for coating application.

Figure 11 shows the adhesion ratios of the cross-cut films of coatings of polyurethane acrylates. As expected, the PCMHEA rich urethane acrylates show very poor adhesion properties. The adhesion to the PVC floor is, however, highest when equal amounts of HPA and PCMHEA are used. It is clear that the formulated coating materials should have good adhesion as well as suitable viscosity and good weatherability and mechanical properties such as tensile properties and hardness. In this work, therefore, it is concluded that the use of the equimolar

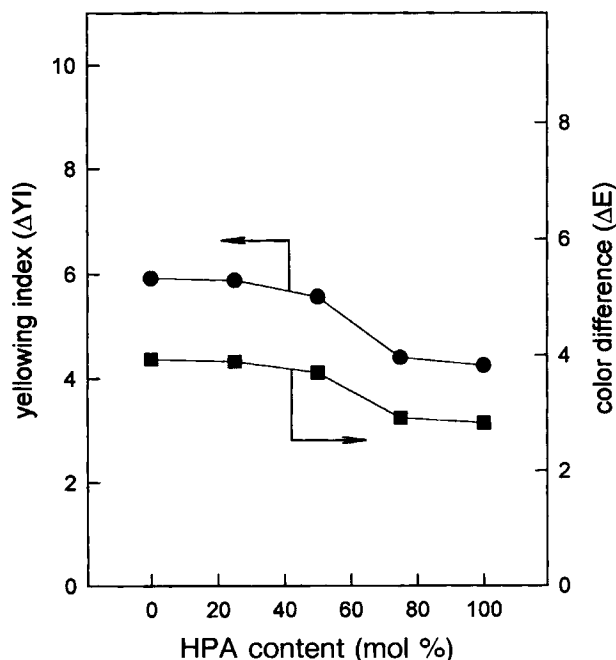


Figure 10 Accelerated weather resistance [(●) yellowing index and (■) color difference] as a function of HPA content for the polyurethane acrylates of HDI isocyanurate type.

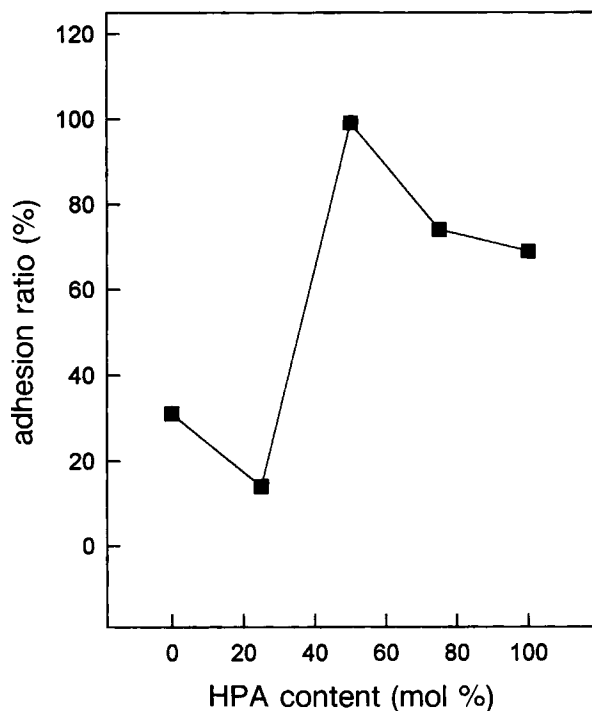


Figure 11 Adhesion ratio of the cross-cut film of coating as a function of HPA content for the polyurethane acrylates of HDI isocyanurate type.

mixture of HPA and PCMHEA is better for the formulation of the UV-curable urethane acrylates in this work than that of 100% HPA, even though the mechanical properties and weatherability of the urethane acrylate prepolymers are better as the HPA contents in the prepolymers are increased.

