

Chain-Extended Polyurethane–Acrylate Ionomer for UV-Curable Waterborne Coatings

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Received 30 June 2000; accepted 21 August 2001

ABSTRACT: Conventional and chain-extended UV-curable waterborne polyurethane–acrylate (PUA) ionomers were prepared from diisocyanate, polyethylene glycol (PEG), dimethylolpropionic acid, and hydroxyethyl methacrylate, and identified with FTIR spectra and 500-MHz $^1\text{H-NMR}$ spectra. The number-average molecular weight (M_n) and polydispersity of chain-extended PUA were determined by gel permeation chromatography. For the synthesis of chain-extended PUA, water was employed as the chain extender. The two kinds of PUA prepolymer could be easily dispersed in water in the form of self-emulsified latex after the carboxyl group attaching to the backbone of PUA was neutralized with tertiary amine. The effects of M_n of PEG, carboxyl content, and type of diisocyanate on the interfacial tension and rheological behavior of PUA dispersions were investigated. The chain-extended PUA prepolymer could photopolymerize to a greater extent than the conventional PUA, as indicated by differential photocalorimetry. The photopolymerization kinetics of chain-extended PUA, based on different substrates, were also investigated. The differential scanning calorimetry analysis for the photo-cured films from PUA dispersions suggested that lower M_n of PEG tended to favor phase mixing between soft and hard segment phases, and higher M_n of PEG would provoke phase separation. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 84: 1818–1831, 2002; DOI 10.1002/app.10384

Key words: photocurable; waterborne; coatings; polyurethane; chain extending

INTRODUCTION

Ultraviolet (UV)-curable waterborne coatings have received increasing attention in the past decade because of their advantages of environmental protection, lower energy consumption, high curing speed, rheological controlling, and adaptation to spraying.¹ Polyurethanes have been popularly employed as binders in waterborne coatings for their prominent performance. Polyurethanes for conventional waterborne coatings have

been investigated extensively. To date, however, the studies on UV-curable waterborne polyurethanes have been insufficiently reported. The conventional polyurethane aqueous dispersions are usually obtained by extra-emulsification or self-emulsification. The former may induce the immigration of extra-emulsifier to the surface of dried film, thus provoking potential health problems.² Self-emulsification of polyurethanes is achieved by introducing hydrophilic groups, such as carboxyl or sulfo groups, and polyethylene oxide segments onto/into the backbone of polyurethanes, by using diol monomers bearing hydrophilic groups to react with polyisocyanate, then dispersing in water after being neutralized with tertiary amine.

The common process for preparation of perfect self-emulsified polyurethanes is using dimethyl-

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Contract grant sponsor: Guangdong Natural Science Foundation; contract grant number: 960019.

Journal of Applied Polymer Science, Vol. 84, 1818–1831 (2002)
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olpropionic acid (DMPA) as hydrophilic monomer to react with diisocyanate.³ The resulting modified polyurethane can be dispersed by water after being neutralized with tertiary amine. The main advantages of this self-emulsification are as follows: the dispersing process does not require strong shear force; fine particles with improved dispersion stability are obtained; the water sensitivity of the films after evaporation of water is reduced; and resistance to nonpolar agents is high.⁴ In this process, sufficient hydrophilic monomer DMPA must be employed to endow the polyurethane dispersion with good stability; however, the dried film may exhibit poor water resistance because of the presence of ionic groups in large content. A balance between dispersibility and water resistance can be achieved by incorporating some polyethylene oxide segments into the backbone of ionic polyurethane.⁵

For polyurethane coatings, a higher number-average molecular weight (M_n) of the resin favors film formation and performance of the coatings. However, polyurethane with high M_n is not easy to be evenly dispersed in water because of its high viscosity, especially after having been neutralized with amine. Generally, the chain-extending procedure could be adopted to increase the M_n while isocyanato-terminated polyurethane is dispersed in water after being neutralized with tertiary amine.⁶ In this study, the chain-extended PUA ionomers, which could be photocured in the presence of photoinitiator after a water flash-off step, were synthesized by using water as the chain extender. The properties of the chain-extended PUA dispersions, photocuring behavior of the prepolymers, and performance of the cured films were investigated by comparing with those of conventional counterparts that contained no chain-extending unit in the backbone of PUA ionomers.

EXPERIMENTAL

Materials

Polyethylene glycol (PEG, M_n = 400, 600, 1000, and 2000, Hong Yun Chemical Co., Guangzhou, China) was dried and degassed at 80°C/1–2 mmHg until no bubbling was observed. Hydroxyethyl methacrylate (HEMA, industrial grade, Huang Yan Chemical Co., Zhejiang, China) was redistilled and the fraction at 70–74°C/15 mmHg was collected as a purified reactant. Dimethylolpropionic acid (DMPA; Perstorp Chemical, Sweden), 2-hydroxy-2-methyl-phe-

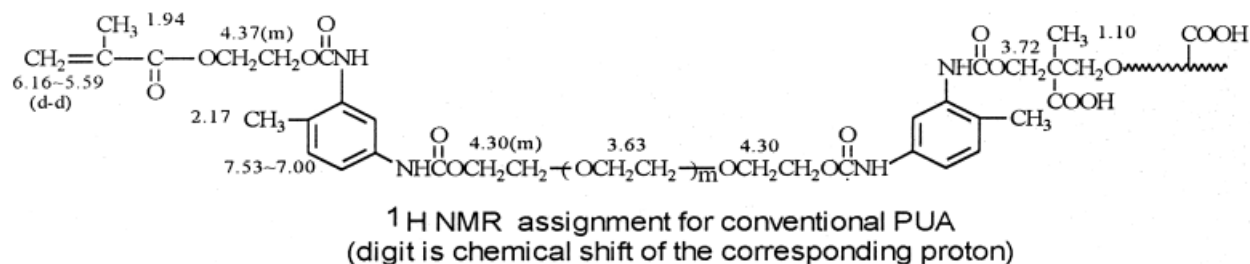
nyl-propan-1-one (photoinitiator Darocur 1173), and 2-hydroxy-4'-(2-hydroxyethoxy)-2-methylpropiophenone (photoinitiator Darocur 2959) were obtained from Ciba Fine Chemical. Triethylamine (TEA, analytical grade), dibutyltin dilaurate (DBTDL), tolylene-2,4-diisocyanate (TDI), and isophorone diisocyanate (IPDI; Fluka Chemical, Ronkonkoma, NY) were used without further purification. Di-*n*-butylamine (chemical pure grade, Xin Hua Reactive Materials Institute, Shanghai, China) was treated with potassium hydroxide pellet and redistilled.

