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UV-curable water-borne polyurethane primers for aluminum and polycarbonate interfaces

S. H. Yoon · B. K. Kim

Abstract Water-borne polyurethane (WPU) primers were synthesized from three types of polyol, viz., poly(propylene glycol), poly(tetramethylene glycol), and polycaprolactone diol (PCL) at two prepolymer molecular weights, and were tested for the adhesion between vinyltrimethoxysilane modified aluminum panel and polycarbonate. It was found that chemical hybridizations of Al panel with WPU via sol–gel reaction were crucial to enhance the adhesion. Among three types of polyol, PCL gave the highest adhesion strength, glassy and rubbery moduli, tensile strength, and glass transition temperature. On the other hand, smaller prepolymer molecular weight gave improved adhesion and improved mechanical properties due to the increased crosslink density and cohesive strength.

Keywords Water-borne polyurethane · Primer · Sol–gel · Adhesion strength

Introduction

Water-borne polyurethanes (WPUs) are environmentally friendly materials which find broad applications in coatings and adhesives for wood and automobiles as well as for numerous flexible substrates such as textiles, leather, paper, and rubber [1–4]. WPUs have received increased attentions because they are non-toxic and non-flammable in addition to the fact that they do not pollute the air [5–8]. In general, WPUs have inferior drying rates and a slower development of adhesion compared to the conventional solvent-borne PUs. In addition, their applications have been limited by the type of raw materials and the manufacturing process. However, problems related to their properties and processing can largely be resolved by proper molecular designs and hybridization with other materials [9–13].

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Water-borne polyurethanes can be cured by UV (UV-WPU) which benefits from the advantages of both 100% UV cure system and WPUs without suffering from any of their obvious disadvantages [14, 15]. Advantages of WPUs, other than the environmentally friendly nature, come from the large molecular weight of the prepolymers. These include tack-free before cure which allows flooring and rolling operations, and high elasticity allowing high deformation coatings such as vacuum forming of crash pad. Advantages of 100% UV cure system include fast process and excellent surface properties of films. The two types of advantages are combined upon casting the WPUs into film, followed by drying and UV curing.

The metalizing painting provides the coatings with soft touch, graceful appearance, and durability, and it finds a number of newer applications including internal and external automobile coatings. The metalizing coating for automobile consists of top coating, metal layer, primer coating, and polymer substrate. Among them, primer is crucial to determine the performance of the whole process. In general, there is little miscibility between metal layer and polymer substrate. Therefore, molecular design and synthesis of primer molecules having strong interactions with the metal as well as the polymer substrate is the key elements to give sufficient adhesive strength.

The organosilane provides an important group of adhesion promoters for coupling organic polymers to aluminum surfaces [16–18]. The adhesion properties of the silane on aluminum depends both on chemical bonding at the silane–aluminum interfaces and weak physical bonding to a rough mechanical interlocking [19–21].

We designed and synthesized WPU primer which was interposed between Al surface and polycarbonate (PC) substrate. Vinyl group of vinyltrimethoxysilane (VTMS) was chemically bonded to the Al surface to introduce chemical reaction between Al and WPU primer. WPU primers were synthesized using three different types of polyol at two different levels of molecular weight to evaluate the WPU–PC miscibility in addition to the effect of WPU–Al chemical hybridization. Such contribution has not yet been found in the open literature.

