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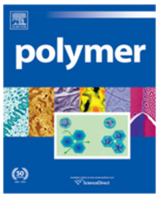

Newly UV-curable polyurethane coatings prepared by multifunctional thiol- and ene-terminated polyurethane aqueous dispersions: Photopolymerization properties

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ABSTRACT

A novel approach toward the preparation of newly UV-curable polyurethane coatings composed of multifunctional thiol- and ene-terminated polyurethane aqueous dispersions is presented. By a synergistic combination of polyurethane dispersions synthesis and thiol-ene chemistry, strategies for the preparation of newly UV-curable polyurethane coatings are developed. Photo-DSC, real-time FTIR, DMA and tensile tests measurements are used to investigate the photopolymerization and mechanical behaviors of newly UV-curable polyurethane coatings. The newly polyurethane coatings have 1.5 times higher polymerization rate and final 99% functional groups conversion in air conditions compared to current urethane-acrylate based UV-curable polyurethane dispersions coatings. UV-cured polyurethane films prepared by this method are also found to exhibit increase in Young's modulus and tensile strength at break by 25% and 10%, respectively. These experiment facts suggest that the incorporation of thiol-ene chemistry to the polyurethane dispersion coatings increase their polymerization rate, producing a high degree of cross-linking. This confirms the preparation of the targeted novel UV-curable polyurethane coatings and reveals the dramatic effect that changes in incorporation of thiol-ene chemistry can have on the photopolymerization behaviors of UV-curable polyurethane dispersions coatings systems.

1. Introduction

In recent years, waterborne coatings using ultraviolet (UV)-curing technology have gained increasing interest due to their environment safety, low energy consumption, high curing speed, cost efficient, low temperature and enhanced performance [1–5]. UV-curable polyurethane (PU) aqueous coatings have been most extensively studied in recent years because of their versatility, environmental friendliness and excellent mechanical performance [6–14]. However, current urethane-acrylate based UV-curable PU dispersions coatings have such major limitations as oxygen inhibition, non-uniform cross-linking, wide mechanical transition ranges and high internal stress levels [15–17]. Owing to unique properties such as significantly less oxygen inhibition and much higher functional group conversion, incorporation of thiol-ene curing chemistry into PU aqueous coatings is a potentially very effective technology that can address the above shortcomings [18,19]. Recently, newly developed UV-curable polyurethane coatings based on multifunctional thiol- and ene-terminated polyurethane dispersions mixtures have been synthesized by our group to explore their possible applications as UV-curable PU coatings [20,21]. It is anticipated that dispersion of both multifunctional thiols and multifunctional enes would exhibit good solution stability while incorporating some thiourethane groups with a higher molecular refractive index component into the resulting cured films. It may be expected that incorporation of stoichiometric amount of multifunctional thiol crosslinkers into urethane-acrylate based PU dispersions coatings could significantly enhance their UV-curing behavior and mechanical properties, and present potential for special industrial applications.

The present paper is a continuation to the previous part of this work [20]. It will describe the photopolymerization and mechanical behaviors of UV-curable PU coatings based on multifunctional thiol- and multifunctional ene-terminated PU aqueous dispersion. The polymerization features, such as photopolymerization rates and thiol/ene group conversions of resulting PU coatings are

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studied in detail using real-time FTIR and Photo-DSC. In addition, the mechanical properties of the resulting UV-cured PU films are studied using DMA and tensile tests measurements. The present study may stimulate a better understanding of the rational incorporation thiol-ene chemistry into polyurethane dispersions systems to generate new UV-curable polyurethane dispersions coatings with improved physical properties, making them widely applicable.

2. Experimental

2.1. Materials

Poly(hexylene adipate-isophthalate) polyester diol (Desmophen 1019-55-OH# 55 and Acid# 2), isophorone diisocyanate (IPDI) (Desmodur-I), and a commercial urethane-acrylate based UV-curing polyurethane dispersion (Bayhydrol® UV VP LS 2282) were used as a principal polyol, polyisocyante and references coatings for PU aqueous dispersions and they were supplied by Bayer Material Science, Pittiesburgh, PA. Photoinitiator of 2-hydroxy-4-(-2-hydroxyethoxy)-2-methylpropionphenone (Irgacure®2959) was from Ciba Chemical Co. Trimethylolpropane tris(3-mercaptopropionate) (TriSH) and trimethylopropane diallyl ether (DiAE) were respectively used as multifunctional thiol and ene monomer, 3-hydroxy-2-(hydroxymethyl)-2-methyl-propanoic acid (DMPA) was used to supplied enough –COOH for dispersion in water, and dibutyltin dilaurate (DBTDL) and triethyl amine (TEA) were received from Aldrich Chemical Co. Acetone (99.5%), toluene (99.5%) and propan-2-ol (99%) were received from Fluka. All the materials were used as received.