Synthesis of Conventional Polyurethane Acrylate Ionomer

PEG and DMPA were added into a three-necked flask equipped with stirrer, thermometer, and reflux condenser under nitrogen atmosphere. TDI containing 0.03% (w/w) DBTDL was slowly dropped into the reactor. The reaction mixture was stirred efficiently and kept at 45°C for 7 h, to ensure an acceptable reaction rate without gelation. The change of isocyanato group (NCO) value during the reaction was determined by di-*n*-butylamine back titration method to find the end point of the reaction. A stoichiometric amount of HEMA was added to cap all of the terminal NCO group. The capping reaction was stopped until the absorption at 2274 cm⁻¹, which is assigned to the absorption of the isocyanato group, disappeared in the FTIR spectra of the reaction mixture. Then a neutralizing agent TEA and water serving as dispersant were added into the kettle to form a white aqueous conventional PUA dispersion with 30% (w/w) solids content.

Synthesis of Chain-Extended PUA Ionomer

The preparation of isocyanato-terminated polyurethane with carboxyl pendant group was similar to the above. IPDI was also used to prepare the prepolymer. Unlike the conventional method for preparing PUA ionomer, in which HEMA was used to entirely eliminate the isocyanato group, only half the stoichiometric amount of HEMA was used to react with the isocyanate. The end point of this step was indicated by the fact that the NCO value did not change with reaction time. Finally, the neutralizing agent TEA and water serving as chain extender and dispersant were added into the system to form chain-extended PUA dispersion with 30% (w/w) solids content. The pH values of the PUA dispersions were around 7.2.



Scheme 1 ¹H-NMR assignment for conventional PUA (digit is chemical shift of the corresponding proton).

Preparation of UV-Cured Films

The UV-cured PUA films were prepared by casting the formulated aqueous dispersion containing 2% (w/w) photoinitiator Darocur 1173 or Darocur 2959 based on the ionomers onto a tin plate or polytetrafluoroethylene plate and then by curing under a medium pressure mercury lamp (125 W; Philips, The Netherlands) after a water flash-off step.

Measurements

Nicolet 205 FTIR (Nicolet Instruments, Madison, WI) and Varian Unity 500 NMR (Varian Associates, Palo Alto, CA) spectrometers were employed to characterize the conventional and chain-extended PUA prepolymer. The M_n and distribution of PUA prepolymer were determined on a Waters-24 GPC (Waters Associates, Milford, MA) equipped with Styragel HR 1-4 columns (Waters Associates) at 25°C. THF was used as the carrier solvent and polystyrene was used as the standard. The water/air interfacial tension for the PUA dispersion with 30% (w/w) solids content was measured by the Du Noüy ring method on JZHY-180 interfacial tension tester (Chengde Testing Machine Factory, China). The rheological behavior of PUA dispersions was investigated by rotary viscometer RHEOTEST2-50HZ-TYPRV 2 (VEB MLW Prüfgeräte Werk, GDR) at ambient conditions. The particle size of the PUA dispersions was measured on a particle analyzer Autosizer Loc (Malvern) by laser light-scattering method. The samples were diluted with deionized water to adjust the viscosity to 0.927 mPa/s. The UV light intensity was measured by a UV-A radiometer, which is sensitive in the wavelength range of 320–400 nm. The photopolymerization kinetics were investigated on a modified CDR-1 DSC (Shanghai Balance Instrument Factory, Shanghai, China) [known as differential photocalorimeter (DPC)] with a Philips 125-W medium pressure mercury lamp as the UV

source. The exothermal rate as a function of irradiation time was recorded under isothermal conditions. The digitized data, based on the trace on a strip chart recorder, were analyzed by Microcal Origin 5.0 software. Darocur 1173 and Darocur 2959 were used as photoinitiators in the photopolymerization kinetics studies. The kinetics of degradation of the cured PUA films were measured using a Shimadzu TGA-50 instrument (Shimadzu, Tokyo, Japan) from room temperature to 600°C at a heating rate of 10°C/min under nitrogen atmosphere. DSC measurement for the cured films was conducted on a TA 2910 modulated DSC (TA Instruments, New Castle, DE) at a heating rate of 10°C/min under nitrogen purging. The dynamic mechanical properties of the cured PUA films were determined using TA 2980 DMA (TA Instruments, New Castle, DE) at a frequency of 1 Hz with a heating rate of 5°C/min. Some physical properties of cured PUA films were measured according to the Chinese National Standard Test Procedures.

RESULTS AND DISCUSSION

Synthesis, Interfacial Tension, and Rheological Behavior

Diisocyanate could react with DMPA and PEG to form isocyanato-terminated polyurethane prepolymer with pendant carboxyl group. The formation of the prepolymer was evidenced by the emergence of the strong absorption at 1230 cm^{-1} (C—O), 1540 cm^{-1} (N—CO), 1620 cm^{-1} (N—H), 1690 cm^{-1} (C=O), 3415 cm^{-1} (N—H), and by the substantially decreased absorption of NCO at approximately 2274 cm^{-1} .⁷ For the conventional PUA, absorption at 1635 and 870 cm^{-1} , assigned to the acryloyloxyl group, emerged in its FTIR spectra.⁸ The formation of chain-extended PUA

Table I Effect of M_n of PEG on Interfacial Tension of PUA Dispersions

M_n of PEG	Interfacial Tension (mN/m)		Average Particle Diameter (nm)	
	Conventional PUA	Chain-Extended PUA	Conventional PUA	Chain-Extended PUA
400	43.6	43.7		
600	41.3	38.3		
1000	40.7	37.6	187	149
2000	37.0	36.4		

could be identified by the emergence of strong absorption at about 1470 cm^{-1} (N—C—N), 1540 cm^{-1} (N—CO), 1620 cm^{-1} (N—H), 1690 cm^{-1} (C=O), and 3415 cm^{-1} (N—H). The $^1\text{H-NMR}$ chemical shifts for the corresponding protons of conventional PUA are marked in the chemical structure (**Scheme 1**).