Experiment

Raw materials

Polycaprolactone diol (PCL diol) was purchased from Sigma-Aldrich whereas poly(tetramethylene glycol) (PTMG) and poly(propylene glycol) (PPG) were kindly donated from KPX chemical(Ulsan, Korea). The polyols were dried and degassed at 80 °C under vacuum for 3 h before use. Isophorone diisocyanate (IPDI, Aldrich) was dried over 4 Å molecular sieves before use. Vinyltrimethoxysilane (VTMS, Aldrich), dimethylol butanoic acid (DMBA), 2-hydroxyethyl acrylate (HEA, Aldrich), triethylamine (TEA, Fluka), dibutyltin dilaurate (Aldrich), α,α'-dimethoxy-α-hydroxy acetophenone (Darocur 1173, Ciba Specialty Chemicals), 1-propanol (Aldrich), 1-butanol (Aldrich), phosphoric acid (Aldrich), and Al 1050 (Q-lab) were used as received.
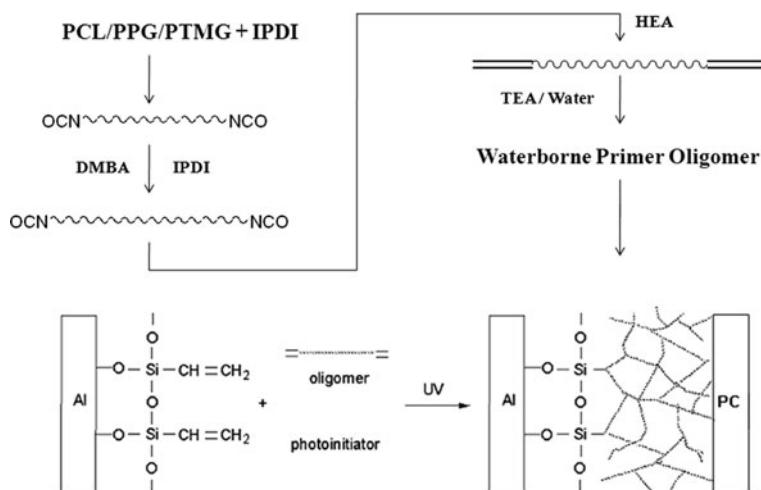
Surface treatment of Al panel

Aluminum panel (4.4×6.0 cm^2) was rinsed with acetone and deionized water, and dried in vacuum oven. Then, it has been immersed in phosphoric acid solution to expose the hydroxyl groups on the surface. The composition of the solution was 1-propanol/1-butanol/deionized water/phosphoric acid = 35/25/22/18 by volume%.

The panel was washed by deionized water, followed by drying in nitrogen flow to prevent surface of the panel from oxidizing. The OH group content of the surface has been indirectly determined by the contact angle measurement. Surface treated Al panel was immersed in ethanol solution with VTMS, water, and HCl for sol–gel reaction (Scheme 1). Reaction proceeded over 3 days at 60 °C, pH 2.

Synthesis of WPU

The recipe for the preparation of WPU is shown in Table 1. Polyol having molecular weight of 600 was charged to a 500 mL four-necked separable flask with a mechanical stirrer, thermometer, and condenser with a drying tube. The reactions were carried out in a constant-temperature oil bath at 70 °C. IPDI and DMBA as ionic center were gradually added to prepare the NCO-terminated PU of desired molecular weight. The NCO-terminated prepolymer was end capped with HEA at 55 °C to obtain the prepolymer of molecular weights of about 5,000 and 10,000, respectively. The prepolymer molecular weight is based on the stoichiometric imbalance between the NCO and OH groups. The progress of reaction has been monitored by FT-IR measurements. Upon completing the end capping reaction, mixture was cooled down to room temperature, and the carboxylic acid groups were neutralized by TEA during the next 2 h. WPU was obtained by adding water to the mixture to a solid content of about 30%. Photo initiator was added to this dispersion

Scheme 1 Overall reaction scheme to prepare WPU primer

Table 1 Recipe for the preparation of WPU (unit: g)

Series	M_c (g/mol)	Polyol (M_n: 600)	IPDI	DMBA	HEA
PCL-5	5,000	18.26	7.80	0.9 (3 wt%)	1.39
PPG-5					
PTMG-5					
PCL-10	10,000	19.25	8.10		0.67
PPG-10					
PTMG-10					

with agitation for 2 h. The resulting products were stable dispersions for over 6 months.

UV curing

WPU was coated at the interfaces between polymer substrate and aluminum panel, followed by compression under 2 kg and drying at 30 °C for 3 h. Then the film was further dried at 80 °C in an electric oven for the next 6 h before it was UV cured. The film as cured under UV lamp (365 nm, 8 W, Crosslink) for 2 h at atmosphere.

