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High solid and high performance UV cured waterborne polyurethanes

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ABSTRACT

High solid and thermally stable waterborne polyurethanes (WPU) were designed and synthesized by introducing imide groups into the hard segment and locating the anionic groups at the chain termini (terminal ions). It was found that the terminal ions gave rise to a much finer dispersion, higher dispersion stability and viscosity, whereas the conventional hard ions (those containing ionic groups in the hard segments) produced greater water swelling. Also, the terminal ions lead to a high-solid content (50%) at a low ionic content (2%), due to the effective exposure of the ionic groups to the particle surface, owing to the high mobility of the ionic groups and low free energy of the chain ends. When imide groups replaced urethane groups in the hard segment, remarkably enhanced mechanical, dynamic mechanical properties and thermal stability were obtained.

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1. Introduction

Waterborne polyurethanes (WPU) are versatile environmentally friendly materials that are increasingly being used in coatings and adhesives for wood and automobiles, as well as for numerous flexible substrates such as textiles, leathers, papers, and rubbers [1–4]. Generally, WPU have inferior drying rates and slower development of adhesion compared to the conventional solvent-borne PU. In addition, their applications have been limited by the raw materials and manufacturing process. However, problems related to their properties and processing can largely be resolved by their proper molecular design and hybridization with other materials [5–9].

In this regard, producing WPU with a high-solid content and low ionic content have been the main technical issue. A high-solid content facilitates fast drying and easy transportation, whereas a low ionic content gives rise to films having high moisture and hydrolytic stability along with fast drying. The ionic groups are hydrophilic in nature and bind water molecules tightly. Therefore, it has been the basic policy to keep the ionic group content as low as possible, in so far as the dispersion remains stable against coagulation.

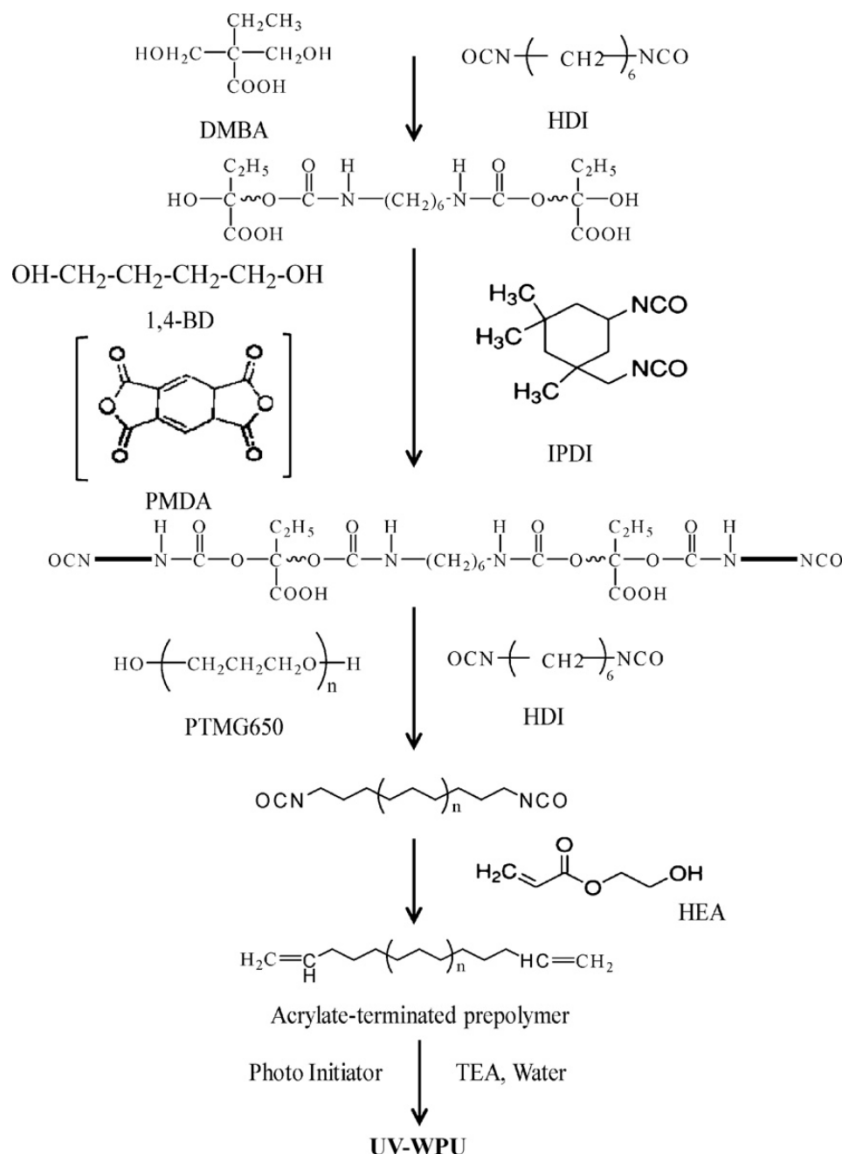
When the dispersion is prepared by the so-called one-shot process [10] or by a prepolymer mixing process [11], ionic centers are incorporated as chain extenders and located among the hard seg-

