

Preparation of Multifunctional Thiol- and Acrylate-Terminated Polyurethane: A Comparative Study on Their Properties in UV Curable Coatings

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ABSTRACT: The multifunctional thiol- and acrylate-terminated polyurethane (PU) has been successfully prepared for using as the main resin in the UV curable coatings. The structure and molecule weight of prepared PUs were analyzed by fourier transformed infrared spectroscopy (FTIR) and gel permeation chromatography, respectively. The results showed that the different terminal multifunctional groups have been grafted onto the PU and their difference in molecule weight was significant. Used as the main resin in coatings, the curing kinetic and percentage conversion of the different UV curing coatings system were investigated by real-time FTIR method, and the effects of terminal functional groups and photoinitiator on the final conversion percentage and conversion rate were also compared. It is observed that the thiol-terminated PU had higher conversion speed and final conversion percentage due to the remarkable effect of mercapto groups on reducing oxygen inhibition during UV curing process. The shrinkage, viscosity, and adhesion of UV curable coatings with thiol- and acrylate-terminated PUs were also investigated and compared, and the results indicated that the former exhibited lower shrinkage and higher adhesion performances than the latter, along with the lower viscosity. © 2014 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* **2014**, *131*, 40740.

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INTRODUCTION

UV curable coating has been widely used in many fields for its high efficiency, low energy consumption, and environmental friendliness.^{1,2} However, the oxygen inhibition of the photopolymerization reaction, resulting from molecular oxygen scavenging radicals, is a deterrent for many potential applications of photopolymerization, which reduces the overall efficiency of UV curable coatings and limits its application.^{3,4} Many physical and chemical methods have been developed to combat the harmful effects of oxygen inhibition. The physical methods include purging the photopolymerization environment with inert gases,^{5–7} isolating the air from UV curable coating by plastic film, increasing the light intensities or photoinitiators contents. While the chemical methods include adopting dual curing technology,^{8,9} and adding effective materials that can consume the oxygen during curing process, such as tertiary amine^{10–14} or thiol.^{15–17}

Thiol has been reported to reduce the effects of oxygen inhibition by undergoing chain transfer with the peroxy radical to

produce a hydrogen peroxide and thiyl radical which can initiate polymerization.¹⁸ Beyond reducing the oxygen inhibition in UV curable coatings, multifunctional thiols have been used to form sulfur linkages in polymer backbones with unsaturated hydrocarbons [e.g., allyl ether, vinyl ether, (meth)-acrylate], epoxies, or isocyanates through click reaction,¹⁹ which is known for its several unique properties, including insensitivity to oxygen inhibition, fast rate, delayed gelation, high crosslink density, and great mechanical property.^{20,21} Therefore, the photo induced thiol-ene radical reaction, especially the thiol-acrylate click reaction has attracted many researchers' interesting during the past decade.²² And the photopolymerization kinetics of different structures of thiol and acrylate have been studied and compared systematically.²³

Despite many potential applications, there are a few drawbacks commonly associated with thiol-acrylate-based UV curable systems, notably odor and self stability,²⁴ which are greatly depended on the molecular weight of the thiol compound and

its concentration in the coatings. The high molecular weight and low concentrations, anchoring thiol on the inorganic particles result in coatings with minimal odor.²⁵ Yang et al.²⁶ prepared multifunctional thiol- and ene-terminated polyurethane (PU) aqueous dispersions, respectively, the double components were separated to resolve the self stability problem. Otts²⁷ added multifunctional thiol into the water PU acrylate dispersion, and results showed that the curing efficiency and mechanical properties of coatings were improved. In addition, several studies for a successful functionalization of photoinitiator via Michael addition with small thiol molecules have been performed.^{28,29} However, to the authors' best knowledge, there are only a few studies comparing the preparation and properties of multifunctional thiol- and acrylate-terminated PU in the UV curable coatings.

The goal of this study was to prepare multifunctional thiol- and acrylate-terminated polyurethane for using in the UV curable coatings. More specifically, polymerization kinetics, the functional groups conversion, volume shrinkage, and adhesion were evaluated for thiol-terminated PU in coatings and the acrylate-terminated PU was used as reference. It can effectively move the industrial application of photo induced thiol-acrylate click reaction for reducing the oxygen inhibition of UV curable coatings.