By UV cure, chemical reactions between the Al panel and WPU primer are introduced.

Characterizations

The number average diameter of the dispersions was measured by a light scattering method (Submicron Particle Size Analyzer, N5, Beckman Coulter), using a He–Ne laser with wavelength 633 nm. The sample was first diluted in deionized water to 0.5%, followed by ultrasonic wave treatment to homogenize the dispersion.

Contact angles of dispersion cast film with deionized water drop were measured with a conventional contact angle goniometer (G-1, Erma). Tests were made at room temperature and at least five runs were made to report the average.

Fourier transform infrared (FT-IR) spectroscopy was used to confirm the end capping of NCO terminal by HEA at a resolution of 2 cm^{-1}.

AR-XPS (Angle-Resolved X-ray Photoelectron Spectroscopy) and standard XPS measurements were done using VG-Scientific ESCALAB 250 spectrometer AL with Cu-Kα X-ray source.

The tensile properties of the cast films were measured at room temperature with a Universal Testing Machine (UTM) at a crosshead speed of 500 mm/min. Adhesion strength was measured according to the lap shear method using UTM. Dynamic mechanical test of the cast films were performed using a dynamic mechanical thermal analyzer (DMTA, Rheometrics DMTA 3E) at 10 Hz, 5 °C/min, 2% strain over a temperature range from −100 to 100 °C.

Results and discussion

FT-IR measurements

The IR spectra of NCO-terminated PU prepolymer and HEA capped one are showed that the absorption peak of NCO at 2,270 cm^{-1} completely disappeared upon capping with HEA (not shown).

Formation of silane layer

Al panel was immersed in phosphoric solution to expose the OH groups on the surface. It is seen that the contact angle decreases from 89° to 68° as the immersion time increases to 180 s. By this time the surface seems saturated with OH (Table 2).

Figure 1a shows standard XPS measurements of the Al panel which was subjected to the sol–gel reaction. There are three characteristic peaks of Si2p from 98 to 102 eV (99.2 eV (Si–C=C), 100.5 eV (Si 2p), 101.4 eV (Si–O–Si)) showing that the sol–gel reactions between VTMS and OH group of the surface of Al panel have occurred.

AR-XPS (Figs. 1b, 2) show that the atomic ratio (Si/C) decreases along the distance from the surface.

Particle size

The effects of polyol and prepolymer molecular weight on the particle size are shown in Table 3. Particle sizes are in the range of 88.7–124.0 nm and increases along the order of