There is no appreciable difference in the chemical shift of protons between the $^1\text{H-NMR}$ spectrum of the conventional PUA and that of the chain-extended PUA. This is attributed to the proximity of chemical structure, except that chain-extended PUA contains a urea group. However, the signal at 3.63 ppm, assigned to the methylene of the PEG segment, for chain-extended PUA is approximately twice as strong as that for the conventional counterpart, implying that the molecular weight of PUA prepolymer may double after being chain extended with water.

The molecular weight and its distribution of the prepolymer play an important role in determining the end-use properties of the coatings.⁹ The GPC analysis showed that the number-average molecular weight of chain-extended PUA prepolymer based on PEG 2000 was 1.05×10^4 , which approximately conforms to the theoretical value of 9880. The error of 6.3% is acceptable. It should be noted that the prepolymer has a polydispersity of 1.22, indicating that the molecular weight distribution of the prepolymer is quite narrow.

Table I shows the effects of M_n of PEG on the interfacial tension of two PUA dispersions. Conventional and water chain-extended PUA dispersions have the same 3.8% (w/w) of carboxyl content. As the M_n of PEG in the prepolymer increases from 400 to 2000, these two kinds of ionomers show a gradual decrease in interfacial tension. This is attributed to the changes of inter-chain physical interactions within the ionomers.

As the soft-segment length of the prepolymers increases, coulombic forces between carboxyl anions become weakened and the hydrophobic segments (acryloyloxy group and TDI segments) interact less. As a result, the molecular chains assume more flexible conformation, thereby enabling the hydrophobic moiety of the chains to become less ordered at the air–water surface. Therefore, the interfacial tension decreases. The conventional and chain-extended PUA dispersions with the same viscosity of 0.927 mPa/s have a relatively small particle diameter (in the order of 10^2 nm) as a result of their lower interfacial tension. This indicates that the hydrophilic functional groups (carboxyl anion) could provide the PUA prepolymers with sufficient aqueous dispersibility.

The effect of varying the carboxyl content of the PUA ionomer on the interfacial tension for the chain-extended PUA dispersions is shown in Table II. The interfacial tension for the PUA prepolymer gradually decreases with the increasing content of carboxylic groups. Increased carboxyl content may lead to the generation of strong electrostatic repulsion, especially for the PUA prepolymer containing relatively short soft segments. As a result, the prepolymer molecular chain may assume more extended conformation,

Table II Effect of Carboxyl Content on Interfacial Tension of Chain-Extended PUA Dispersions from PEG 400

Carboxyl Content (wt %)	Interfacial Tension (mN/m)
2.37	48.1
3.19	45.6
3.80	43.7
4.27	39.8

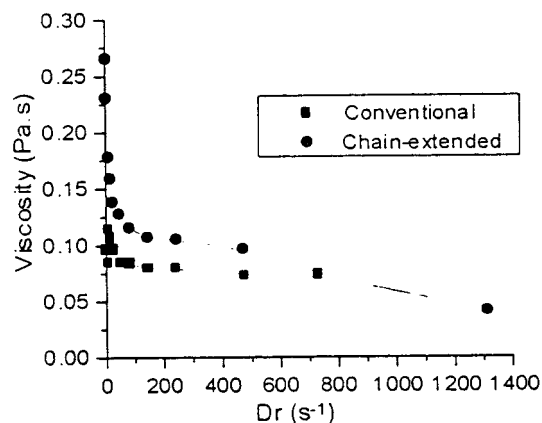


Figure 1 Effect of prepolymer structure on rheological behavior of PUA dispersions from PEG 1000.

which causes the hydrophobic segments to loosely arrange at the air–water interface. Therefore, the interfacial tension reduces.

It is well known that the rheological behavior of a fluid can be described by the exponential equation $\tau = KD^n$, where τ is the shear stress; D is the shear rate; n is the flow index, the value of which is 1 for a Newtonian fluid; and K is the viscosity coefficient. The greater the value of K , the higher the apparent viscosity for the fluid.

Figure 1 shows the rheological behavior of PUA dispersions based on PEG 1000 and TDI. The viscosity for the dispersions decreases with the increased shear rate, indicating that the PUA dispersions exhibit shear thinning or pseudoplastic behavior.

At a lower shear rate, chain-extended PUA dispersion has greater viscosity than that of its conventional counterpart, whereas the viscosity for both dispersions drops to the same value when the shear rate reaches 1300 s^{-1} . This implies that the chain-extended PUA dispersion deviated, to a greater extent, from Newtonian flow behavior than the conventional counterpart. As shown in

Table III, the chain-extended PUA dispersion has a lower flow index. In the course of flowing, the increased shear rate leads to the orientation of the prepolymer molecular chain, thus destroying the associated structure such as hydrogen bonding. As a result, the flow resistance decreases and the viscosity reduces. In addition, the chain-extended PUA dispersion exhibits greater thixotropy than the conventional counterpart. This is ascribed to a lot of physical crosslinking in the chain-extended PUA prepolymer. The crosslinkings are broken down by mechanical shear and, as in pure plastic flow, are reestablished after shearing is discontinued.

It is desirable to possess such pseudoplastic behavior and thixotropy in terms of coatings application, especially for spraying. When the coatings are sprayed from the spray head at a high velocity, the greater shear rate causes the reduction of apparent viscosity of the coatings. The coatings with lower viscosity, resulting from their good flow ability, can be evenly dispersed into fine spraying, thus giving a shiny and generous coat. During storage, the high viscosity of the coatings facilitates transportation efficiency and economic benefit.