EXPERIMENTAL

Materials

Isophorone diisocyanate (IPDI) purchased from Bayer and polyoxypropylene diol (PPG, $M_w = 1000$) purchased from Tianjin Petrochemical Corporation were used to prepare PU. Allyl pentaerythritol ether (APE) and pentaerythritol tetra (3-mercaptopropionate) (tetrathiol) were used to terminate the PU. Dibutyl tin dilaurate (DBTDL) and triethylamine (TEA) were used as catalysts for the hydroxyl-isocyanate and thiol-isocyanate reaction, respectively, and both of them were purchased locally. Tripropylene glycol diacrylate (TPGDA) and trimethylolpropane triacrylate (TMPTA) were provided by UCB chemicals. 1-hydroxy-cyclohexyl-phenyl ketone (HCPK) from Ciba-Geigy was used as a free radical photoinitiator. All other chemicals were analytical pure reagents and used as received without further treatment.

Synthesis of Multifunctional Thiol- and Acrylate-Terminated PU

A 250 mL, four-necked flask equipped with a mechanical stirrer, nitrogen purging system, thermometer and a refluxing device was used as a reactor. First, PPG (50.0 g, 0.05 mol) with $M_w = 1000$ was degassed *in vacuo* for 1 h at 110°C. After the temperature was reduced to 60°C, then 22.2 g (0.1 mol) IPDI and a drop of DBTDL were added into the reactor and the mixture was stirred at 70°C until the isocyanate (NCO) content reached about 5.8 wt %. So the isocyanate group (NCO)-terminated prepolymer was obtained. The multifunctional thiol-terminated PU was obtained by dropping the above prepolymer into the 48.9 g (0.1 mol) tetrathiol at room temperature within 10 min and a drop of TEA was used as catalyst. The mixtures were further reacted at 60°C for 1 h. The complete consumption of NCO was confirmed by the disappearance of the fourier transformed infrared spectroscopy (FTIR) isocyanate peak at

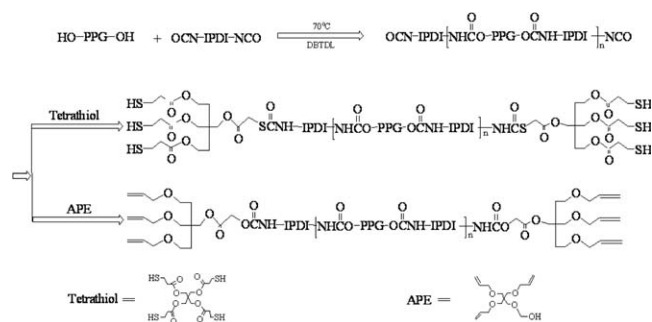


Figure 1. The synthesis scheme of thiol- and acrylate-terminated PU.

2250 cm^{-1} .^{19,30} While the multifunctional acrylate-terminated PU was obtained by adding 25.6 g (0.1 mol) APE into the NCO-terminated prepolymer at 70°C, and a drop of DBTDL was used as catalyst. The mixture was stirred at 70°C until the NCO groups can not be detected in FTIR. The synthesis scheme was given as shown in Figure 1.

Preparation of UV Curable Coatings with the Prepared PU

The UV curable coatings in this study were a mixture of obtained polymer, TPGDA, TMPTA, and HCPK. The mass fraction for TPGDA, TMPTA, and HCPK were fixed as 50, 45, and 5, respectively. Different levels (10, 20, 30, and 50 mass fraction) of multifunctional thiol- or acrylate-terminated PU were used as base resin. The obtained mixtures were blended under stirring at room temperature and the different UV curable coatings were prepared.

Instrument and Characterization

FTIR spectra were recorded on a FTIR (Nicolet 360) with KBr pellets. The molecular weights of products and the square ratio of different components were determined by gel permeation chromatography (GPC) equipped with a waters 1515 isocratic HPLC pump and 2410 RI detector. THF was used as the solvent, and numerical values for the molecular weights were generated by comparison to a polystyrene calibration curve.