$$PPG10 < PPG5 < PTMG10 < PCL10 < PTMG5 < PCL5$$

For the same prepolymer molecular weight, the order is agreed with the difference in solubility parameter between water and polyol as noted from 8.63(PCL), 8.90 (PTMG), 12.6 (PPG), and 23.4 (water) (cal/cm^3)$^{1/2}$. It seems that miscibility of polyol in water, i.e., the hydrophilicity primarily governs the particle size of WPU.
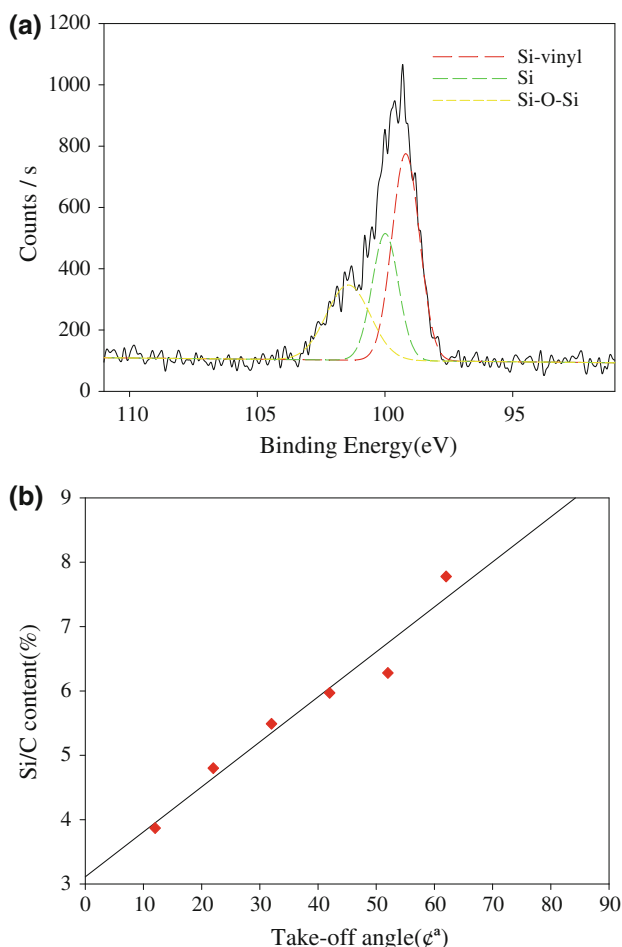
Regarding the effect of prepolymer molecular weight, higher molecular weight prepolymer (10,000) gave smaller particle size than the lower one (5,000) regardless of the type of polyol. This may imply that higher flexibility of the polymer chain makes breakup of the dispersed phase into small drops easier and formation of micelle structure would be more feasible, leading to the decreased particle size.

Mechanical properties

The stress–strain behavior of the WPU cast films are shown in Fig. 3. The WPU made of PCL diol shows the greatest modulus, strength, and lowest elongation at

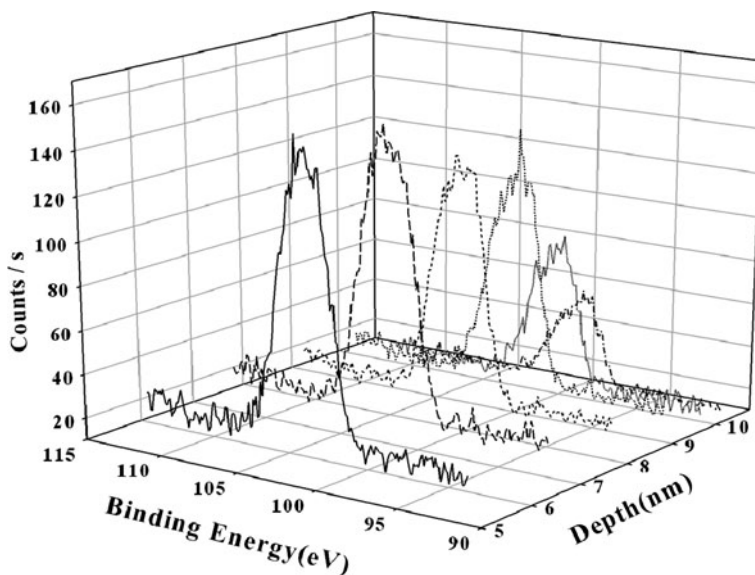**Table 2** Change of contact angle according to the immersion time

Immersion time (s)	0	30	60	90	120	150	180	210
Contact angle (°)	89	86	84	78	75	72	68	68

Fig. 1 Si 2p XPS spectra for treated Al (**a**) and Si/C content according to depth from the surface of treated Al (**b**)

break while PPG based one shows the opposite tendency, regardless of the prepolymer molecular weight. The PTMG based one shows the intermediate behavior. Since the relatively small molecular weight of polyol (500) does not allow soft segment crystallization of PCL, strong hydrogen bonding existing in PCL seems the primary reason for the observed properties. On the other hand, better chain fitting of PTMG molecules over PPG due to its regular structure should provide the material with superior mechanical properties.

Regarding the effect of prepolymer molecular weight, lower prepolymer molecular weight gives higher modulus, strength, and lower elongation at break. This is primarily based on the increased crosslink density to follow in dynamic mechanical properties.