Figure 2 shows the rheological behavior of chain-extended PUA dispersions from PEG with different M_n . With the increased shear rate, the viscosity for PUA dispersion from PEG of lower M_n decreases gradually, whereas that from PEG of greater M_n (2000) reduces more drastically. The increasing soft-segment length leads to more flexible molecular chains, among which physical crosslinking such as chain entanglement and hydrogen bonding between urethano and urea groups can be readily formed. In the static state, the PUA dispersion has greater viscosity. When the shear rate increases, the physical crosslinks are broken down, thus leading to the drastic decrease in viscosity. This implies that the PUA

Table III Effect of Different Synthetic Methods on the Rheological Parameters of PUA Dispersions

Sample	M_n of PEG	Flow Index (n)	Viscosity Coefficient (K)	Extent of Thixotropy ($\times 10^2 \text{ Pa s}^{-1}$)
Conventional	1000	0.94	0.11	2.9
	2000	0.86	0.20	7.1
Chain-extended	1000	0.84	0.24	12.0
	2000	0.85	0.19	11.2

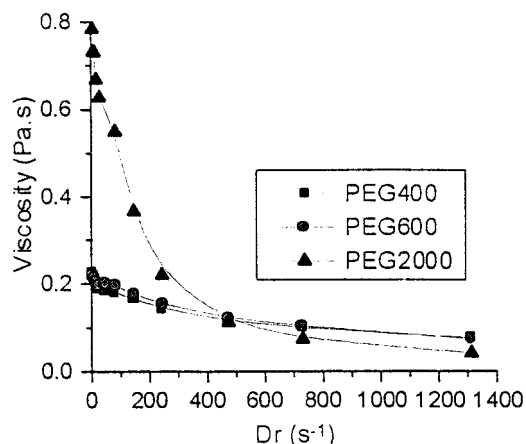


Figure 2 Effect of M_n of PEG on rheological behavior of chain-extended PUA dispersions.

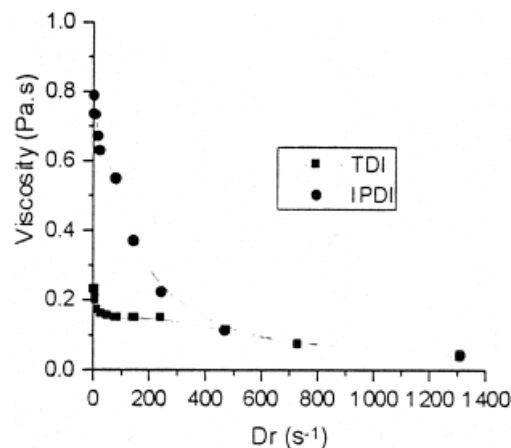


Figure 3 Effect of diisocyanate type on rheological behavior of PUA dispersions from PEG 1000.

dispersion from PEG with higher M_n exhibits shear thinning or pseudoplastic behavior, more distinct than that from PEG with lower M_n .

The hard segment of PUA prepolymer also plays an important role in determining the viscosity of the dispersion. Figure 3 compares the rheological behavior of TDI- and IPDI-based PUA dispersions. The IPDI-based PUA dispersion displays more pronounced pseudoplastic behavior than that of the TDI-based one. Chain entanglement and hydrogen bonding between urethano and urea linkages can be more readily formed in the IPDI-based prepolymer chains because of the flexibility of the chains. These phenomena account for the deviation of the IPDI-based PUA dispersion from Newtonian flow behavior.

The effect of carboxyl content on rheological parameters of chain-extended PUA dispersions from PEG 400 is shown in Table IV. As the carboxyl content increases, flow index generally decreases, whereas viscosity coefficient and the extent of thixotropy vary without obvious regularity. This indicates the complexity of the effect of carboxyl content on the rheological behavior of the PUA prepolymer.

Viscosity, one of those properties that depend on the size of the chains, is strongly affected by chain conformation.¹⁰ As the ionic groups at the chain increase, the mutual repulsion of the same charges causes expansion of the chain, which may result in increasing the viscosity of the PUA dispersion. Moreover, interchain associations resulting from hydrogen bonding between urethano and/or ureylene groups make the chains assume more expanded conformation, which is also responsible to the increase of the viscosity. However, because of intrachain associations caused by the formation of hydrogen bonding, the PUA ionomers may form compact aggregates, thus decreasing the viscosity. Therefore, the viscosity of the PUA dispersion is the consequence of the competition among the above factors. It is naturally difficult to predict the trend of the viscosity (i.e., the change of viscosity coefficient and thixotropy) for the PUA dispersions with varying carboxyl content.

It is important to measure the viscosity of dispersions as a function of solids content, because in the case of UV-curable aqueous resins, water must be evaporated before UV irradiation. Thus,

Table IV Effect of Carboxyl Content on Rheological Parameters of PUA Dispersions from PEG 400

Carboxyl Content (wt %)	Flow Index (n)	Viscosity Coefficient (K)	Extent of Thixotropy ($\times 10^2 \text{ Pa s}^{-1}$)
2.37	0.89	0.12	3.6
3.19	0.87	0.35	4.0
3.80	0.76	0.53	8.7
4.27	0.79	0.30	2.9

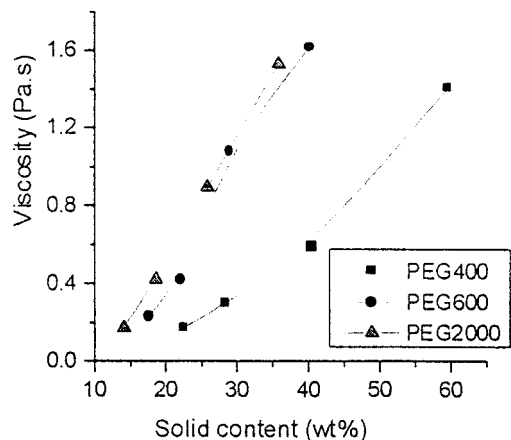


Figure 4 Effect of solids content on viscosity of PUA dispersions.

a higher solid content with the same viscosity is beneficial in terms of energy efficiency.¹¹ Figure 4 shows the effect of solids content on the viscosity of the chain-extended PUA dispersions at a low shear rate of 27 s^{-1} . Regardless of the M_n of PEG in the prepolymer, the viscosity increases with the solids content. This behavior corresponds to the characteristics of condensed polymer solution. However, the viscosity is still relatively low within a very broad range of solids content, which is advantageous to achieve high solids coatings.