ments. Consequently, the mobility of the ionic segments is very much limited by the rigidity of the hard segments, and the ionic groups are hardly exposed to the particle surfaces. This necessitates more ionic groups to produce a stable dispersion, yet little has been published in the literature concerning this issue. We previously introduced ionic groups in the soft segments [12]. By doing this, the viscosity of the prepolymer was greatly decreased, leading to the breaking up of the production of fine particles and decreased water swelling of the cast film.

Conventionally, the molecular weight of the PU is increased by the chain extension of isocyanate-terminated prepolymers using short diols. These chain extensions produce many urethane linkages which are vulnerable to thermal decomposition and limit the application. Consequently, various attempts have been made to improve the thermal stability of PU [13,14]. The most widely accepted approach is to introduce thermally stable heterocyclic groups into the HS. Among them, polyimide (PI) has remarkable heat resistance and superior mechanical and durable properties. It is expected that the thermal properties of PU could be improved by introducing imide groups into the backbones of solvent-borne PU [15,16] and WPU as well [17].

We introduced imide groups into the HS of WPU as follows. First, isophorone diisocyanate (IPDI) was reacted with pyromellitic dianhydride (PMDA) to build up the HS of the PU consisting of imide groups. Then, soft segments were built on the chain termini of the HS. Finally, ionic diols were built at the chain termini of the SS. The results compared favorably with WPU extended by diols and those with hard ions, in terms of the dispersion characteristics and

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Scheme 1. Synthesis procedure for UV-WPU carrying ionic groups in the hard segment.

surface, mechanical, dynamic mechanical and thermal properties of the cast films.

2. Materials and methods

2.1. Materials

Polytetramethylene ether glycol (PTMG, $M_n = 650$, KPX Chemicals, Korea) and 1,4-butanediol (1,4-BD, Aldrich) were dried and degassed at 80°C under a vacuum for 2 h before use. Extra pure grades of pyromellitic dianhydride (PMDA, Aldrich) and dimethylol butanoic acid (DMBA, Aldrich) were dried at 50°C for 48 h in a vacuum oven. Extra pure grades of 1,6-hexamethylene diisocyanate (HDI, Aldrich), isophorone diisocyanate (IPDI, Aldrich), 2-hydroxyethylacrylate (HEA, Aldrich) as an end capping agent, dibutyltin dilaurate (DBTL, Aldrich), and α,α' -diethoxy- α -hydroxy acetophenone as photo initiator (Darocur 1173, Ciba Specialty Chemicals), were used as received. Triethylamine (TEA, Fluka) was dried over 4 Å molecular sieves before use.

