

MODIFIED ULTRAVIOLET-CURABLE WATER DISPERSIBLE POLYURETHANE-ACRYLATES*

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Abstract Three kinds of UV-curable self-emulsified polyurethane-acrylate (PUA) prepolymer, i.e., conventional, chain extended and grafted PUAs, were prepared. The relatively small particle size of the PUA dispersions indicates that the PUA prepolymers exhibit sufficient aqueous dispersibility. The PUA prepolymers can substantially lower the interfacial tension of water. Chain-extended PUA dispersions exhibit pseudoplastic behavior and thixotropy to a greater extent than do their conventional counterpart. The chain-extended and grafted PUA photocure to higher conversion than do the conventional PU equivalent. The results of DSC measurement suggest that there exists phase mixing between the hard and the soft segment phases for the PUAs based on PEG 400 that is the comparatively short soft segment in the prepolymer. For the PUA prepolymers based on PEG having higher M_n values, chain-extending and grafting could impede the phase separation between the hard and the soft segment domains. The adhesion, impact strength and flexibility of the photocured films were tested.

Key words UV-curable coatings, Water dispersible, Polyurethane, Acrylate, Graft

INTRODUCTION

Ultraviolet (UV)-curable water dispersible coatings have received much attention in the past decade due to their merits in environmental protection, lower energy consumption, high curing speed, rheology controlling and adaptation to spraying^[1]. Polyurethanes used for conventional water dispersible coatings have been investigated extensively. However, the studies on UV-curable water dispersible polyurethanes have been scarcely reported. The conventional polyurethane aqueous dispersions are usually obtained through the use of diol monomers bearing hydrophilic groups, such as dimethylolpropionic acid (DMPA)^[2]. The major advantages of this self-emulsification include: the dispersing process does not require strong shear forces and fine particles with improved dispersion stability may be obtained^[3, 4].

Acrylic polymers have been widely used as binders for coatings due to their prominent outdoor stability and lower costs. Great efforts have been dedicated to the combination of polyurethanes with acrylic polymers to increase the performance-to-cost ratio of the coatings. One of the popular methods is to blend polyurethanes with acrylic polymers. However, good compatibility cannot be acquired easily through such simple physical blending^[5]. Hybridization or grafting between the two polymers can produce improved compatibility and a higher performance-to-cost ratio^[6]. But UV-curable, dispersible hybrid systems are not easy to attain. Grafting offers a method for obtaining UV-curable water dispersible polyurethane/acrylic polymer complex systems^[7].

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EXPERIMENTAL

Materials

Polyethylene glycol (PEG, M_n = 400, 600, 1000 and 2000) was dried and degassed under vacuum. hydroxyethyl methacrylate (HEMA, industrial grade) was redistilled, glycidyl methacrylate (GMA, Fluka) and methyl methacrylate (MMA) were redistilled under vacuum after the removal of inhibitor, di-*n*-butylamine was treated with KOH pellets and redistilled. DMPA (Perstorp), 2-hydroxy-2-methyl-phenyl-propan-1-one (Darocur 1173, Ciba), tolylene diisocyanate (TDI), dodecyl mercaptan, dibutyltin dilaurate (DBTL) and triethylamine (TEA) were used without further purification.

Synthesis of Conventional PUA Dispersions

TDI, containing 0.03 wt% DBTL, was dropped into a flask containing PEG and DMPA under a nitrogen atmosphere. The reaction temperature was kept at 45°C and maintained for 7 h. The changes in the NCO value during reaction were determined by the di-*n*-butylamine back titration method to find the end point of reaction. Thus, isocyanato-terminated polyurethanes with pendant carboxyl groups were obtained. A stoichiometric amount of HEMA was added to eliminate all the NCO groups until the FTIR absorption peak of NCO at 2274 cm^{-1} disappeared. Water was added to the system under stirring following neutralizing of the polyurethanes with TEA. In this way, a conventional polyurethane-acrylate dispersion with a 30% solid content was obtained.

Synthesis of Chain-extended PUA Dispersions

The method for preparing isocyanato-terminated polyurethanes with pendant carboxyl groups is the same as that described above. Half of the stoichiometric amount of HEMA was used to react with the isocyanates. The end point of this step was indicated by the fact that the NCO value did not change with reaction time. Finally, TEA and water were added to the kettle to form an aqueous dispersion with a 30% solid content.