The photopolymerization kinetics of UV curable coatings was studied by real-time infrared spectroscopy, which was performed using a Nicolet Magna-IR System 750 spectrometer with a DTGS-KBr detector. The detail characterizing method is undergone according to the previous reports.^{31,32} Each of the IR spectra obtained from the spectrometer is an average of three scans and the time to acquire each spectra was 10 s. The spectra were obtained one after another to ensure that the UV curing process was analyzed in real time. The kinetic conversion can be calculated from the decay of the stretching vibrations of the acrylate functional groups at 810 cm^{-1} , and the carbonyl group at 1700 cm^{-1} was used as an internal standard as this peak remained unchanged during the course of the experiment. All experiments were performed at 25°C. The initiation light source was a 200 W medium pressure mercury lamp, which gave a UV light intensity at the sample of 50 mW/cm^2 and the main wavelength of 365 nm.

The viscosities of coating were measured by a NDJ-79 rotation viscometer (Shanghai Scientific Instrument, China) at 25°C.

To measure the volumetric shrinkage of the UV curable coatings, the coating samples were glued onto glass substrates and

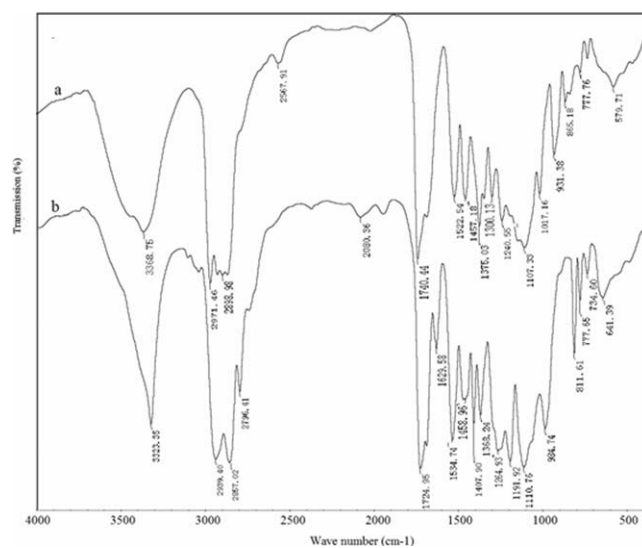


Figure 2. FTIR spectra of multifunctional thiol- (a) and acrylate- (b) terminated PU.

cured by spot curing equipment with the light intensity of 80 mW/cm² for 300 s. After complete curing of the cured films for about 24 h, the volumetric shrinkage of sample was determined by measuring the density change of each resin sample before and after UV curing according to the following equation.³³

$$\text{Shrinkage (\%)} = \frac{1/d_{\text{after}} - 1/d_{\text{before}}}{1/d_{\text{before}}} \times 100\%$$

where d_{before} is the density of sample before curing and d_{after} the density of a resin after curing. The densities of the cured samples were determined by the displacement method by using a Mettler AX105DR density determination kit.

This adhesion test was performed in accordance with DIN ISO 1520. First, the coatings were coated onto the 2 × 25 mm² tinplate, and the adhesion testing of the resulting cured films was done by scribing the coated area with a cross-hatch cutter, applying 3M 610 tape to the cross-hatched area and rapidly pulling from the cross-hatched area. The cross hatches were judged by their appearances and marked with notes from 0 (not flaked off) to 5 (>65% flaked off).

RESULTS AND DISCUSSION

Preparation and Characterization of Multifunctional Thiol- and Acrylate-Terminated PU

To investigate the antioxidant inhibition of thiol-terminated PU, we first prepared the prepolymer by PPG and IPDI, then the prepolymer was terminated by multifunctional thiols, at the same time, the multifunctional acrylate-terminated PU was prepared and used as reference. FTIR is a simple and powerful tool to detect the reaction. Figure 2 shows the FTIR spectra of thiol- and acrylate-terminated PU. Both figures show no band at about 2250 cm⁻¹, suggesting NCO has completely reacted. In addition, there are several strong bands between 3305 and 3361 cm⁻¹ (relating to NH), between 1625 and 1655 cm⁻¹ (relating to C=O), between 1542 and 1560 cm⁻¹ (relating to NH) as well as between 1226 and 1255 cm⁻¹ (also relating to

NH), suggesting the formation of the urethane-urea.³⁴ As shown in Figure 2, acrylate-terminated PU shows absorption peak at 1635 and 810 cm⁻¹, associated with the CH=CH₂ stretching band, whereas the thiol-terminated PU shows absorption peak centered at 2570 cm⁻¹, attributed to the S—H functional groups.¹⁶ It can be concluded that the functional groups have been successfully grafted onto the terminus of PU.