Effect of Diluent Content

Diluents are used in UV-curable systems to mainly provide 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. Figure 12 shows the effect of the diluent contents on the storage modulus for the HDI isocyanurate/PCD prepolymers. Here the coating films were formulated from HPA50/PCMHEA50 mixed hydroxyacrylates. As the diluent content increases, the modulus E' decreases. The result may be related to the decreased structural order resulting from the difficulty in regular molecular packing because of the long side chains, leading to decreasing maximum loss peak (E'') and maximum $\tan \delta$ with increasing diluent for the formulations with PEGDA (see also Fig. 13).

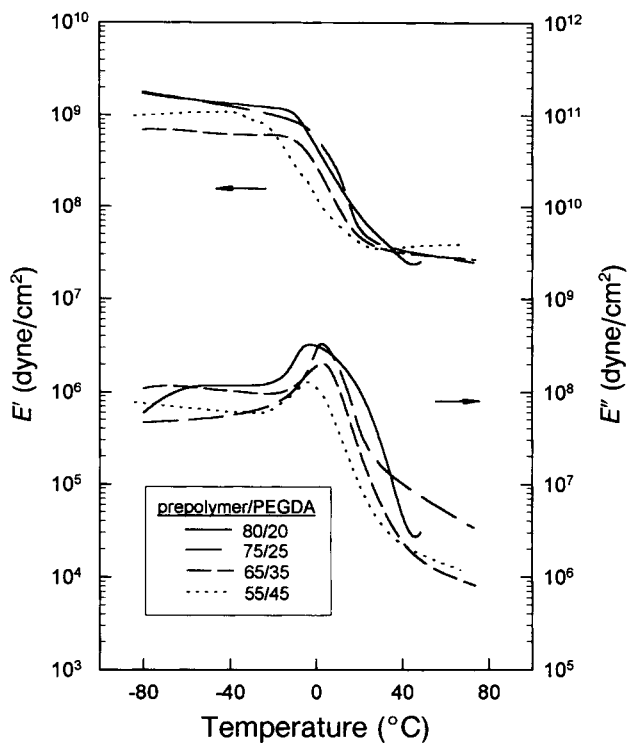


Figure 12 Moduli (storage modulus and loss modulus) as a function of temperature for the polyurethane acrylates of HDI isocyanurate type with different weight percent of prepolymer/PEGDA.

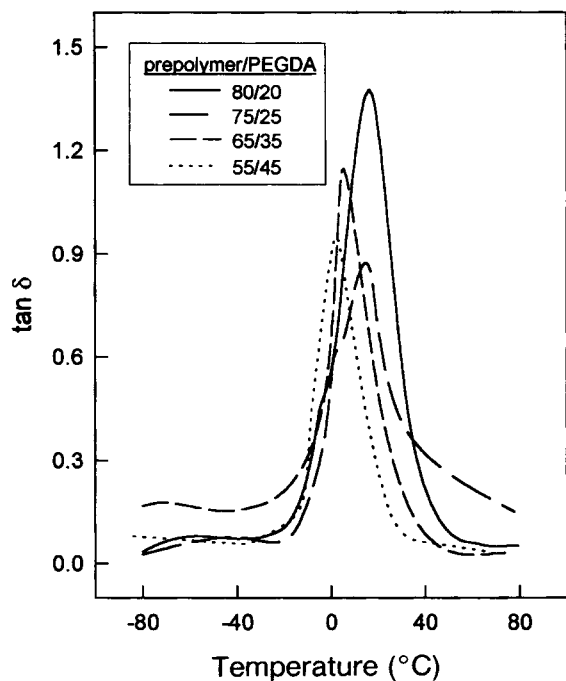


Figure 13 $\tan \delta$ as a function of temperature for polyurethane acrylates of HDI isocyanurate type with different weight percent of prepolymer/PEGDA.