Fig. 2 XPS depth profile of treated Al

Table 3 Particle sizes and adhesion strength of WPU primers

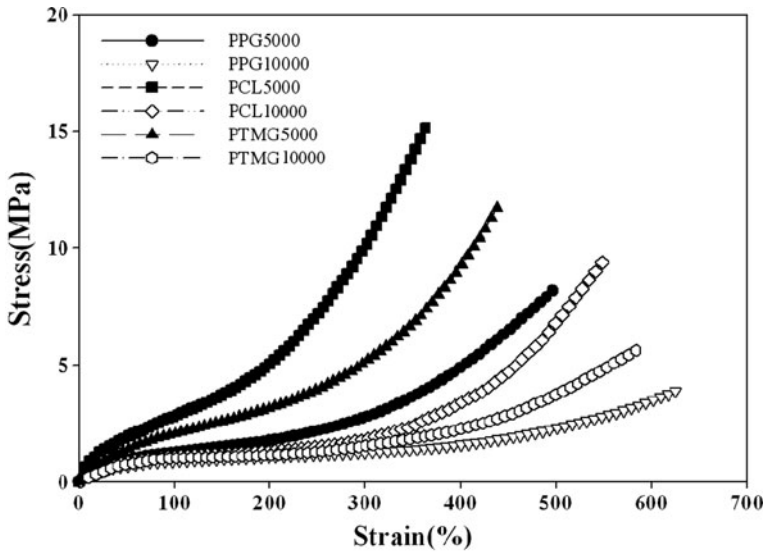|		PTMG-5	PTMG-10	PPG-5	PPG-10	PCL-5	PCL-10
Particle size (nm)		118.7	103	94.5	88.7	124	110.9
Adhesion strength (kgf/cm^2)	Treated Al	4.163	2.484	3.537	1.935	5.489	3.931
	Untreated Al	1.575	0.618	1.297	0.425	2.158	1.058

Dynamic mechanical properties

The dynamic mechanical properties of the WPU cast film are shown in Fig. 4. Rubbery plateaus are well defined for all of the samples. This is an indication that all the WPUs have networked structure which was introduced by the UV cure of HEA termini of the prepolymers. The plateau modulus is in the increasing order of

$$PPG10 < PTMG10 < PCL10 < PPG5 < PTMG5 < PCL5$$

As expected, higher molecular weight prepolymer gives smaller plateau modulus. This is in accordance with the ideal rubber theory as:

$$G_N^o = \frac{\rho RT}{M_c}$$

where G_N^o is the rubbery modulus, M_c is the molecular weight between cross-links, ρ is the density, T is the absolute temperature, and R is the gas constant. The molecular weight of HEA capped prepolymer corresponds to the Mc since HEA termini served as crosslink site under UV cured. Consequently, larger prepolymer gives smaller modulus in rubbery state. At the same prepolymer molecular weight,

Fig. 3 Stress–Strain behavior of WPU films

intermolecular interactions, viz. the hydrogen bond strength should take an important role in determining the rigidity, unless the thermal energy (kT, k = Boltzmann constant) dominate the secondary force.

On the other hand, the tanδ peak temperature of the WPU corresponding to the glass transition temperature (T_g) increases in the order of