Synthesis of GMA-MMA Copolymer

The solution copolymerization of GMA and MMA was carried out at 75°C in methyl ethyl ketone (MEK) solution under a nitrogen atmosphere. Benzoyl peroxide was used as the initiator and dodecyl mercaptan as chain-transfer agent. The polymerization lasted for 8 h.

Synthesis of Graft-modified Polyurethane/Acrylate Prepolymer

The GMA-MMA copolymer with epoxy concentration of 0.704 mmol/g was added to the reactor containing conventional PUA prepolymer and stirred at 45°C for 7 h. The molar ratio of carboxyl in PUA to epoxy in copolymer was controlled at 16.1:1 or 9.6:1. TEA was added dropwise to neutralize the unreacted carboxylic groups of the resultant solution. During the time that MEK was distilled from the solution, water was added dropwise to the system. Thus, a milky dispersion of grafting modified polyurethane-acrylate prepolymer was obtained.

Preparation of UV-cured Films

UV-cured films of PUAs were prepared by casting the formulated aqueous dispersion containing 2 wt% photoinitiator, Darocur 1173, based on the prepolymer, onto a tin plate or a poly(terafluoroethylene) plate at room temperature. Curing was conducted under a medium pressure mercury lamp (125 W), after a water flash-off step.

Measurements

FTIR spectra were recorded using a Nicolet 205 FTIR spectrometer. The water/air interfacial tension of the PUA dispersions having a 30 wt% solid content was measured by the Du Noüy ring method on a JZHY-180 interfacial tension tester. The rheological behavior of the PUA dispersions having a 30 wt% solid content or otherwise stated, was investigated using a Rheotest2- 50Hz-TYPRY2 rotary viscometer at ambient condition. Particle size of the PUA dispersions was measured with a particle analyzer Autosizer Loc (Malvern). The samples were diluted with de-ionized water to adjust the viscosity to 0.927 mPa·s.

A modified CDR-1 DSC, differential photocalorimeter (DPC), was used to measure the exothermal rates of

irradiated samples^[8]. The light intensity was measured by a UV-A UV-radiometer, which is sensitive in the wavelength range of 320–400 nm. Exothermal rates as a function of time were observed under isothermal conditions for continuous illumination reactions. The digitized data based on the trace on a strip chart recorder were analyzed with the software Microcal Origin 5.0 on a PC. Conventional DSC measurements of the cured PUA films were carried out under nitrogen purging (50 mL/min) and at a heating rate of 10 K/min from –100 to 100 °C on a TA 2910 Modulated DSC. Some physical properties of the cured PUA films were measured according to The Chinese National Standard.

RESULTS AND DISCUSSION

Characterization of PUA Prepolymer

The formation of the PUA prepolymer is evidenced by the emergence of the strong absorption peaks at about 1540 cm^{-1} (NH–CO), 1620 cm^{-1} (N–H) and 1690 cm^{-1} (C=O) and by the substantially decreased absorption peaks at approximately 2270 cm^{-1} (NCO)^[9]. The formation of the chain-extended PUA prepolymer could be demonstrated by the emergence of the strong absorptions at about 1470 cm^{-1} (N–C–N), 1540 cm^{-1} (NH–CO) and 1690 cm^{-1} (C=O) and by the weak absorption peaks at approximately 2270 cm^{-1} (NCO). The number-average molecular weight (M_n) of the chain-extended PUA prepolymer based on PEG 2000 was determined to be 1.05×10^4 , and the corresponding polydispersity was 1.22. The pendant carboxyl groups of the conventional PUA prepolymer can react with the epoxy groups of GMA-MMA copolymer to produce a grafted PUA prepolymer. The characteristic absorption band of epoxy group at 910 cm^{-1} did not appear in the IR spectrum of the grafted PUA, indicating all the epoxy groups were consumed.

The molar ratio of PEG/DMPA/TDI for the preparation of PUA prepolymers, content of carboxyl group and content of methacryloxyoxyl group in prepolymers are shown in Table 1.