2.2. UV-curable PU coatings based on multifunctional thiol- and ene-terminated PU aqueous dispersions

Multifunctional thiol-terminated and ene-terminated PU aqueous dispersions were prepared by a procedure described in the literature [20,21]. Under nitrogen atmosphere, the polyester diol (76.9 g, 0.075 equiv), DMPA (3.42 g, 0.05 equiv), Desmodur-I (22.68 g, 0.2 equiv), DBTDL and acetone (85.6 g, 20.8 wt% based on total dispersion) were added, and stirring continued until a homogenized mixture was obtained. The mixture was heated at 60 °C for about 3–8 h to afford an isocyanate terminated prepolymer. The isocyanate content during the reaction was monitored using a standard dibutylamine back titration method. Upon reaching the theoretical –NCO value, the prepolymer was chain terminated by TriSH for 4–12 h at 30 °C. In the final chain terminated step the ratio of thiol groups (from TriSH) to isocyanate groups was 3.0/1.0. While the DiAE was also used as chain terminated, the ratio of C=C groups (from DiAE) to isocyanate groups was 2.0/1.0. The PU prepolymers were finally neutralized by triethyl amine (DMPA equiv) by stirring for 30 min while maintaining the temperature at 50–55 °C. Dispersions of thiol- and ene-terminated PU prepolymer in water were carried out by slowly adding water to the neutralized PU prepolymers at 45–50 °C over 30 min with an agitation speed of 750 rpm. Acetone from the resulting PU dispersions was removed at 35 °C on a rotary evaporator. The final solid content was 39 wt%. At the end, a defoamer (Foamstar-I) was added, and stirring continued for 15 min at a speed of 250 rpm.

The multifunctional thiol- and ene-terminated PU dispersions were mixed at equivalent thiol/ene molar ratio with 1.5 wt% photoinitiator of Irgacure®2959, and stirring continued for 15 min at a speed of 250 rpm. The samples were then stored in the dark. The PU dispersions mixtures were then cast onto an aluminium plate with a thickness of approximately 70 μm. Film formation was carried out at room temperature. Water was then allowed to evaporate at temperatures between 25 and 80 °C in an oven. The coatings were cured by passing the sample five times under a Fusion medium pressure mercury lamp (600 mW/cm^2) at a speed of 10–20 m/min. The polymerization rate of the double bonds and thiol groups were determined from the decrease of the IR band at 940 cm^{-1} ($CH{=}CH_2$ twisting vibration) and 2570 cm^{-1} (S–H twisting vibration).

For comparison, we prepared Bayhydrol® UV VP LS 2282 based UV-curing polyurethane dispersions coatings by the same method described above. The Bayhydrol® UV VP LS 2282 was mixed with 1.5 wt% Irgacure®2959, and stirring continued for 15 min at a speed of 250 rpm. The PU dispersions were then cast onto an aluminium plate with a thickness of approximately 70 μm. Film formation was carried out at room temperature. Water was then allowed to evaporate at temperatures between 25 and 80 °C in an oven. The coatings were cured by passing the sample five times under a Fusion medium pressure mercury lamp (600 mW/cm^2) at a speed of 10–20 m/min.