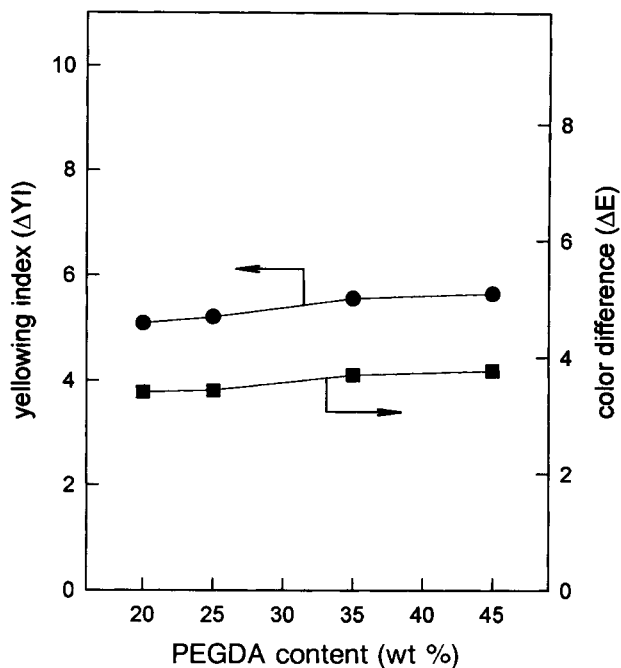


Figure 14 Accelerated weather resistance [(●) yellowing index and (■) color difference] as a function of PEGDA content for the polyurethane acrylates of HDI isocyanurate type.

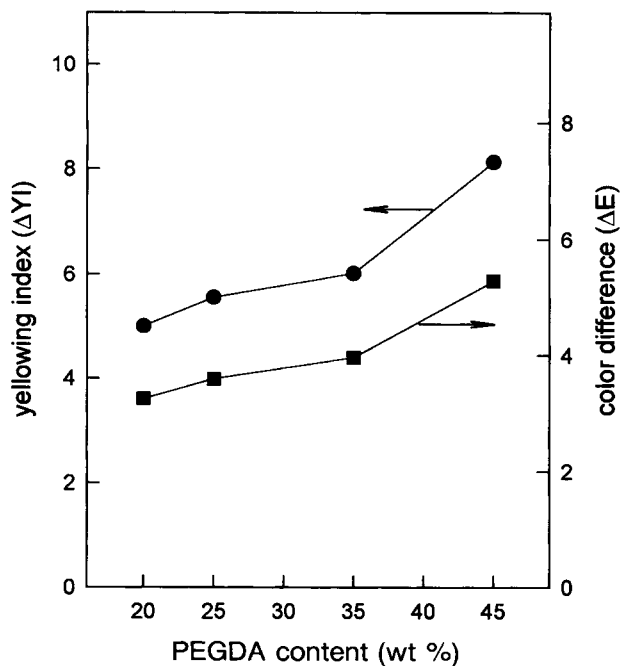


Figure 15 Thermal resistance [(●) yellowing index and (■) color difference] as a function of PEGDA content for polyurethane acrylates of HDI isocyanurate type.

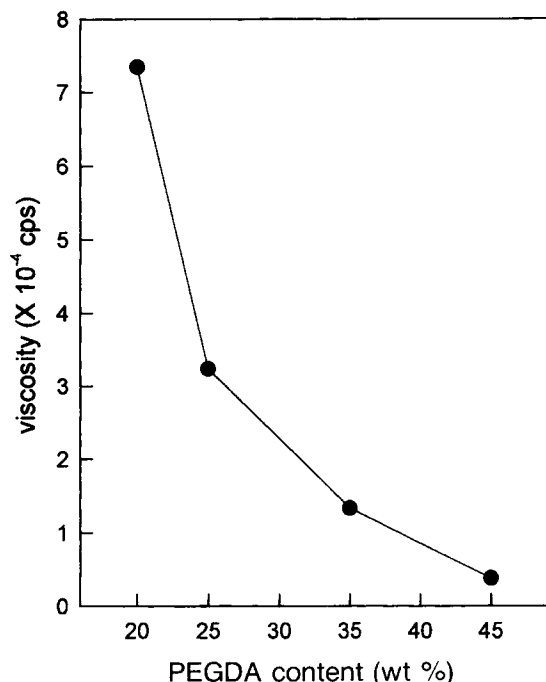


Figure 16 Viscosity as a function of PEGDA content for the polyurethane acrylates of HDI isocyanurate type.