2.2. Molecular design and synthesis of waterborne polyurethanes

To introduce the ionic groups into the hard domains (called hard ion), a systematic routine was followed, as shown in Scheme 1. An excess amount of HDI was reacted with DMBA to produce the desired molecular weight (this is controlled by the molar imbalance of the reactants). The HDI was the choice of diisocyanate to make the ionic segments flexible. Then, the hard segments (1,4-BD or PMDA + IPDI) were built on the NCO termini of these prepolymers to produce the desired molecular weight. Finally, the soft segments (PTMG + HDI) having NCO groups were built on the termini of these prepolymers. This NCO terminated prepolymer was capped with HEA.

The first step in the synthesis of the terminal ions (Scheme 2) was to build up the isocyanate-terminated hard segments from IPDI and 1,4-BD or PMDA. Then, the soft segments were built on these hard segments. The ionic segments carrying NCO termini were finally added to the termini of the soft segments.

A 500 ml round-bottomed, four-necked separable flask with a mechanical stirrer, thermometer, condenser with a drying tube, and a pipette outlet were used for the reaction. The reactions were

Table 2
Dispersion sizes, viscosities of WPU and contact angles of UV-WPU films.

Series	Dispersion size (nm)	Contact angle (°)	Viscosity (cP)
HB4	176.3	72.5	12.3
TB4	56.2	81.4	23.4
TB3	108.6	85.3	31.5
TB2	220.1	87.2	41.7
TP3	140.8	80.3	35.4

and conductivity change during the emulsification process are well documented elsewhere [19–21]. The resulting product was a stable dispersion with a solid content ranging from 30% to 50%. A 4 wt.% of photo initiator with respect to the polymer amount in the dispersion was added before the dispersion was cast on a polyethylene film and partially dried. Then the film was cured under UV using an UV lamp (365 nm, 8W, Crosslink) for 2 h at atmosphere

2.3. Characterizations

The number average diameters of the dispersions were measured by a light scattering method (Beckmann Coulter #5, Particle Size Analyzer) using a He–Ne laser with a wavelength of 633 nm. The sample was first diluted in deionized water to 0.5%, followed by ultrasonic wave treatment to homogenize the dispersion. The dispersion viscosities were measured with a Brookfield viscometer using an LV.2 spindle. Films were prepared by casting the dispersion onto Teflon, followed by drying at 30 °C for 24 h. The resulting films were heated overnight in an oven at 50 °C under 2–3 mm Hg. The contact angles of the dispersion cast films with a deionized water drop were measured with a conventional contact angle goniometer (G-1, Erma). The tests were conducted at room temperature and at least three runs were made to obtain the average. The swelling of the films was measured by immersing them in water at room temperature. The percentage of swelling for a particular film was determined by measuring its weight increase as a function of time,

$$\% \text{ swell} = \frac{W - W_0}{W_0} \times 100$$

where W_0 is the weight of the dried film and W is its weight after water absorption. The tensile properties were measured with a universal testing machine (Lloyd LRX) at a crosshead speed of 500 mm/min using specimens prepared according to ASTM D-1822. The tests were performed at room temperature and at least three runs were carried out for each material to obtain the average value. The dynamic mechanical properties were measured with a Dynamic Mechanical Thermal Analyzer (Rheometric Scientific, DMTA MK-IV). The experiments were carried out at 10 Hz, 4 °C/min, and 3% strain over the temperature range from –40 to 100 °C. TGA analysis was performed using a TGA Q50 (thermogravimetric analyzer) (TA instrument). The samples were placed in an alumina crucible and heated at 5 °C/min under a N_2 atmosphere, where the flow rate of N_2 was 60–40 ml/min.