The reaction between NCO and OH or SH is easily to carry, but the expected polymer with narrow molecule weight distribution is usually difficult to control. As for APE, there is only one active hydroxyl group, which is used only for terminal agent for preparing PU. Therefore, the mole ratio of 1 : 2 between NCO-terminated prepolymer and APE can ensure the expected PU product is obtained effectively. It has been previously reported that tertiary amine-catalyzed thiol-isocyanate reactions give a single thiocarbamate product with no side products.^{35,36} The NCO and SH can react to form thiourethane structure without other structures. However, four same thiol groups of tetrathiol make it not only can be used as terminal agents but also as extender or crosslinker during the click reaction between tetrathiol and NCO-terminated prepolymer. Therefore, the perfect six thiol functional oligomer cannot be effectively obtained. The final products are the mixture of multiple thiol-terminated polymers; therefore, the adding order is dropping NCO-terminated prepolymer into the tetrathiol within 10 min, and the temperature is controlled at room temperature, the TEA is used as catalyst. To further understanding the reaction and final products, the quantitative analysis of functional groups and molecule weight analysis are useful to understand the reaction progress and the final product.

The thiol concentration of thiol-terminated PU, determined by the method of Ellman,³⁷ is 1.95 mmol/g, which is lower than the theoretical thiol content of 2.48 mmol/g. While the acrylate groups of acrylate-terminated PU, determined by the iodometric method, is 2.82 mmol/g, which is near to the theoretical value of 3.07 mmol/g. As expected, the tetrathiol used as crosslinker is almost inevitable. The GPC results showed that the average molecule weight of NCO-terminated prepolymer is about $M_n = 1560$ g/mol. While the thiol-terminated PU had higher average molecule weight ($M_n = 6452$ g/mol) and broader distribution than acrylate-terminated PU ($M_n = 3570$ g/mol), which indicated that portion tetrathiol was used as extender or crosslinker in the reaction. According to the molecular weights and functionality of the PU and the acrylates, the concentration of thiol and acrylate functional groups was calculated as shown in the Table I.

Photopolymerization Kinetics of UV Curable Coatings

Both real-time FTIR and photo-DSC are the powerful analytical methods for monitoring UV initiated curing processes which proceed within a fraction of a second. However, the limitation of photo-DSC is its long response time and necessary knowledge on the theoretical enthalpy of reaction. Especially for the coatings with different amounts of acrylate functional groups, the theoretical enthalpy is not constant, which led to much inconvenience in calculating conversion. Consequently, we chose the real-time FTIR method to study the kinetics of UV curing

Table I. The Concentration of Thiol and Acrylate Functional Group in the Different UV Curing System

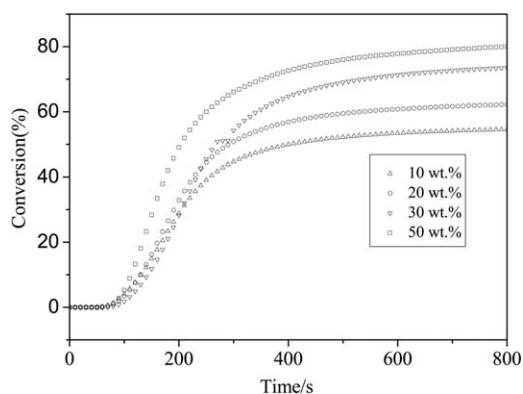
| Oligomer kind and content (%) | | —SH concentration (mmol/g) | —CH=CH ₂ concentration (mmol/g) |
|-------------------------------|----|----------------------------|--|
| Thiol-terminated PU | 10 | 0.177 | 5.80 |
| | 20 | 0.325 | 5.32 |
| | 30 | 0.450 | 4.91 |
| | 50 | 0.650 | 4.25 |
| Acrylate-terminated PU | 10 | 0 | 6.05 |
| | 20 | 0 | 5.79 |
| | 30 | 0 | 5.56 |
| | 50 | 0 | 5.19 |

process in this work according to our previous method.³⁸ The acrylate double bonds conversion is obtained according to the following:

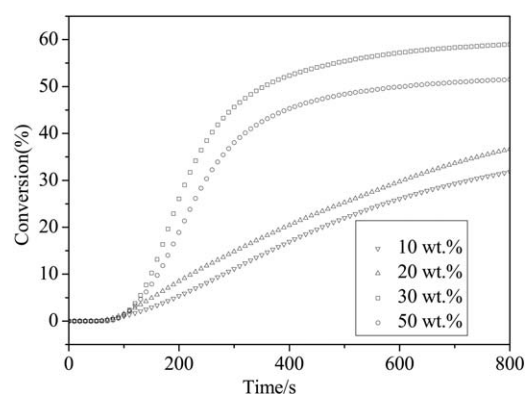
$$\text{Conversion (\%)} = \frac{A_{0(\text{C}=\text{C})}/A_{0(\text{C}=\text{O})} - A_{t(\text{C}=\text{C})}/A_{t(\text{C}=\text{O})}}{A_{0(\text{C}=\text{C})}/A_{0(\text{C}=\text{O})}}$$

where $A_{0(\text{C}=\text{C})}$ and $A_{t(\text{C}=\text{C})}$ are the integrated area of acrylate double bonds in the range of 1533–1673 cm^{-1} at the initial time and the time t , respectively. Meanwhile, $A_{0(\text{C}=\text{O})}$ and $A_{t(\text{C}=\text{O})}$ are the integrated area of carbonyl group absorption peak in the range of 1688–1828 cm^{-1} at the initial time and the time t , respectively.

The prepared polymer, the main resin of UV curable coatings, had significant influences on the properties of coatings. To determine the effect of thiol- and acrylate-terminated PU on acrylate polymerization, the monomer used in this study was fixed as TMPTA and TPGDA with mass ratio of 50 : 45, and 5% HCPK was used as photoinitiator. The UV curable compositions containing 10, 20, 30, and 50 wt % of thiol- and acrylate-terminated PU were detected using real-time FTIR. Based on the FTIR results, the conversion percentage versus time plots for coatings with thiol-terminated PU and acrylate-terminated PU was given in Figures 3 and 4, respectively.

**Figure 3.** The influences of amount of thiol-terminated PU on the acrylate double bonds conversion of UV curable coatings.

With increasing thiol- or acrylate-terminated PU from 10 to 50 wt % in UV curable coatings, the percentage conversion (which are related to the crosslink density) increased progressively for thiol-terminated PU, while first increased and then decreased for acrylate-terminated PU. It can be ascribed that the comprehensive effect of the functionality of resins, viscosity, and oxygen inhibition. First of all, the UV curing process is usually realized by forming the crosslink structure with the resin as backbone and with monomer as dilutes. The functionality and the functional groups content of resin play an important role during the UV curing process. Generally, the higher functionality leads to higher curing speed, the ideal multifunctionality of prepared PU exhibited faster curing speed than the active monomer TPGDA and TMPTA. Consequently, the curing speed of the coatings increased with the increasing prepared PU with the content from 10 to 30 wt %. Second, the viscosity of UV curable coatings is a key factor that determines the mobility of coating and the oxygen diffusing rate into the formations.¹³ Most of the UV curable resins have a relatively high viscosity, especially for the polymer with higher functionality. The higher viscosity will lead to lower molecular mobility, and therefore, the oxygen existing in the coatings is hard to release. Consequently, the polymerization speed and the final conversion percentage are decreased. However, the increasing resins content lead to the higher viscosity and higher functionality, which are competing and conflicting factors to influence the curing speed of coatings. After the content of resins reached 50 wt %, the viscosity of UV curable coatings reached about 1000 mPa s and the effect of viscosity prevailed than the functionality of resins, as a result, the UV curable formations with 50 wt % acrylate-terminated PU exhibited lower curing speed and conversion than that with 30 wt %. However, the thiol-terminated PU exhibited sustainable increasing trend rather than the opposite trends. It can be attributed to the last but the most important factor, antioxygen inhibition effect of thiol group. It is well known that the thiol group can reduce oxygen inhibition of UV curable coatings by forming active peroxide radicals via thiol-acrylate click reaction. Multifunctional thiol-terminated PU not only provided many active positions for thiol-acrylate click reaction, which increased the curing speed and final conversion, but also reduced the initial crosslink speed by the long chain of