UV Curing

Figure 5 shows the DPC curves characterizing the curing behavior of the conventional and chain-

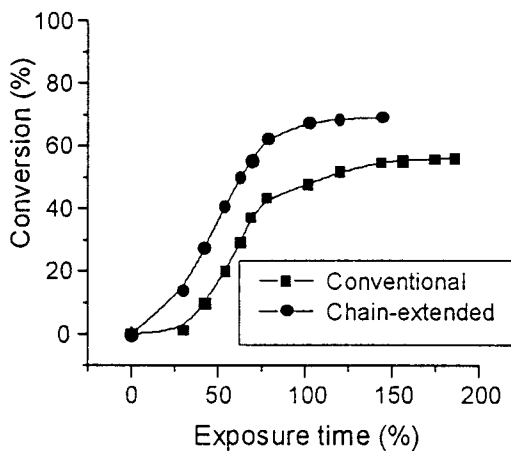


Figure 5 Comparison of DPC curves for the curing of the PUA prepolymers (initiator content, 1.0 wt %; incident light intensity, 0.490 mW/cm^2).

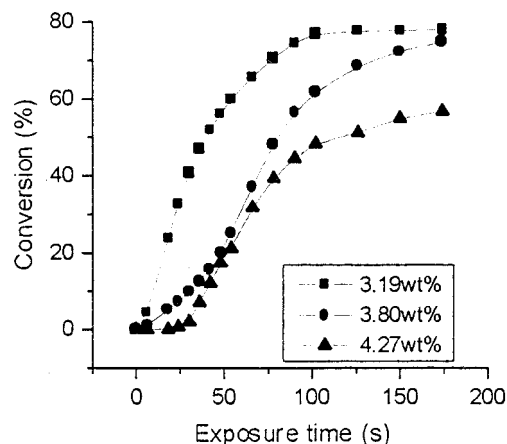


Figure 6 Effect of carboxyl content on curing kinetics of chain-extended PUA from PEG 400.

extended PUA prepolymers. It is obvious that for the chain-extended PUA prepolymer, a sharp exothermal peak is generated after an induction time of 3 s and the maximum of reaction rate is reached in the relatively short time of 12 s, whereas the conventional PUA prepolymer displays less exothermal peaks and requires a longer time to obtain the maximum rate.

Figure 5 illustrates the S-shape for the plots of conversion versus exposure time. It can be seen that for the chain-extended PUA, the conversion increases drastically with exposure time in the early stage, indicating the early occurrence of gel effect and autoacceleration. Because of relatively greater numbers of crosslinking (chain entanglement and hydrogen bonding between urethano and/or urea groups) in the prepolymer, the viscosity of the reacting system may increase drastically with the enhanced conversion, which makes termination by radical combination difficult and thus gives rise to striking autoacceleration. The chain-extended PUA prepolymers have a greater final conversion of cure than that of the conventional prepolymer. This implies that the modification in the chemical structure of the PUA prepolymer is conducive to a greater extent of cure at room temperature, which is of great significance in terms of saving energy.

Figure 6 illustrates the effect of carboxyl content on curing kinetics of the chain-extended PUA prepolymers from PEG 400. As the carboxyl content in the prepolymer increases, the strengthened electrostatic repulsion between the ionic centers makes the chain propagation reaction exceedingly difficult.¹² The reaction rate of chain

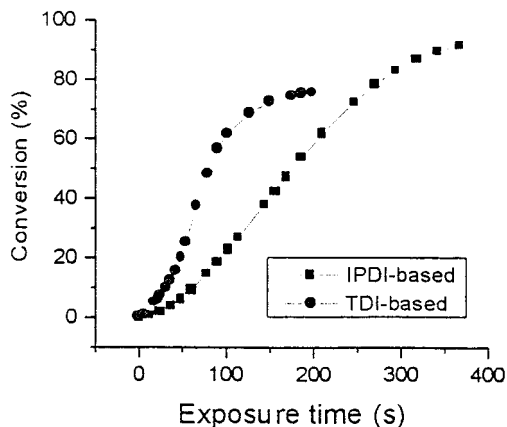


Figure 7 Effect of diisocyanate type on curing kinetics of chain-extended PUA from PEG 400.

termination also decreases to a certain extent. As a result, the curing reaction may proceed less progressively and the final conversion of cure decreases.

Figure 7 shows the conversion of cure for the TDI- and IPDI-based PUA prepolymers from PEG 400 as a function of exposure time. With the increase of irradiation time, the conversion for the TDI-based PUA drastically increases to a maximum of 75.4% at 200 s, whereas the curing reaction for IPDI-based PUA proceeds more steadily. This is attributed to the difference in the chain mobility between these two prepolymers. The moderate rigidity in the hard segments for the TDI-based PUA reduces the molecular chain mobility, causing the gel effect and autoacceleration to occur earlier. In contrast, there is a less striking gel effect during the course of curing for the IPDI-based PUA as a result of its chain flexibility.

However, this dissimilarity in the curing behavior attributed to different diisocyanate types is alleviated for the PUA from PEG 2000, as shown in Figure 8. This implies that the increased soft segments attenuate the effect of the diisocyanate segment on chain mobility. It also can be seen that the IPDI-based PUA has a higher final conversion or extent of cure than that of its TDI-based counterpart. Thus, it is possible that the cured product from IPDI-based prepolymer may develop more integrated phase domains, as demonstrated by its liability to phase separation, discussed previously.

The effect of M_n of PEG on curing kinetics of the chain-extended PUA prepolymers is shown in Figure 9. In general the flexibility of the molecular chain, resulting from the increased length of

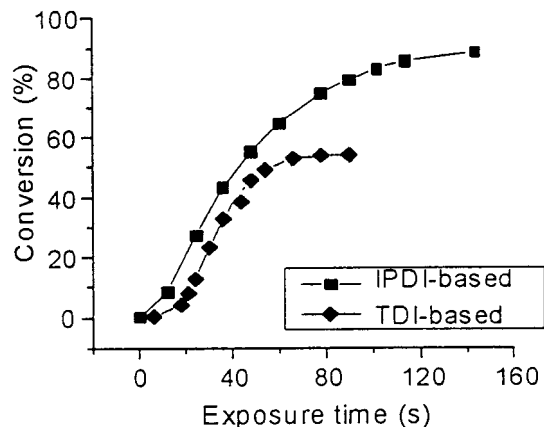


Figure 8 Effect of diisocyanate type on curing kinetics of chain-extended PUA from PEG 2000.

soft segments, may enhance the mobility of chain radicals. On the other hand, the aggravated phase separation of the cured PUA resultant with the increased soft-segment length restricts the movement of the radicals through different phase domains. The occurrence of the gel effect and autoacceleration for the reacting system depends to a greater extent on the interplay of these opposing factors. Therefore, it is not surprising that there is no obvious regularity in the effect of M_n of PEG on the curing kinetics of the PUA prepolymers.