3. Results and discussion

3.1. Dispersion size

The dispersion size increases in the following order, depending on the position of the ionic group (in Table 2):

$$TB4 < TB3 < TP3 \ll HB4 \ll TB2$$

In this notation as defined in Table 1, T designates terminal ion, H hard ion, B 1,4-BD extended, and P PMDA extended, and the number designates the ionic content in wt.%. The particle size in the

terminal ions was much smaller than that in the hard ions. This indicates that the concentration of ionic groups at the surface is much higher with the terminal chain than with the hard chain. This can be explained by considering the chain rigidity of the hard segments, the chain flexibility of the soft segments, and the high mobility and low free energy of the chain ends [22]. If the conformation change needs less energy, more ionic groups are exposed to the surfaces during the dispersion. This gives smaller particles with greater dispersion stability. It is noted that TB2 has a comparable particle size to that of the commercially available WPUs, although it has a much higher solid content (50%) at a lower ionic group content (2%). This shows the importance of the molecular design of the WPUs. Also, the dispersion size of TB3 is much smaller than that of TP3, suggesting that the flexibility of the chains adjacent to the ionic groups is important in determining the mobility of the ionic groups. This is more understandable by considering that the overall hydrophilicity of TB3 is lower than that of TP3. It is worth mentioning that very small amounts of well-exposed ionic groups may be sufficient to make high-solid dispersions with sufficient stability.

3.2. Dispersion viscosity

The dispersion viscosity (in Table 2) increases in the following order:

$$HB4 < TB4 < TB3 < TB2$$

The dispersion viscosity is often described by a power law:

$$\eta = 1 + C_1\phi + C_2\phi^2 + \dots$$

where η is the relative viscosity, ϕ is the effective volume fraction of the dispersed phase, and C_1 and C_2 are constants. The order of the dispersion viscosity is agreed with the solid content of the dispersion (TB2 = 50, TB3 = 40, TB4 = HB4 = 30%) since high solid gives high-solid volume fraction. At the same solid content, smaller particle (TB4) gives greater dispersion viscosity than the larger particle (HB4) due to the larger effective volume fraction. This shows that the higher order terms are significant, as well as the first order term, in the above equation. It can be concluded that the smaller particles have a greater dynamic volume under motion at the same solid content and give a greater dispersion viscosity.

3.3. Contact angle

The contact angles of the dispersions (Table 2) increase in the following order:

$$HB4 < TP3 < TB4 < TB3 < TB2$$

The fact that the WPU with the hard ions exhibits the lowest contact angle is likely due to the localized polarity of the hard segments and the ionic groups at the surfaces. A decrease in the ionic concentration decreases the surface polarity, thereby increasing the contact angle.

3.4. FTIR characterization

Fig. 1 shows two types of dispersion cast films having the same ionic content. The shift of the C=O stretch (about 1740 cm^{-1}) to a lower frequency is greater with HB4 than with TB4. This indicates that the intermolecular interactions via hydrogen bonds are more pronounced with the hard ions due to the greater soft segment–hard segment phase separation induced by the greater cohesion of the hard segments.

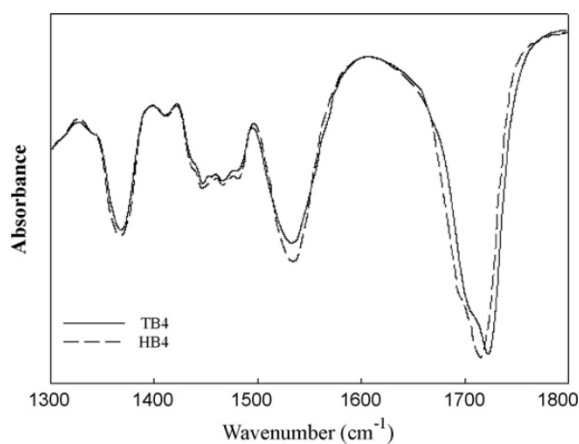


Fig. 1. IR spectra of UV-WPU films having ionic groups at the chain termini (TB4) and in the hard segments (HB4).

3.5. Swelling in water

The swelling of the films in water is shown in Fig. 2. HB4 has the greatest equilibrium and rate of swelling, due to the localized polarity at the surfaces. TB2, having the lowest ionic content, shows the smallest equilibrium and rate of swelling. Between the two terminal ions, the swelling is faster for TP3 than for TB3. This is due to the localized polarity at the surfaces.