2.3. Characterization

Real-time FTIR spectra were recorded on a modified Bruker 88 FTIR spectrometer. UV light from an Oriel lamp system equipped with a 200 W, high-pressure mercury-xenon bulb was channeled through an electric shutter and fiber optic cable in the sample chamber filled with dry air. Experiments were performed at ambient temperature at UV light intensity of 14 mW/cm^2. The Real-time FTIR setup is shown in previous literatures [22,23]. Photo differential scanning calorimetry (photo-DSC) was carried out using a Perkin–Elmer DSC 7 modified by adding a shuttered 450 W medium pressure mercury lamp from Ace Glass. The details of the setup and procedure can be seen in the published papers [24,25]. The samples were measured in air. A dynamic mechanical thermal analysis (DMA) measurements were performed using a TA Instruments DMA 2980 at 1 Hz scanning with a 5 μm amplitude over the temperature range of −50–150 °C at 2 °C min^{-1}. DMA was conducted using the cantilever bending mode with specimen dimensions set at 35 mm × 12 mm × 4 mm ($L \times W \times H$). T_g was taken as the temperature at the peak of the tan (δ) curve in the glass transition region. The samples were measured in air. Tensile property measurements were obtained with a Mechanical Testing machine (MTS-Alliance RT/10) according to ASTM D882, using a 100 N load cell with a specimen gauge length of 40 nm at a cross-head speed of 25 mm/min. A width-thickness ratio of 8 was used for the tensile testing. Five tests were run each sample, and an average value is reported. Films were evaluated (Persoz and pencil hardness) after curing and annealing. Annealing was conducted by heating in an oven at 85 °C for 2 h. This annealing resulted in further conversion of unreacted C=C functionalities. For annealed films, the pencil hardness (ASTM D-3363) and Persoz pendulum hardness (ASTM D-4366 using a BYK-Gardner pendulum hardness tester with a square frame pendulum) values were the average of five tests.

3. Results and discussion

3.1. Photopolymerization behaviors of UV-curable coatings based on multifunctional thiol- and ene-terminated polyurethane aqueous dispersions

Photopolymerization behaviors of UV-curable coatings based on multifunctional thiol- and ene-terminated polyurethane aqueous dispersions are investigated by monitoring the disappearance of the thiol groups at 2570 cm^{-1}, allyl ether at 940 cm^{-1}, and acrylate at 1630 cm^{-1}. Formulations are prepared at the 1:1 stoichiometric ratio of thiol to ene functionalities to ensure that the reaction mixtures would be polymerized completely during the reaction. The conversion of double bond and thiol groups at a given time is calculated from the change in the absorption peak area as a function of time [10–12,18]. Fig. 1 shows the photopolymerization rate and double bond conversion vs irradiation time plot for the sample with multifunctional thiol- and ene-terminated PU dispersions mixtures (50 mol% thiol and 50 mol% ene based on functional groups). Taking the derivative of the double bond conversion vs time plot results in the polymerization rate (in terms of min^{-1}) vs time plot. The double bond group conversion increases rapidly (1–2 min) after the sample is exposed to light. Within 20 min, ene groups conversion reaches about 99%. The increase in the polymerization rate is due to the rapid thiol-ene polymerization reaction [19–21].

Fig. 2 shows a comparison between the double bonds conversion vs time of multifunctional thiol- and ene-terminated PU dispersions mixtures (50 mol% thiol and 50 mol% ene based on functional groups) and Bayhydrol® UV VP LS 2282 based UV-curable polyurethane dispersions coatings. It is clear from this figure that the incorporation of thiol-ene chemistry to the polyurethane dispersion coatings can significantly affect their photopolymerization behaviors evidenced by the C=C conversion between this two UV-curable polyurethane dispersions coatings as shown in Fig. 2. Within 25 min, almost 99% double bonds of multifunctional thiol- and ene-terminated PU dispersions mixtures are converted (Fig. 2a) while only about 89% of the acrylate double bonds polymerizes (Fig. 2b) under the same photolysis conditions and irradiation time. As mentioned previously, this suggests that allyl ether groups be consumed only by a free-radical copolymerization reaction with the thiol groups since allyl ethers are known not to readily homopolymerize [23,26], while the acrylate double bonds participates exclusively in homopolymerization.

The photopolymerization rates (R_p, min^{-1}) values along with final reaction C=C and S–H conversions values in resulting multifunctional thiol- and ene-terminated PU dispersions mixtures are summarized in Table 1. R_p is calculated as initial rates from the slope of C=C conversions vs time plot at low percent conversion. The final 99% C=C conversion and 99% S–H conversion in the sample containing multifunctional thiol- and ene-terminated PU dispersions mixtures may result from an insignificant increase in R_p (from maximum value of 0.165 min^{-1} for Bayhydrol® UV VP LS 2282 based PU coatings to maximum value of 0.224 min^{-1} for multifunctional thiol- and ene-terminated PU dispersions mixtures based PU coatings). This experimental fact suggests that the incorporation of thiol-ene chemistry to polyurethane dispersion coatings systems enhance their photopolymerization behaviors, producing relatively high C=C and S–H groups conversion at earlier time (1–2 min). This enhancement in the C=C groups conversion and photopolymerization rate is confirmed by photo-DSC investigation, which will be discussed later.