**Figure 4.** The influences of amount of acrylate-terminated PU on the acrylate double bonds conversion of UV curable coatings.

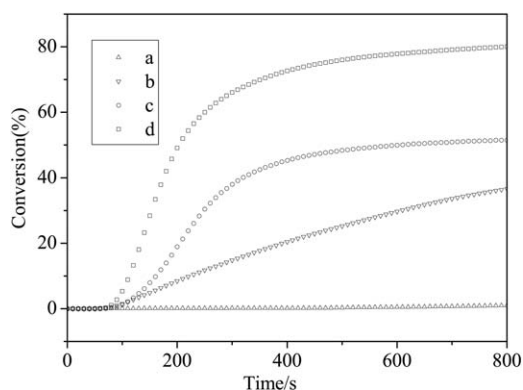


Figure 5. The influences of photoinitiator on the acrylate double bonds conversion of the UV curable coatings (a) 50 wt % acrylate-terminated PU without photoinitiator, (b) 50 wt % thiol-terminated PU without photoinitiator, (c) 50 wt % acrylate-terminated PU with 5% HCPK, and (d) 50 wt % thiol-terminated PU with 5% HCPK.

PU and reduced the awful odor of small molecular thiol compounds.

Effect of Photoinitiator on the Thiol-Acrylate Polymerization

It can be easily concluded that the thiol-acrylate polymerization exhibits lower oxygen inhibition than traditional photo induced acrylate polymerization. In addition, the previous research reported that the thiol-acrylate can be polymerized without additional photoinitiator by adding some small molecule thiol.³⁹ To further identify the similar properties of the thiol-terminated PU, the UV curing kinetics of coatings containing 50 wt % thiol- or acrylate-terminated PU, with and without photoinitiator, were investigated and compared, respectively. Figure 5 shows conversion rate of coatings containing thiol- and acrylate-terminated PU with and without photoinitiator. As for the UV curable system without photoinitiator, the conversion curve is nearly to a straight line for coatings based on acrylate-terminated PU, indicated that there is almost no curing reaction with about 15 min UV light irradiation. However, the coatings based on thiol-terminated PU exhibited obvious exothermic process and the final conversion can reach about 40%, which is only 10% lower than the coatings based on acrylate-terminated PU with 5% HCPK. The trends are same and more significant

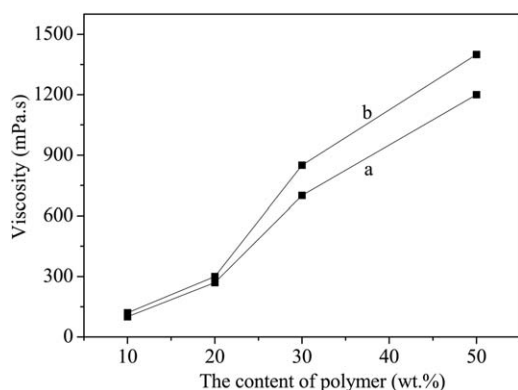


Figure 6. The effect of thiol- (a) and acrylate- (b) terminated PU on the viscosity of UV curable coatings.