3.6. Mechanical and dynamic mechanical properties

Fig. 3 shows the stress–strain curves obtained for the various WPU cast films. When the conventional urethane groups in TB3 are replaced by imide groups in TP3, Young's modulus and tensile strength increase and the elongation at break decreases. The improved mechanical strength of the film with the imide HS is due to the combined effects of the increased hydrogen bondings (one imide group has two carbonyl groups), the dipole interactions of the imide rings present in the HS, and the rigid structure of the HS [23]. HB4 has by far the lowest modulus and strength, presumably due to the greater micro phase separation, as noted from its dispersion characteristics and swelling behavior. The phase separation is shown more clearly by the dynamic mechanical measurements discussed below. Except for TP3, all of the samples show similar stress–strain behavior. This implies that the positions and concentrations of the ionic groups do not have a significant effect on the mechanical properties of the cast films.

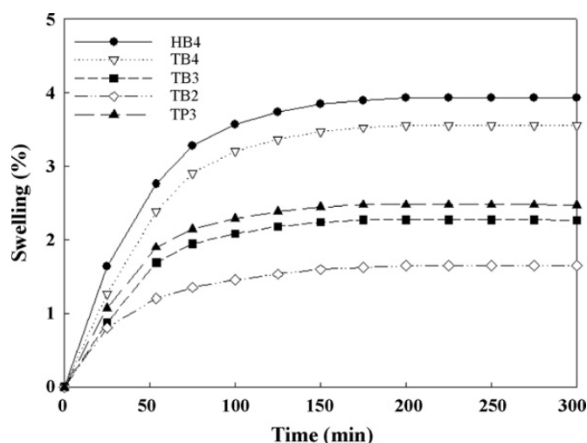


Fig. 2. Swelling of UV-WPU films vs. immersion time in water.

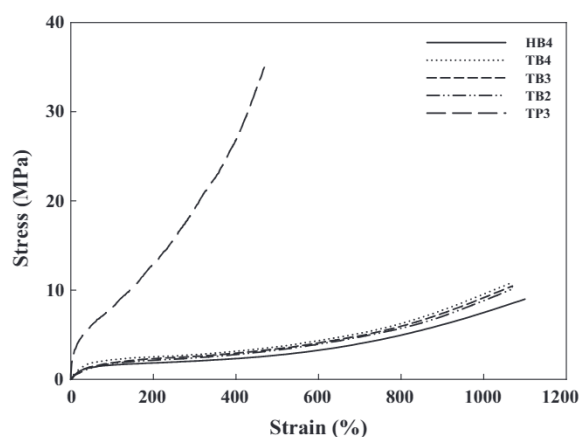


Fig. 3. Stress–strain behaviors of UV-WPU films.

Fig. 4 shows the storage modulus (E') and $\tan \delta$ values for the WPU cast films. All of the samples show two transitions and two $\tan \delta$ peaks indicative of soft segment–hard segment phase separation. Notably, HB4 shows the greatest phase separation based on the difference in the peak temperatures, due to the aggregation of the hydrophilic groups of the HS. The storage modulus increases and the rubbery plateau region extends to a higher temperature when the urethane groups are replaced by imide groups in the UV cured WPU (TP3 vs. TB3) [17].

3.7. Thermal properties

The thermal stability of the UV cured PUD was evaluated by TGA analysis. The typical TG and DTG curves of the UV cured PUD are shown in Fig. 5. Generally, the thermal stability of a polymer is determined by the strength of its weakest bond. It is known that