The photoinitiator is one of the important factors in determining the extent of cure for the dried film. Figure 10 compares the curing kinetics for two PUA systems from different photoinitiators, that is, Darocur 1173 and Darocur 2959. It is apparent that a relatively high conversion of cure (>90%) can be achieved for these systems. It

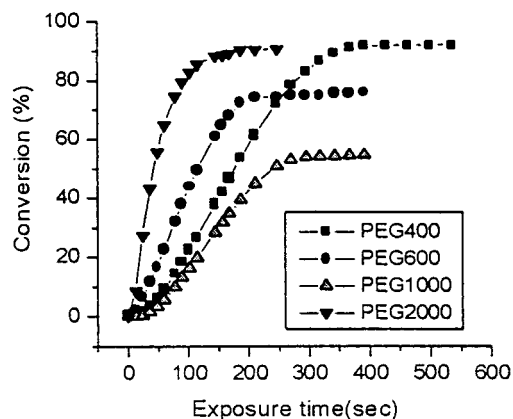


Figure 9 Effect of M_n of PEG on curing kinetics of chain-extended PUA prepolymers.

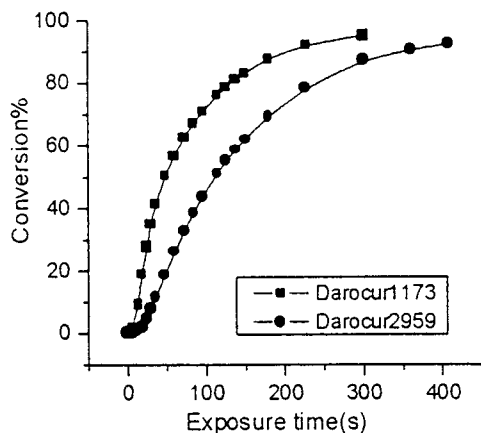


Figure 10 Effect of photoinitiator type on the curing kinetics of the chain-extended PUA prepolymers containing 1.0 wt % photoinitiator.

takes less time for the system based on Darocur 1173 to attain final conversion. This is presumably attributable to the good miscibility of Darocur 1173 (a liquid) with water-based systems after water flash-off.¹³ In spite of its greater aqueous solubility, the solid state of Darocur 2959 may cause it to be less evenly dispersed in the system, thus requiring prolonged time to reach a greater extent of cure. This corresponds with the argument proposed by Green¹⁴ that the photoinitiator with greater hydrophilicity offers good dispersibility in the waterborne system, which is not definitely achieved in the dried film prior to curing.

Glass Transition

It is well known that polyurethanes possess two-phase morphology resulting from phase separation between the hard segment phase and the soft segment phase. The factors that affect the extent of phase separation include copolymer composition, block length, and inter- or intramolecular interactions.¹⁵ There are three possible intermolecular physical interactions within polyurethane ionomers: (1) coulombic forces between ionic groups; (2) hydrogen bonding between urethane and/or urea groups; and (3) association of hydrophobic segments. Thermal and mechanical properties of PU ionomers are subject to the changes of these factors.

As to the water chain-extended polyurethane ionomers, increasing the DMPA/PEG molar ratio increases both the hard-segment content and the ionic group content. The increased hard-segment

(TDI–DMPA) content tends to promote irregularity in the packing of the hard segments, resulting in domains of lower density and order. These hard segments are likely to mix with polyether segments, especially in the case of PEG with lower M_n of 400. On the other hand, because of lower DMPA content, the formation of the ionic multiplets or clusters cannot lead to a driving force strong enough to generate microphase separation. Therefore, only a single glass transition is observed in these polyurethane ionomers over the range of 2.37 to 4.27% (w/w) carboxyl content. With the increase of DMPA content, the amount of PEG incorporated in the PU structure is reduced in stoichiometric fashion. The strengthened coulombic interaction resulting from this relatively increased hard-segment content is attributed to higher T_g and broader transition zone for the PUA ionomers (as shown in Table V).

Table VI shows the effect of M_n of PEG on glass transition of chain-extended PUA-cured films. Irrespective of the type of diisocyanate, there are two glass-transition zones for all PUA ionomers, except those with PEG 400. Generally, the shorter the segments, the more compatible the hard and soft segments.¹⁶ When the phase mixing of hard and soft segments is relatively complete, the backbone mobility of soft segments is restricted by the hard segments within the soft segments, and the hard segments are solubilized by the soft segments within hard segments, and lose their effectiveness as filler or a physical crosslink.¹⁷ Therefore, for the PUA ionomers from PEG 400, only a single glass transition is observed as a result of this phase mixing of hard and soft segments.

In the case of those PUA from PEG with higher M_n , however, soft segments are more likely to be phase separated with hard segment. This leads to the existence of two glass-transition zones. The low glass-transition temperature (T_{gs}) is attributed to the soft-segment phase, whereas the high

Table V Effect of Carboxyl Content on Glass Transition of Chain-Extended PUA-Cured Films

Carboxyl Content (wt %)	T_g (°C)	T_{onset} (°C)	T_{end} (°C)	ΔT_g (°C)
2.37	4	-18	20	38
3.19	39	-6	67	73
3.80	41	-2	81	83
4.27	48	15	93	78

Table VI Effect of M_n of PEG on Glass Transition of Chain-Extended PUA-Cured Films