The general mechanical properties such as hardness of several formulated UV-curable coatings are summarized in Table I. The effect of diluent content on the mechanical properties is clearly seen from the table. In general, the tensile properties of the formulated coatings were decreased with increasing PEGDA contents. The effect of diluent contents on the weatherability of the urethane acrylates is shown in Figure 14 in terms of ΔYI and ΔE . The result shows that the weatherability is poorer as the diluent contents are increased, even though the difference is not significantly large. The thermal resistance of the final formulation also shows the same trend as that of the weatherability, as shown in Figure 15.

It has been reported that for the UV-cured polymers low viscosity (below 20,000 cps) is required for use in floor coating. Figure 16 shows the viscosity for the urethane prepolymer formulation of different PEGDA compositions. The viscosity was decreased with increasing PEGDA. 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 35% PEGDA can only be used for the final formulation. The viscosity for the urethane prepolymer formulation of 45% PEGDA is too low to be applied for coatings. In Figure 17 the adhesion ratios of the cross-cut films of coatings of polyurethane acrylates is illustrated. The adhe-

sion to the PVC floor is highest when 35 wt % PEGDA is used. The highest adhesion may be thought to come from the best coating condition of the PVC floor due to the optimum viscosity values in the PEGDA composition, because the coating is impossible if the coating material possesses too high and too low viscosities. The general mechanical properties and viscosity behavior are better when the contents of PEGDA is lower; therefore, we determined the optimum diluent composition for the coating formulation as 35 wt %.

CONCLUSIONS

The UV-curable urethane acrylates for floor coating were formulated from urethane prepolymer, four different polyisocyanates (IPDI adduct, HDI adduct, HDI biuret, and HDI isocyanurate) and two different hydroxyacrylates (HPA, PCMHFA), diluent, and photoinitiator. We used 1-hydroxy cyclohexylphenyl ketone as a photoinitiator with PEGDA as a diluent. The properties of the urethane acrylate coating, such as hardness, tensile properties, adhesion, weatherability, and viscosity were dependent on the type of urethane prepolymer and the overall composition of the prepolymer/diluent.

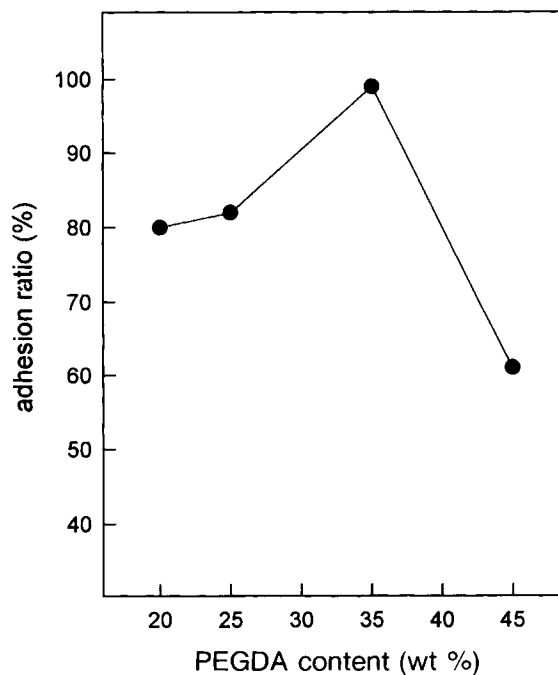


Figure 17 Adhesion ratio of the cross-cut film of coating as a function of PEGDA content for the polyurethane acrylates of HDI isocyanurate type.

The gel content of the UV-curable urethane acrylates reached about 90% within 0.5 s. The dynamic mechanical studies showed the properties of those polyurethane acrylates with various acrylates and diluents were well correlated with their T_g behaviors. It was found that the urethane acrylate containing HDI isocyanurate as a polyisocyanate showed fairly good tensile properties, hardness, adhesion, and weatherability properties. The polyurethane acrylates prepared with an equimolar mixture of HPA and PCMHEA showed balanced coating properties, good adhesion, and weatherability. It was observed that the adhesion was best as a PVC floor coating with appropriate viscosity (below 150 P at 25°C) when 35% diluent was used.

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