Table 1. Calculated results of the PUA prepolymers

PUA prepolymer	PEG M_n	PEG : DMPA : TDI (molar ratio)	Content of carboxyl		Molar content of methacryloxyoxyl (mmol/g)
			(wt%)	(mmol/g)	
Conventional PUA	400	1 : 1.16 : 2.87	4.17	0.927	1.157
	600	1 : 1.25 : 3.33	4.20	0.933	1.043
	1000	1 : 2.10 : 4.13	4.18	0.929	0.910
	2000	1 : 3.69 : 6.25	4.18	0.929	0.784
Chain-extended PUA	400	1 : 1.00 : 2.67	4.18	0.929	0.620
	600	1 : 1.30 : 3.07	4.19	0.931	0.549
	1000	1 : 1.90 : 3.86	4.19	0.931	0.474
	2000	1 : 3.36 : 5.75	4.17	0.927	0.383
Grafted PUA polymethacrylate* 20% (W/W)	400	1 : 1.13 : 2.84	2.66	0.591	0.920
	600	1 : 1.46 : 3.28	2.65	0.589	0.842
	1000	1 : 2.07 : 4.10	2.66	0.590	0.724
	2000	1 : 3.68 : 6.24	2.65	0.588	0.622

* The content of epoxy in acrylate copolymer is 0.704 mmol/g

Interfacial Tension and Rheological Behavior

The effect of different prepolymer structures on the interfacial tension and on the particle size of the PUA dispersions based on PEG 1000 was compared as shown in Table 2. The three kinds of PUA ionomers can substantially lower the interfacial tension of water. The interfacial tension for the chain-extended PUA dispersions is lower than that of their conventional counterpart. In the case of the chain-extended PUA, the doubled length of the PUA chains improves the flexibility of the molecular chain, which weakens the Coulombic forces between the ionic centers and renders the hydrophobic segments less associated. The three PUA dispersions with the same viscosity of 0.927 mPa·s have a relatively small particle diameter in the order of 2×10^2 nm due to their lower interfacial tension. This indicates that the water-solubilizing functional groups (carboxyl groups) could provide the PUA prepolymers with sufficient aqueous dispersibility.

The rheological behavior of a fluid can be described by the following equation.

$$\lg \tau = \lg K + n \lg D \quad (1)$$

Here τ is the shear stress, D is the shear rate, n is the flow index, K is the viscosity coefficient. The greater the value of K , the higher is the apparent viscosity for the fluid.

Table 2. Effect of prepolymer structure on the characteristics of PUA dispersions from PEG 1000

Sample	Interfacial tension (mN/m)	Average particle diameter (nm)
Conventional	40.2	187
Chain-extended	37.6	149
Grafted*	42.9	167
Deionized water	72.0	—

* The content of GMA/MMA copolymer is 20% (W/W).

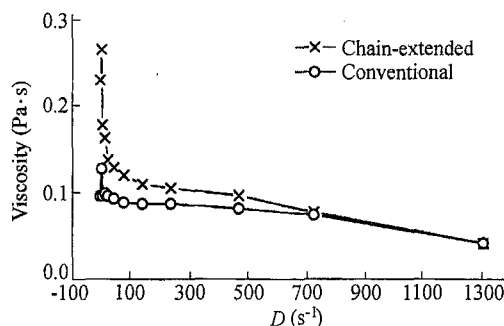


Fig. 1 Effect of prepolymer structure on rheological behavior of PUA dispersions from PEG1000

Figure 1 shows the rheological behavior of conventional PUA dispersions and of chain-extended PUA dispersions. The viscosity of the dispersions decreases with the increase of shear rate, indicating that the PUA dispersions exhibit shear thinning, pseudoplastic behavior. At a lower shear rate, chain-extended PUA dispersion has a higher 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} . As shown in Table 3, 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 chains, thus destroying the associated structure such as hydrogen bonding and chain entanglement. In addition, the chain-extended PUA dispersion exhibits greater thixotropy than its conventional counterparts.

Table 3. Effects of different synthetic methods on the rheological parameters of PUA dispersions

Synthetic method	M_n of PEG	Flow index n	Viscosity coefficient K	Extent of thixotropy ($10^2 \text{ Pa}\cdot\text{s}^{-1}$)
Conventional	1000	0.94	0.11	2.9
	2000	0.86	0.20	7.1
Chain-extending	1000	0.84	0.24	12.0
	2000	0.85	0.19	11.2

UV-curing of PUA Prepolymers

Figure 2 illustrates the S shape of the plots of conversion versus exposure time. The chain-extended and grafted PUA prepolymers have a greater final conversion of cure than 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.