Sample	M_n of PEG	T_g (°C)	T_{onset} (°C)	T_{end} (°C)	ΔT_g (°C)
TDI-based	400	41	-2	81	—
	600	10	-11	31	38
		48	22	84	
	1000	8	-4	18	42
		50	36	70	
	2000	-15	-25	-4	70
55		29	78		
IPDI-based	400	-4	-18	4	—
	600	-8	-23	-3	53
		45	20	60	
	1000	-8	-23	17	54
		46	38	67	
	2000	-17	-31	-4	67
		50	33	66	

glass-transition temperature (T_{gh}) is attributed to the hard-segment phase. As the M_n of PEG increases, the phase separation of soft and hard segments becomes more remarkable, as indicated by the shifting tendency of T_{gs} and T_{gh} . For the TDI-based PUA, as the M_n of PEG increases from 600 to 2000, T_{gs} gradually moves toward a lower temperature, whereas T_{gh} gradually shifts to an elevated temperature. The difference between T_{gs} and T_{gh} (ΔT_g) increases from 38 to 70°C. This is also the case for the glass transitions of the IPDI-based PUA. However, either T_{gs} or T_{gh} of IPDI-based PUA is lower than that of its TDI-based counterpart because of the chemical structure of diisocyanate. Incorporation of phenyl into the backbone relatively decreases the rotation of single bonds. Consequently, the molecular chains become more rigid, which results in higher T_g . In addition, it should be noted that all of these ionomers have a ΔT_g of over 50°C, indicating that IPDI-based ionomers tend to form a well-defined phase separation once PEG in the soft segment has M_n of over 600.

The effect of M_n of PEG on the glass transition of conventional PUA-cured films is similar to that of chain-extended counterparts. As shown in Table VII, PUA ionomer based on PEG 400 exhibits only a single glass transition as a result of the phase mixing of soft and hard segments. When M_n of PEG increases from 600 to 2000, phase separation between soft and hard segments becomes more pronounced, as indicated by the gradually lowered T_{gs} and enhanced T_{gh} . Accordingly, the change in specific heat of soft- and hard-segment domains gradually increased, respectively.

Thermal Stability

Thermal stability of a coating is vital for its long-term use. In general, polyurethane is not a very thermally stable polymer. The TGA weight loss curve of a typical PU ionomer exhibits two distinct regions of weight loss revealed in the differential weight loss (DTGA) curve. The first part of the degradation correlates with the hard segment (TDI-DMPA-HEMA segment), whereas the second peak reflects the degradation of the soft segment (PEG segment).¹⁸ The onset and maximum peak temperatures of the first step, $T_{1\text{on}}$ and $T_{1\text{max}}$, respectively, as well as the equivalents of the second step, $T_{2\text{max}}$, can qualitatively characterize the degradation of the PUA ionomers.

Activation energy for thermal degradation can be obtained from the measured TGA data using three different analytical methods.¹⁹ Because the mechanism changes during the degradation of polyurethanes, activation energy not only is a function of the chemical structure of polymers but

Table VII Effect of M_n of PEG on Glass Transition of Conventional PUA-Cured Films

M_n of PEG	T_g (°C)	T_{onset} (°C)	T_{end} (°C)	ΔT_g (°C)
400	10	0	34	34
600	20	1	36	35
	63	52	100	48
1000	-1	-14	8	22
	76	50	95	45
2000	-18	-27	-8	19
	90	51	113	62

Table VIII Effect of Carboxyl Content on TGA Parameters of Chain-Extended PUA-Cured Films from PEG 400

Carboxyl Content (wt %)	T_{1on} (°C)	T_{1max} (°C)	T_{2max} (°C)	Residue at 450°C (%)	E_a (kJ/mol)
2.37	228	264	331	10.0	181
3.19	229	278	327	10.1	114
3.80	236	267	320	10.7	77
4.27	244	280	315	10.6	102

also varies with the conversion. The method proposed by Flynn²⁰ is widely applied to calculate the degradation activation energy of PUA because of its simplicity and convenience. This method is applicable only for low conversions, between 1 and 9% of nonisothermal differential weight loss (DTGA) method, with a constant heating rate β . The conversion α is defined by $\alpha = 1 - W(t)/W_0$, where W_0 and $W(t)$ represent initial weight and weight at any time t during the degradation process, respectively. According to Flynn,

$$\frac{d}{d\alpha} \left[T^2 \frac{d\alpha}{dT} \right] = \frac{E_a}{R} + 2T$$

where T is the Kelvin temperature, E_a is the activation energy, and R is the gas constant.

As described previously, the PUA ionomer whose soft segment is composed of PEG 400 does not exhibit distinct microphase separation between the soft- and hard-segment domains. When the carboxyl content in the ionomer increases, the

coulombic forces generated between the ionic centers may increase accordingly and are responsible for the improved thermal stability of PUA. As shown in Table VIII, the greater the carboxyl content, the higher the T_{1on} and the lower the T_{2max} , as well as the greater residue at 450°C. It would be expected that activation energy also increases with the increased carboxyl content; unfortunately, this is not confirmed. This may explain why the difference in carboxyl content is not great enough to show an obvious difference in activation energy. In addition, the selected analytical method allows certain errors in calculation.

Soft-segment length plays an important role in determining the kinetics of thermal degradation for the PUA-cured films. Table IX summarizes the effect of varying M_n of PEG on the TGA parameters of two kinds of PUA-cured films, conventional and chain-extended PUA. Increasing M_n of PEG will augment phase separation between soft- and hard-segment domains. As a result, the first and

Table IX Effect of M_n of PEG on TGA Parameters of PUA-Cured Films

Sample	M_n of PEG	T_{1on} (°C)	T_{1max} (°C)	T_{2max} (°C)	Residue at 450°C (%)	E_a (kJ/mol)
Conventional	400	221	311	393	11.9	104
	600	214	266	362	14.2	236
	1000	209	289	408	14.9	149
	2000	205	289	410	14.4	167
Chain-extended (TDI-based)	400	236	267	320	10.7	77
	600	236	297	362	14.1	93
	1000	230	288	393	15.2	154
	2000	215	288	409	14.4	234
Chain-extended (IPDI-based)	400	235	315	—	6.1	76
	600	218	299	357	5.6	83
	1000	228	296	384	6.6	120
	2000	225	298	398	8.3	178

Table X Crosslink Density of Two Kinds of PUA from PEG 1000

Type of PUA	Crosslink Density ν_e ($\times 10^3$ mol/m ³)
Conventional	0.82
Chain extended	0.66

second weight loss zones, which respectively are assigned to hard- and soft-segment thermal degradation, migrate outward.

