Synthesis and Characterization of UV-Curable Waterborne Polyurethane–Acrylate Ionomers for Coatings

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ABSTRACT: A new kind of ultraviolet (UV)-curable waterborne polyurethane–acrylate (PUA) ionomer, prepared from toluene diisocyanate (TDI), polyethylene glycol (PEG), dimethylolpropionic acid (DMPA), triethylamine (TEA), and 2-hydroxyethyl methacrylate (HEMA), was synthesized by the modified prepolymer mixing process in which water serves as a chain-extender and dispersant. Fourier transform infrared (FTIR) spectra demonstrated the formation of the PUA ionomers both in dispersions and in their corresponding cured films. Surface tension of the PUA dispersions decreased as the DMPA-to-PEG mole ratio increased. The investigation of rheological behavior of the PUA dispersions suggested that all the dispersions belong to pseudoplastic fluid and display the characteristic of common polymer dispersions. Differential scanning calorimetry (DSC) analysis showed that the increasing DMPA-to-PEG mole ratio may result in a higher T_g and a broader transition zone for the hard segment. The results of TGA for the PUA-cured films indicated good thermal stability with no appreciable weight loss until well above 200°C. Measurement of physical properties showed that all the PUA-cured films exhibited excellent adhesion, gloss, flexibility, and impact strength, as well as pendulum hardness, depending upon hard segment content. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 73: 2869–2876, 1999

Key words: UV curing; waterborne coatings; polyurethane–acrylate ionomers

INTRODUCTION

Ultraviolet (UV)-curable waterborne coatings have received considerable attention in the past decade due to their merits in environmental protection and lower energy consumption. Polyurethane (PU) coatings are one of the well-documented polymeric systems. They have gained widespread acceptance because of their overall balance of properties, such as high impact and tensile strength, abrasion resistance, and toughness, along with excellent resistance to chemicals and solvents.[1,2] The chemistry of waterborne urethanes has been reported in much literature.[3–5] An aqueous polyurethane dispersion is a binary colloidal system in which particles of polyurethane are dispersed in a continuous phase (water). The particle sizes tend to be of the order of 10 or 10^2 nm and have a high surface energy. This results in a strong driving force for film formation, following the evaporation of water.

Conventional polyurethanes are not compatible with water. Therefore, functional groups have to be incorporated into the polymer backbone to provide aqueous dispersibility and stability. In general, waterborne urethanes can be classified according to the nature of their water-soluble dispersing groups, which may be anionic (acids), cationic (bases), or nonionic (hydrophilic polyether chains). Anionic dispersions are commercially predominant. They are commonly prepared by a prepolymer mixing process. An excess of a difunctional diisocyanate, such as toluene diisocyanate (TDI) or isophorone diisocyanate (IPDI), is reacted with a polyoxyethylene diol and a dispersing diol, such as dimethylolpropionic acid (DMPA), to form an urethane prepolymer

that is dispersed with water in the presence of a tertiary amine. Finally, the excess isocyanate may be extended with water or a polyamine. Typically, the finished urethane dispersion has a pH 7–8 and a solids content of 30–40%.

In the meantime, the UV curing technique saves energy and offers rapid curing rate for dispersions. UV-curable waterborne polyurethane dispersion can be prepared by tipping the urethane prepolymer with acrylic functionality, such as 2-hydroxyethyl acrylate (HEA) or 2-hydroxyethyl methacrylate (HEMA), and then formulating with water and a photoinitiator.[6] Using a similar method, a kind of modified UV-curable waterborne polyurethane acrylate (PUA) ionomers for coatings were synthesized; and the effects of varying molar ratios of DMPA to poly(ethylene glycol) (PEG) 400 on the rheological behavior of the ionomer dispersions, as well as the thermal and physical properties of their corresponding cured films, were investigated.