Glass Transition of Cured PUA Films

Polyurethanes usually possess two-phase morphology resulting from phase separation between the hard and the soft segment phase. Factors that affect the extent of phase separation include the copolymer composition, the block length and the inter- or intramolecular interactions^[10]. Table 4 shows the glass transition temperatures of conventional, chain-extended and grafted PUA-cured films. There exists only one glass transition zone for the PUA-cured films based on PEG 400. Generally the shorter the segments, the more compatible are the hard segments and the soft segments^[11]. 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 segment domains, whereas the hard segments solubilize in the soft segments and lose their effectiveness as a filler or a physical crosslink^[12].

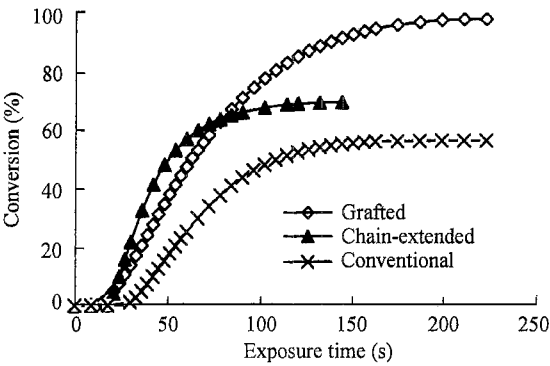


Fig. 2 Effect of the structure of PUA prepolymers (based on PEG 1000) on the photocuring kinetics

Table 4. Glass transition of conventional, chain-extended and grafted PUA-cured films					
PUA	M_n of PEG	T_{onset} (°C)	T_{end} (°C)	T_g (°C)	ΔT_g (°C)
Conventional	400	0	34	10	–
		52	100	63	43
	1000	–14	8	–1	77
		50	95	76	
	2000	–27	–8	–18	108
		51	113	90	
Chain-extended	400	–2	81	41	–
		22	84	48	38
	1000	–4	18	8	42
		36	70	50	
	2000	–25	–4	–15	70
		29	78	55	
Grafted	400	30	56	46	–
		12	30	27	–
	1000	–6	26	14	22
		35	58	36	
	2000	–28	2	–15	65
		15	73	50	

In the PUA-cured films based on PEG with higher M_n , however, the soft segments are more likely to be phase separated with the hard segments. This leads to the existence of two glass transition zones. The low glass transition temperature (T_{gs}) is attributed to the soft segment phase, while the high glass transition temperature (T_{gh}) is due to the hard segment phase. For conventional PUA-cured films, as the M_n of PEG is increased from

600 to 2000, T_{gs} gradually moves towards a lower temperature, while T_{gh} gradually shifts to an elevated temperature. The difference (ΔT_g) between T_{gs} and T_{gh} increases from 43 to 108°C. As to the chain-extended PUA-cured films, the difference (ΔT_g) between T_{gs} and T_{gh} increases from 38 to 70°C. This suggests that chain-extension may impede the phase separation between the hard segment domains and the soft segment domains.

As to the grafted PUA system, acrylate copolymers contribute to the hard segment domains, since they are relatively readily miscible with the hard segments of PU through chemical bonding and hydrogen bonding. As a result, a huge homogeneous hard segment phase, which mainly governs the microstructure of the grafted PU ionomer, is formed. When the length of soft segment is rather short, the backbone mobility of soft segment is greatly restricted by the hard segment domain. Thus, the soft segment characteristic disappears. For the grafted PUA-cured films based on PEG 1000 and 2000, however, the glass transition of soft segment phase still exists. This is because the soft segments are too flexible to be entirely restricted by the hard segment domain. But in comparison with the PUA ionomer prior to grafting, i.e., conventional PUA, T_{gs} of the grafted PUA occurs at elevated temperature. On the other hand, the glass transition of hard segments shifts to a lower temperature because of the improved compatibility between the hard and the soft segment domains that result from the incorporation of acrylate copolymer.

Physical Properties of PUA-Cured films

A comparison of the physical properties of PUA-cured films is shown in Table 5. All of these PUA-cured films possess excellent crosshatch adhesion, impact strength and flexibility. However, the pendulum hardness for these cured films differs significantly due to the distinct interchain physical interactions within PUA network structure. Chain-extension may induce high interchain interaction through hydrogen bonding between the increased urethane and/or urea linkages, while incorporation of acrylate copolymer into the PU may also generate more interchain interaction through hydrogen bonding via the urethane groups and the carboxyl groups. This will enable the hard segments to dominate the properties of PUA-cured films, thus giving higher pendulum hardness values.