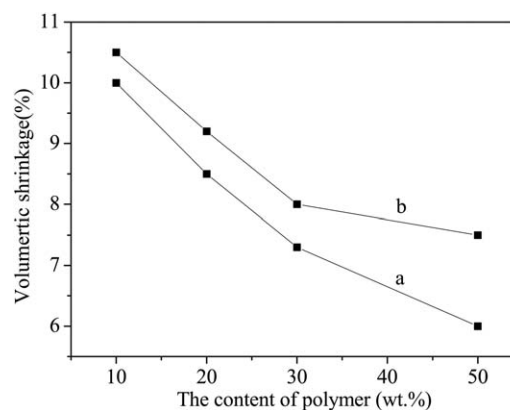


Figure 7. The effect of thiol- (a) and acrylate- (b) terminated PU on the volumetric shrinkage of UV curable coatings.

for the systems with 5% photoinitiator HCPK, the final conversion is about 80% for coatings based on thiol-terminated PU with 5% HCPK, while the value is only 50 wt % for corresponding acrylate-terminated PU. It can be concluded that the terminal mercapto groups of PU can play the similar role in the thiol-acrylate polymerization.

Effects of PU on the Properties of UV Curable Coatings

Viscosity. Figure 6 shows the viscosity variation with the increasing content of prepared PU. It can be seen that the viscosity of coatings increased with the increasing amount of PU and the difference between thiol- and acrylate-terminated PU is not clear, especially for the lower content. When the content of PU reached 50 wt %, the viscosity of coatings with acrylate-terminated PU was 1400 mPa s, and 1200 mPa s for the coatings with thiol-terminated PU. The thiol-terminated PU shows slight lower viscosity but higher molecule weight than the acrylate-terminated PU. It is possibly ascribed to the lower rotational energy barrier of C—S in thiol-terminated PU than C=C in acrylate-terminated PU. Consequently, the mobility of former macromolecule is better and therefore results in lower viscosity.

Shrinkage and Adhesion

It is well known that thiol-ene click reaction exhibits dramatically lower volume shrinkage and shrinkage stress due to the step-growth mechanism and the delayed gel point

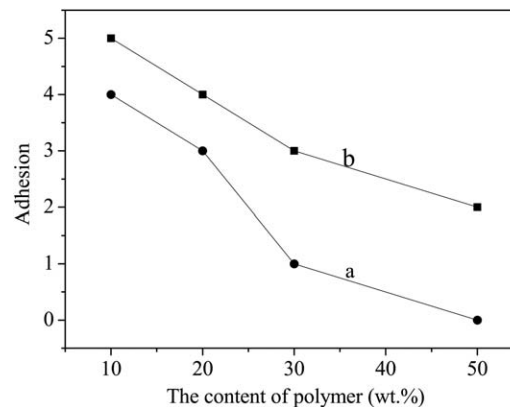


Figure 8. The effect of thiol- (a) and acrylate- (b) terminated PU on the adhesion strength of UV curable coatings.

conversion,^{40,41} the thiol-terminated PU is also no exception. As expected, the shrinkage stress of thiol-terminated PU is actually less than the corresponding acrylate-terminated PU as shown in Figure 7. With the increasing amounts of thiol-terminated PU from 10 to 50 wt %, the reduction of volumetric shrinkage is from 0.5 to 1.5 compared with acrylate-terminated PU.

The higher thiol content can delay the gel point more significantly, as a result, much of the shrinkage occurs prior to gelation and this phenomenon dramatically reduces the shrinkage stress in the final polymer material. The lower shrinkage property brings, as a consequence, better adhesion to surfaces (as shown in Figure 8) because of the decrease in the buildup of stress during the formation of films.⁴²

CONCLUSIONS

The multifunctional thiol- and acrylate-terminated PU were prepared and characterized, respectively. Results show that the terminal functional groups of PU are 1.95 mmol/g mercapto groups and 2.82 mmol/g acrylate groups.

With the different levels of prepared PU as main resin in UV curable coatings, their differences in curing kinetics, viscosity, volumetric shrinkage, and adhesion were investigated. The thiol-terminated PU exhibited significant better properties than corresponding acrylate-terminated PU, including remarkable antioxidant inhibition, and the coatings even can be cured without photoinitiator after UV irradiation; relative lower shrinkage of 6% with 50 wt % prepared PU, and outstanding adhesion property. It can be attributed to the advantages brought by the thiol-ene click reaction between thiol-terminated PU and acrylate dilutes during UV curing process.

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