EXPERIMENTAL

Materials

PEG 400 was dried and degassed at 80°C/1–2 mmHg until no bubbling was observed. HEMA (Industrial grade) was distilled, and the fraction at 72°C/15 mmHg was collected as a purified reactant. DMPA (Aldrich Chemical) and 2-hydroxy-4′-(2-hydroxyethoxy)-2-methylpropiophenone (Darocur 2959 from Ciba-Geigy), as well as analytically pure TDI, dibutyltin dilaurate (DBT), and triethylamine (TEA), were used without further purification.

Synthesis of the Modified PUA Dispersions

The modified PUA ionomers were synthesized by three-step processes according to the following reaction scheme:

$$HO-(CH_2CH_2O)_n-H + HOCH_2\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle COOH}{|}}{C}}CH_2OH + OCN-R-NCO$$

(PEG)　　　　　　　(DMPA)　　　　　　　(TDI)

$$\downarrow$$

TDI—PEG—TDI—DMPA—TDI—PEG—TDI

$$\downarrow HEMA$$

HEMA—TDI〜〜〜DMPA〜〜〜TDI

$$\downarrow H_2O, TEA$$

HEMA—TDI〜〜〜NHCONH〜〜〜TDI〜〜〜HEMA
　　　　　$COO^-HN^+Et_3$　　$COO^-HN^+Et_3$

First, PEG and DMPA were added into a three-neck glass reactor equipped with a stirrer, thermometer, and reflux condenser under a N_2 atmosphere. Then TDI containing 0.03 wt % DBT was dropped into the reactor at 45°C. This temperature was maintained for 7 h to ensure an acceptable rate of reaction. The change of the NCO value during reaction was determined by the di-n-butylamine back titration method to find the end point of reaction. Second, unlike the conventional method of preparing PUA ionomers in which HEMA was used to eliminate all the NCO groups, only half of stoichiometric amount of HEMA was needed 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, a neutralizing agent TEA and water serving as a chain-extender and dispersant were added into the kettle to form an aqueous dispersion with 30% solids content. The reaction end point of this step was determined by the disappearance of the infrared (IR) peak of NCO.

Preparation of UV-Cured Films

The UV-cured PUA films were formed by casting the formulated aqueous dispersion with 2 wt % photoinitiator Darocur 2959 based on the ionomer onto a tin plate at room temperature and then by curing the dispersion under a medium pressure mercury lamp (125 W).

Measurements

IR spectra of PUA ionomers and cured films were recorded using a Nicolet 205 Fourier transform infrared (FTIR) spectrometer. The interfacial tension of water/air was measured by Du Noüy ring method (JZHY-180 interfacial tension tester made by Chengde testing machine factory). The rheological behavior of PUA dispersions was investigated by a RHEOTEST2-OHZ-TYRRY2 rotational viscometer at ambient conditions. Thermo-

Table I PUA Film Test Procedures

Property	Procedure
Gloss	GB1743-79
Pendulum hardness	GB/T1730-93
Adhesion	GB1720-79
Impact strength	GB/T1732-93
Flexibility	GB/T1731-93

Figure 1 FTIR spectrum of PUA ionomer.

gravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed to characterize the thermal properties of the cure films. The kinetics of degradation of the PUA films was measured using a SHIMADZU TGA-50 from room temperature to 600°C at a heating rate of 10°C/min and a nitrogen flow rate of 50 mL/min. DSC measurements were carried out with nitrogen purging the sample cell (50 mL/min) and at a heating rate of 10°C/min from −100 to 100°C on a Dupont 2910 Modulated DSC. Some physical properties of the PUA films were measured according to the Chinese National Standard Test procedures listed in Table I.[7]

RESULTS AND DISCUSSION

Formation of PUA Prepolymer and Cured Film

When a moderate amount of water was added to the urethane containing a NCO group on one end and HEMA on the other, a chain-extended poly-

urethane prepolymer could be produced according to the following reaction process:

$$\sim\sim\text{NCO} + \text{H}_2\text{O} \longrightarrow$$

$$\sim\sim\text{NH}_2 + \text{CO}_2$$

$$\sim\sim\text{NCO} \longrightarrow \sim\sim\text{NH}-\overset{\overset{\text{O}}{\|}}{\text{C}}-\text{NH}\sim\sim$$