Table 5. Effect of chemical structure on physical properties of PUA-cured films from PEG 1000

Sample	M_n of PEG	Adhesion (grade)	Pendulum hardness*	Impact strength (kg/cm ²)	Flexibility (mm)
Conventional	400	2	0.50	>50	1
	600	2	0.31	>50	1
	1000	2	0.28	>50	1
	2000	1	0.24	>50	1
Chain-extended	400	1	0.65	>50	1
	600	2	0.59	>50	1
	1000	2	0.52	>50	1
	2000	2	0.47	>50	1
Grafted	400	2	0.87	>50	1
	600	2	0.90	>50	1
	1000	1	0.86	>50	1
	2000	1	0.57	>50	1

* The value for glass is 1.00.

The effects of the M_n of PEG on the physical properties of PUA-cured films are also shown in Table 5. For the conventional and chain-extended PUA-cured films, the pendulum hardness readily reduces with the increase in M_n of PEG. This is ascribed 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^[13]. As to the grafted PUA-cured films, the pendulum hardness also generally reduces, but to a lesser extent than the conventional and chain-extended ones. This can be attributed to the augmented phase separation with the increasing soft segment length.

CONCLUSIONS

The formation of conventional, chain-extended and grafted self-emulsifiable PUAs is indicated by FTIR spectra. The PUA prepolymers can substantially lower the interfacial tension of water. The chain-extended PUA dispersions exhibit pseudoplastic behavior and thixotropy to a greater extent than their conventional counterpart. The chain-extended and grafted PUAs photocure to a higher conversion than the conventional equivalent. There exists phase mixing between the hard segment phase and the soft segment phase for the PUA-cured films based on PEG 400 which has a shorter soft segment in the prepolymer. For the PUA-cured films from PEG with higher M_n , phase separation between hard segment and soft segment domains takes place, but chain-extension and grafting can impede the phase separation. Chain-extended and grafted PUA-cured films have superior pendulum hardness than that of conventional PUA-cured films. Regardless of the type of PUA, the pendulum hardness decreases with the increase of soft segment length.

REFERENCES

- 1 Garratt, P.G. and Klimesch, K.F., *Eur. Polym. Paint Colour J.*, 1994, 184 (4343): 30
- 2 Satgur, R., McMahon, J. and Padget, J.C., *Surf. Coat. Inter.*, 1994, 10: 424
- 3 Kim, B.K., *Colloid Polym. Sci.*, 1996, 274: 599
- 4 a) Kim, J.Y. and Suh, K.D., *Macromol. Chem. Phys.*, 1996, 197: 2429
b) Song, M.E., Kim, J.Y. and Suh, K.D., *J. Appl. Polym. Sci.*, 1996, 62: 1775
c) Park, N.H., Suh, K.D. and Kim, Y.J., *J. Appl. Polym. Sci.*, 1997, 64: 2657
- 5 Bechara, I. and Bonney, F., *Mod. Paint Coatings*, 1997, March: 34
- 6 a) Kim, B.K. and Lee, J.C., *J. Appl. Polym. Sci.*, 1995, 58: 1117
b) Nair, P.R., Nair, C.P.R. and Francis, D.J., *Eur. Polym. J.*, 1997, 133 (1): 89
c) Hegedus, C.L. and Kloiber, K.A., *J. Coatings Technol.*, 1996, 68 (860): 39
- 7 Yang, J.W., Zeng, Z.H. and Chen, Y.L., *Chinese J. Materials Research*, 2000, 14 (1): 109
- 8 Chen, Y.L., Zheng, M. and Liang, Z.X., *Applied Chemistry (Ch)*, 1994, 11 (2): 27
- 9 Lee, J.J., Chi, Z.K. and Charg, H.H., *J. Appl. Polym. Sci.*, 1995, 57: 1005
- 10 a) Xiao, H., Xiao, H.X. and Frisch, K.C., *J. Appl. Polym. Sci.*, 1994, 54: 1643
b) Eisenberg, A., Herd, B. and More, R.B., *Macromolecules*, 1990, 23: 4098
- 11 a) Sung, C., Smith, T.W. and Sung, N.H., *Macromolecules*, 1980, 13: 117;
b) Lee, M. Y., Lee, J.C. and Kim, B., *Polymer*, 1994, 35: 1095
- 12 Abouzahr, S. and Wilkes, G.L., *J. Appl. Polym. Sci.*, 1984, 29: 2695
- 13 Yang, W.P., *Polym. Mater. Sci. Eng.*, 1992, 66: 216