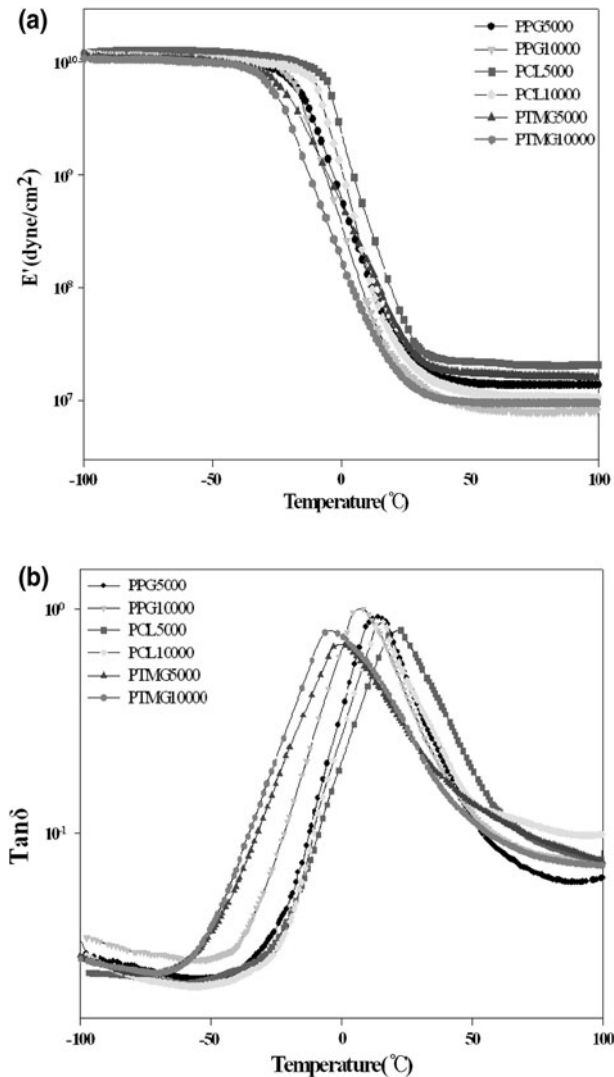$$PTMG10 < PTMG5 < PPG10 < PTMG5 < PCL10 < PCL5$$

The higher T_g of lower prepolymer molecular weight is a direct response of the increased crosslink density. However, the higher T_g of PPG based WPU over the PTMG based one implies that soft segment segment-hard segment phase mixing is favored with PPG segment. This seems reasonable since PPG having less cohesive structure than the regular PTMG is more vulnerable to micro phase mixing with IPDI-DMBA hard segment.

Adhesion strength

The adhesion strengths of the WPUs are given in Table 3. Regardless of the type of polyol being used and prepolymer molecular weight, the VTMS treated panels show approximately threefold higher adhesion strength than the untreated one. This implies that the interface adhesion between the metal and primer is critical in determining the adhesion of metal penal-primer-polymer. That is, chemical hybridization of metal with primer via sol–gel reaction seems crucial to enhance the poor adhesion of organic primer on the metallic surface.

The effect of polyol type on adhesion should mainly come from the intermolecular interaction between WPU primer and PC substrate. In this regard,

Fig. 4 Temperature dependence of storage modulus (E') (**a**) and mechanical loss factor (tanδ) (**b**) of WPUs

PCL is expected to give the highest adhesion with PC due to the structural similarity and strong hydrogen bond between the ester groups of WPU and PC. Among the ether types of polyol, PTMG based WPU gave higher adhesion strength than PPG based one. This is most likely due to the strong cohesion and high glass transition temperature of PTMG based one, as noted from the effect of prepolymer molecular weight. Low molecular weight prepolymer showing high glass transition temperature and mechanical strength gave high adhesion strength.

Conclusions

Water-borne polyurethane primers have been designed and synthesized for use in aluminum–PC interface. It was found that the surface treatment of Al panel in phosphoric acid and chemical hybridization of Al panel with WPU via sol–gel reaction were crucial to enhance the adhesion.

Among three types of polyol being used to prepare the WPU, PCL gave the highest adhesion strength in addition to highest glass and rubbery state moduli, tensile strength, and glass transition temperature. The highest adhesion was due to the structural similarity with substrate while the others due to the strong intermolecular interaction via hydrogen bonding.

On the other hand, PPG gave the lowest properties due to the structural irregularity and weak hydrogen bond. However, better mixing of PPG soft segments with IPDI–DMBA hard segments augmented the T_g of PPG based WPU over PTMG based one.

Smaller prepolymer molecular weight gave improved adhesion as well as other mechanical properties due to the increased crosslink density and cohesive strength.

The particle size was mainly governed by the solubility parameter and crosslink density of the polymer, i.e., smaller difference in solubility parameter and smaller crosslink density gave better dispersion and smaller particle.

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