At the same time, a great number of CO_2 bubbles were given off from the reactants. The termination of these reactions may be discerned by no emission of carbon dioxide. In addition, the formation of the polyurethane prepolymer could be illustrated by the emergence of the strong absorption peaks at about 1470 cm^{-1} (N—C—N), 1540 cm^{-1} (NHCO), 1620 cm^{-1} (NH), 1690 cm^{-1} (C=O), 3415 cm^{-1} (N—H),[8] and by the substantially decreased absorption peaks at approximately 2270 cm^{-1} (NCO), as given in the spectrum of Figure 1.

Figure 2 FTIR spectrum of PUA-cured film.

In order to investigate the curing of acrylates, the absorption bands of acrylate at 1635 cm^{-1} were generally used. Figure 2 showed the IR spectrum of the cured film. In comparison with that of the urethane acrylate prior to UV irradiation, the sharp C=C absorption band at 1635 cm^{-1} depleted after UV irradiation.

Rheological Behavior of PUA Dispersions

The effect of varying DMPA-to-PEG molar ratios on the surface tension of PUA dispersions was shown in Table II. The surface tension of PUA ionomer dispersions gradually decreased as the amount of DMPA in the ionomer increased. This indicated that the more carboxyl groups the systems contained, the finer the particles they formed according to the relationship for the attainable particle diameter in a dispersion process described by Wu.[9] It is also interesting to point out that, like surfactant, the PUA ionomer present in water could substantially lower the surface tension of water. For this reason, it is advantageous to use the PUA ionomers for the preparation of self-emulsified waterborne UV-curable polymer coatings.

The shear-thinning behavior of the PUA dispersions could be observed from shear stress for the dispersions as a function of shear rate, given in Figure 3. In the lower shear rate zone, the shear stress for the dispersions increased with

Table II Surface Tension for the PUA Dispersion

Sample	DMPA to PEG (Mol Ratio)	Carboxyl Amount (Wt %)	Surface Tension (mN/m)
Deionized water	—	—	72.0
A-1	0.50	2.37	48.1
A-2	0.75	3.19	45.6
A-3	1.00	3.79	43.7
A-4	1.25	4.27	39.8

Figure 3 Dependence of shear stress on shear rate for PUA dispersions.

Figure 4 Dependence of viscosity on shear rate for PUA dispersions.

the increasing of the shear rate, while the shear stress became almost constant in the higher shear rate zone, indicating that the PUA dispersions belong to pseudoplastic fluid.

It is well known that rheological behavior of fluid can be described by the following power law equation:

$$\tau = K \cdot D^n \tag{1}$$

where τ is the shear stress, D is the shear rate, n is the flow index and equals 1 for Newtonian fluid, and K is the viscosity coefficient. The greater the K, the higher the apparent viscosity for the fluid.

Equation (1) is transformed into the following logarithmic form:

$$\log \tau = \log K + n \log D \tag{2}$$

where n and K can be calculated from the slope and the intercept of the plot of $\log \tau$ versus $\log D$, respectively.

Table III showed some rheological parameters of the PUA dispersions. All the dispersions had flow index less than one, implying that the rheological behavior of the PUA systems deviates from Newtonian flow. A low viscosity coefficient suggested that the PUA systems display low apparent viscosity.

In the coating system, thixotropy is normally generated by the fracture of some loose associated structure that is established during the static cycle and destroyed by stress. The extent of thixotropy is measured by constructing a so-called thixotropic hysteresis loop. The corresponding shear stress is measured when a series of increasing shear rate was imposed on the tested liquid. Then the same measurement is taken for the reverse step; that is, the corresponding shear stress is measured when the shear rate was gradually decreased. Consequently, the extent of thixotropy is signified by the area enclosed in the thixotropic hysteresis loop. Table III indicated that all the PUA dispersions possessed more or less thixotropy, which is conducive to develop waterborne UV-curable PUA coatings. The thixotropy of the