It is obvious that the TDI-based chain-extended PUA is superior in thermal stability to the IPDI-based counterpart. The hard segments of the TDI-based PUA contain a rigid aromatic structure, which provides the PUA ionomer with better thermal stability. On the other hand, compared with TDI-based PUA, the liability of IPDI-based PUA to phase separation also contributes to the lower thermal stability.

Crosslink Density

Dynamic mechanical analysis (DMA) is a quick and direct method for the determination of crosslink density of highly crosslinked, unpigmented thermoset coatings from modulus measurements carried out at temperatures well above the T_g .²¹ The relationship between rubbery plateau modulus and crosslink density is very simple²²:

$$\nu_e = G'/RT = E'/3RT$$

where ν_e is the crosslink density, that is, the number of moles of elastically effective network chains per cubic centimeter of sample; G' is the shear storage modulus; E' is the tensile storage modulus; R is the gas constant; and T is the Kelvin temperature.

Table X compares crosslink density of two kinds of PUA-cured films from PEG 1000. It is obvious that crosslink density ν_e decreases in the order of conventional > chain-extended PUA. This presumably depends on the difference in their microphase structures. As described previously, conventional PUA exhibits a well-defined phase separation between soft and hard segments. Because the functional groups used to crosslink lie at the end of hard segments, they are less affected by the soft segments or the other moieties of hard segments. The outcome is that

the resultant crosslinked network has a higher fraction of elastically effective chains and thus shows a greater value of ν_e . For the water chain-extended PUA, the reactivity of the functional groups may be obstructed by the relatively strong interchain physical interaction in the hard segments. Accordingly, there will be more imperfect chains such as dangling ends, loops, and sol in the crosslinked network, which account for the lower crosslink density.

Polyurethanes have found use in a variety of coatings because of the wide range of physical properties obtained through formulating variations in polyurethane coatings.²³ Therefore, it is essential to investigate the relationship between the composition and physical properties of polyurethane coatings.

Table XI shows the effect of M_n of PEG on physical properties of the cured PUA films. It can be seen that the cured PUA films exhibit good adhesion, impact strength, and flexibility. The pendulum hardness for these films reduces with the increase of M_n of PEG. This is attributed to the decrease in the ratio of the effective hard to soft segments and the reduced number of urethane linkages in the hard-segment domain.²⁴ Accordingly, a decrease in the hardness of coatings can be expected. In addition, hardness for the IPDI-based chain-extended PUA-cured films, which are liable to phase separation, decreases to a greater degree than that for TDI-based ones. Table XI also shows that the cured films from conventional PUA exhibit lower hardness than that from chain-extended PUA. This may be ascribed to the lower concentration of hard segments in conventional PUA. There is no direct correlation between gloss and M_n of PEG for the cured films. It seems that the cured films from TDI-based chain-extended and conventional PUA show superior gloss to that of the IPDI-based chain-extended PUA.

The effect of carboxyl content on physical properties of chain-extended PUA-cured films is shown in Table XII. As more carboxyl groups are incorporated into the PUA backbone, adhesion, gloss, impact strength, and flexibility vary only slightly, whereas pendulum hardness increases substantially. This may be attributed to the higher hard-segment fraction from incorporating a higher content of DMPA, which induces greater interchain interaction through coulombic forces and hydrogen bonding.

Table XI Effect of M_n of PEG on Physical Properties of PUA-Cured Films

Sample	M_n of PEG	Adhesion (grade)	Pendulum Hardness ^a	Gloss (60°)	Impact Strength (kg/cm ²)	Flexibility (mm)
Chain-extended PUA						
TDI-based	400	1	0.65	143	>50	1
	600	2	0.59	104	>50	1
	1000	2	0.52	87	>50	1
	2000	2	0.47	90	>50	1
IPDI-based	400	2	0.87	79	>50	1
	600	2	0.85	94	>50	1
	1000	2	0.44	93	>50	1
	2000	1	0.21	78	>50	1
Conventional	400	2	0.50	138	>50	1
	600	2	0.31	107	>50	1
	1000	2	0.28	114	>50	1
	2000	1	0.24	102	>50	1

^a The value for glass is 1.00.

CONCLUSIONS

The conventional and chain-extended PUA ionomers were synthesized and identified with FTIR, ¹H-NMR spectroscopy, and GPC. The two series of PUA dispersions have much lower interfacial tension than that of pure water, small particle size, obvious thixotropy, and relatively low viscosity even at high solids content. These properties favor film formation, storage, and spraying of PUA dispersions. The chain-extended PUA can be photocured to a greater extent than that of the conventional PUA and the photopolymerization conversion of the former, based on flexible IPDI, is higher than that of the PUAs based on rigid TDI. PEG with higher M_n involved in the PUA may promote the phase separation between hard-segment and soft-segment domains, but there may be phase mixing between the hard and soft segments in the cured PUA films, based on PEG

with lower M_n (such as PEG 400), resulting from the short length of PEG involved and the phase separation depressed by the interaction between hard urethano groups. The chain-extending unit (urea group) involved in PUA alleviates the phase separation. Chain extending is an effective method to enhance the thermal stability of cured PUA films. The thermal stability of the cured films from the chain-extended PUA increases with the carboxyl content. Increasing M_n of PEG involved may cause the first and second weight loss zones (assigned to the thermal degradation of hard and soft segment, respectively) to shift outward because of the enhanced phase separation. The cured PUA films possess satisfactory adhesion, impact strength, and flexibility. The cured films from the chain-extended PUA exhibit superior pendulum hardness to that from conventional ones, but show slightly lower gloss. Irrespective of the type of PUA, pendulum hardness

Table XII Effect of Carboxyl Content on Physical Properties of Chain-Extended PUA-Cured Films

Carboxyl Content (wt %)	Adhesion (grade)	Pendulum Hardness ^a	Gloss (60°)	Impact Strength (kg/cm ²)	Flexibility (mm)
2.37	1	0.24	125	>50	1
3.19	1	0.42	135	>50	1
3.80	1	0.65	143	>50	1
4.27	2	0.81	134	>50	1

^a The value for glass is 1.00.

reduces with the increase of the soft-segment length. Incorporation of more carboxyl content may enhance the hardness of the films from chain-extended PUA as a result of the great interchain interaction through coulombic force and hydrogen bonding.

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