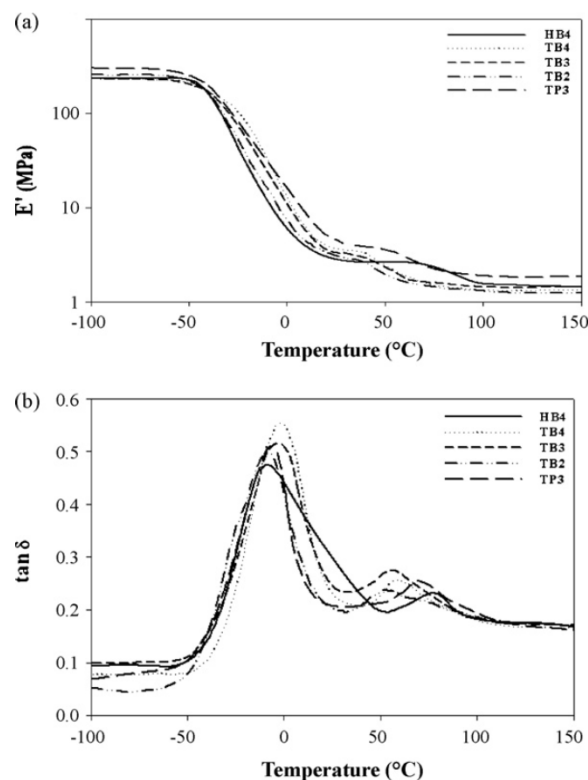


Fig. 4. Storage modulus (a) and $\tan \delta$ (b) of UV-WPU films.

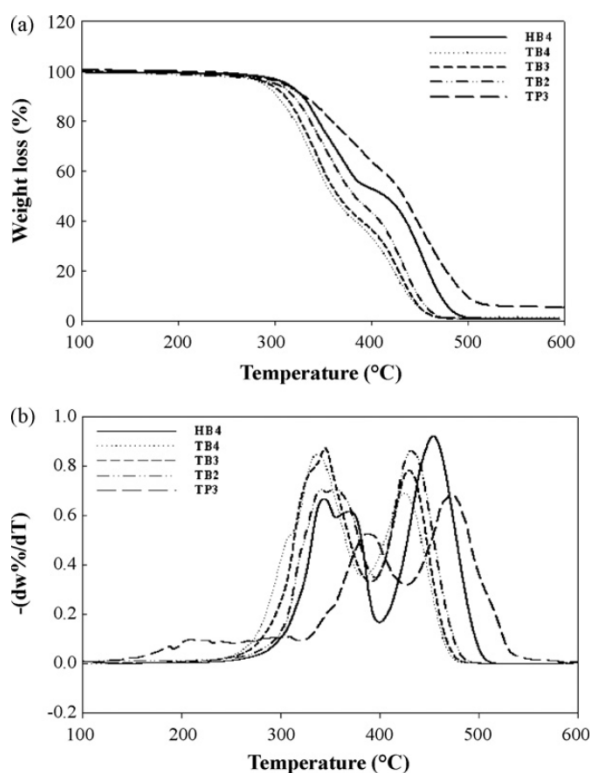


Fig. 5. TG (a) and DTG (b) curves of UV-WPU vs. temperature.

the HS is more prone to thermal decomposition than the SS in PUs. Therefore, the incorporation of imide groups into the HS is expected to improve the initial decomposition temperature of the PU. However, the thermal stability increases throughout the temperature range with the addition of imide HS. This is an indication of the partial mixing of the soft and hard segments [17]. Based on the temperature corresponding to 30% weight loss, the decomposition temperature was increased by about 50 °C for TP3.

4. Conclusions

Thermally stable, high-solid content UV cured WPUs were molecularly designed and synthesized by introducing imide groups into the hard segment and anionic groups at the chain termini of flexible soft segments.

As compared with the conventional hard ions, the terminal ions gave rise to a much finer dispersion with high stability and viscosity, due to the effective migration of the ionic groups toward the particle surface (as noted from the contact angle data), where the migration was favored by the combined effects of the flexible nature of the soft segment and low free energy of the chain ends. Consequently, it was possible to obtain a stable WPU with a high-solid content (50%) at a low ionic content (2%). Moreover, it is believed that this is achieved by the proper molecular design regarding the positions of the ionic groups.

When the imide groups replaced the urethane groups in the hard segment, remarkably enhanced hardness, tensile modulus, strength and thermal stability were obtained. Notably, the thermal stability was increased throughout the temperature range com-

pared to that of the initial decomposition. This implies that the imide HS and SS are partially miscible, thereby rendering the two different types of segments resistant to thermal attack.

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