Table III Rheological Parameters for the PUA Dispersions

Sample	Flow Index	Viscosity Coefficient (Pa s)	Extent of Thixotropy (Pa s^{-1})
A-1	0.89	0.12	3.6×10^2
A-2	0.87	0.35	4.0×10^2
A-3	0.76	0.53	8.7×10^2
A-4	0.79	0.30	2.9×10^2

Table IV Glass Transition Temperatures of PUA-Cured Films

Sample	T_g (°C)	$T_{g\,onset}$ (°C)	$T_{g\,end}$ (°C)
A-1	5	−16	21
A-2	38	0	67
A-3	40	−6	64
A-4	50	2	77

Figure 5 DSC traces for PUA ionomers with varied DMPA-to-PEG mole ratios.

PUA dispersions can be explained in terms of structural changes in the macromolecular chains of the PUA systems. The free flow of the systems were restrained by the increased chain interactions due to the formation of hydrogen bonds between urethano groups (—NH—CO—O—) and/or ureylene groups (—NH—CO—NH—) in the macromolecular chains. When the systems were subjected to a higher shear rate, these hydrogen-bonding associations were broken down. However, as the shear rate diminished, such association failed to be established at once, but regained slowly. Therefore, the PUA dispersions exhibited certain thixotropic behavior.

The effect of shear rate on the viscosity of the PUA dispersions with varying DMPA-to-PEG mole ratios was shown in Figure 4. It clearly illustrates that the viscosity of all the PUA ionomer dispersions decreased as the shear rate gradually increased. This is attributed to the pseudoplastic behavior, which usually arises in common polymer dispersions.

It should be noted that the viscosity for the PUA dispersions with fixed shear rate did not successively increase or decrease with the increase of the DMPA-to-PEG mole ratios. Viscos-

ity, one of those properties depending 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 ionomer dispersion. Moreover, interchain associations due to 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 ionomer is the consequence of the competition among the above factors. It is naturally difficult to predict the trend of the viscosity for the PUA dispersions with varying DMPA-to-PEG mole ratios.

Thermal Properties of PUA Cured Films

It is well known that the factors that affect the extent of phase separation include the copolymer composition, the block length, and inter- or intramolecular interactions.[11] As to the polyure-

Figure 6 TGA and DTGA curves of sample A1 at a heating rate of 10°C/min.

thane ionomers, increasing the DMPA-to-polyol 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 because of the increase in the concentration of the pendant ionic groups. These hard segments are likely to mix with polyether segments.[12] On the other hand, the formation of the ionic multiplets or clusters is also a driving force for the microphase separation.[13] In these polyurethane ionomers, the ionic group content increases with increasing DMPA-to-PEG ratios. Therefore, the Coulombic interaction attributes to higher T_g and broader transition zone for the hard segment, as shown in Table IV and Figure 5.

In general, the TGA weight loss curve of PU ionomer exhibit two distinct regions of weight loss that are reflected in the differential weight loss (DTGA) curve. It is well established that the amount of weight loss of the first region was correlated with the hard-segment concentration, sug-

gesting that degradation of PU ionomer started in the hard segment.[14,15] As shown in Figure 6, the first part of the degradation correlates with hard segment (TDI–DMPA–HEMA segment), while the second peak reflects the degradation of the soft-segment (PEG segment). The onset and maximum peak temperatures of the first step, T_{1on} and T_{1max}, as well as the equivalents of the second step, T_{2on} and T_{2max}, can qualitatively characterize the degradation of the PUA ionomers. Table V summarizes TGA parameters of the PUA ionomers. The results indicate good thermal stability for the PUA iono-

Table V   TGA Parameters of the PUA Ionomers

Sample	T_{1on} (°C)	T_{1max} (°C)	T_{2on} (°C)	T_{2max} (°C)
A-1	228	264	288	331
A-2	229	278	299	328
A-3	236	267	294	320
A-4	244	280	291	315

Table VI Physical Properties of the PUA-Cured Films

Sample	Adhesion (Grade)	Pendulum Hardness[a]	Gloss (60°)	Impact Strength (kg/cm^2)	Flexibility (mm)
A-1	1	0.24	124.7	>50	1
A-2	1	0.42	134.7	>50	1
A-3	1	0.65	142.9	>50	1
A-4	2	0.81	134.3	>50	1

[a] The value for glass is 1.

mers with no appreciable weight loss until well above 200°C. The onset temperatures for hard-segment degradation range from 228 to 244°C, while the equivalents for soft-segment degradation fall in between 287 and 299°C. However, it is not easy to interpret the trend of the degradation behavior for the PUA ionomers with increasing DMPA-to-PEG mole ratios because of the complicated morphology of the samples and experimental deviation.

Physical Properties of PUA Cured Films

Table VI showed some physical properties of the PUA-cured films. It can be seen that the cured films exhibited excellent adhesion, gloss, impact strength, and flexibility. In addition, the PUA-cured films became harder with increasing hard-segment content. Therefore, these PUA ionomers should be useful for various applications in which excellent overall properties are required, such as wood lacquers and plastic coatings.

CONCLUSION

A new kind of UV-curable waterborne polyurethane–acrylate ionomers for coating, prepared from TDI, PEG, DMPA, TEA, and HEMA, were synthesized by the modified prepolymer mixing process in which water served as a chain extender and dispersant. FTIR spectra identified the formation of the PUA ionomers both in dispersions and their corresponding cured films. The surface tension of all the dispersions measured by the Du Noüy ring method was much lower than that of water. As the DMPA-to-PEG mole ratio increased, the surface tension decreased. The rheological behavior of the PUA dispersions investigated by rotational viscometer suggested that all the dispersions belong to pseudoplastic fluid and display the characteristic of common polymer dispersions. DSC analysis showed that increasing the DMPA-to-PEG mole ratio may result in a higher T_g and a broader transition range

for the hard segment because of the Coulombic interaction between the ionic multiplets or clusters. The TGA response for the PUA ionomers indicated good thermal stability with no appreciable weight loss until well above 200°C. Measurement of physical properties showed that all the PUA cured films exhibited excellent adhesion, gloss, flexibility, and impact strength, as well as pendulum hardness, depending upon hard-segment content.

REFERENCES

1. Stenson, P. H. Mod Paint Coat 1990, 6, 44.
2. Schwalm, R.; Hanßling, L.; Reich, W.; Beck, E.; Enenkel, P.; Menzel, K.; Keil, E. Mod Paint Coat 1997, 9, 42.
3. Satgura, R.; McMahon, J.; Padget, J. C.; Coogan, R. C. Surf Coat Int 1994, 10, 424.
4. Dieterich, D. Prog Org Coat 1981, 9, 281.
5. Tirpak, R. E.; Markusch, P. H. J Coat Tech 1986, 58, 49.
6. Kim, H. D.; Kim, T. W. J Appl Polym Sci 1998, 67, 2153.
7. Coatings and Paint Standard Assembly; Chinese Standard Publisher: Beijing, China, 1997.
8. Socrates, G. Infrared Characteristic Group Frequencies; John Wiley & Sons: Chichester, UK, 1980; p. 78.
9. Wu, S. Polym Eng Sci 1987, 27, 335.
10. Billmeyer, F. W. Textbook of Polymer Science; John Wiley & Sons: New York, 1984; p. 218.
11. Hourston, D. J.; Williams, G.; Satguru, R.; Padget, J. D.; Pears, D. J Appl Polym Sci 1997, 66, 2035.
12. Xiao, H.; Xiao, H. X.; Frisch, K. C.; Malwitz, N. J Appl Polym Sci 1994, 54, 1643.
13. Eisenberg, A.; Herd, B.; More, R. B. Macromolecules 1990, 23, 4098.
14. Petrovic, Z. S.; Zavargo, Z.; Flynn, J. H.; Macknight, W. J. J Appl Polym Sci 1994, 51, 1087.
15. Song, Y. M.; Chen, W. C.; Yu, T. L.; Linliu, K.; Tseng, Y. H. J Appl Polym Sci 1996, 62, 827.