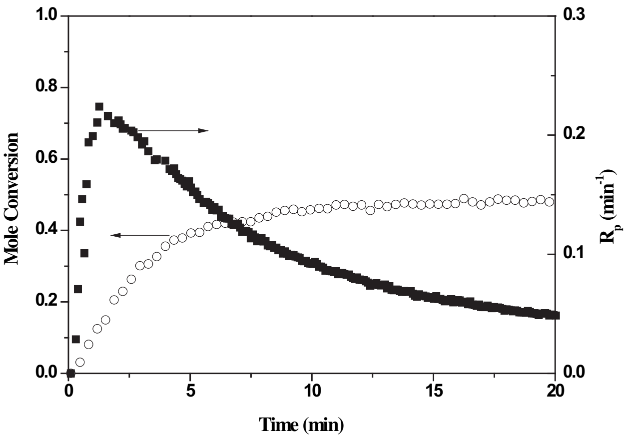

Fig. 1. Real-time FTIR polymerization rate (■) and mole conversion (○) of double bonds of multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures (50 mol% ene and 50 mol% thiol based on functional groups) in air condition as a function of irradiation time with 1.5 wt% Irgacure®2959 using unfiltered UV light source. Light intensity is 14 mW/cm^2.

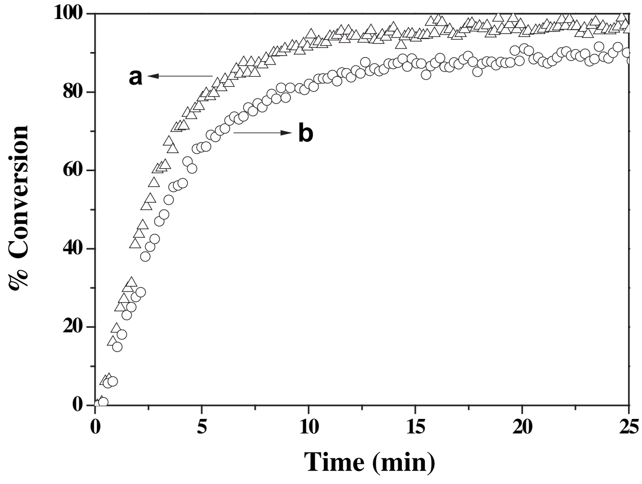

Fig. 2. Real-time FTIR conversion of double bonds of (a) multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures (50 mol% ene and 50 mol% thiol based on functional groups) (△) and (b) Bayhydrol® UV VP LS 2282 based PU aqueous dispersions (○) as a function of irradiation time with 1.5 wt% Irgacure®2959 using unfiltered UV light source in air condition. Light intensity is 14 mW/cm^2.

Fig. 3 shows the photo-DSC exotherms used to construct the photopolymerization rate and polymerization kinetics for the sample with multifunctional thiol- and ene-terminated PU dispersions mixtures (50 mol% thiol and 50 mol% ene based on functional groups) in air condition. Photo-DSC data will show that peak maximum is related to the maximum rate of photopolymerization. The maximum rate of photopolymerization for multifunctional thiol- and ene-terminated PU dispersions mixtures coatings is 8.82 W/g (Fig. 3a), a value much higher than 5.83 W/g that measured for Bayhydrol® UV VP LS 2282 based UV-curable PU dispersions systems (Fig. 3b). The autoacceleration difference in the exotherm plot observed for the two samples after UV light exposure is certainly consistent with the real-time FTIR results in Fig. 1. On the basis of this experimental fact, one can say that the incorporation of thiol-ene chemistry to the polyurethane dispersions synthesis can increase the polymerization rates of double bonds groups in resulting polyurethane dispersions, producing more multifunctional groups conversion in UV radiation condition in these systems.

Table 1
Photopolymerization rates, maximum C=C and S–H conversions values in multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures (50 mol% ene and 50 mol% thiol based on functional groups).[a]

Sample component[b]	Maximum polymerization rate (R_p, min^{-1})[c]	Maximum % C=C conversion	Maximum % S–H conversion
PUD-1	0.224	99	99
PUD-2	0.165	89	/

[a] Samples are cured under 14 mW/cm^2 UV light.

[b] PUD-1: Multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures, PUD-2: Bayhydrol® UV VP LS 2282 based PU aqueous dispersions.

[c] Polymerization rate: initial slope of % C=C conversion vs time plot.

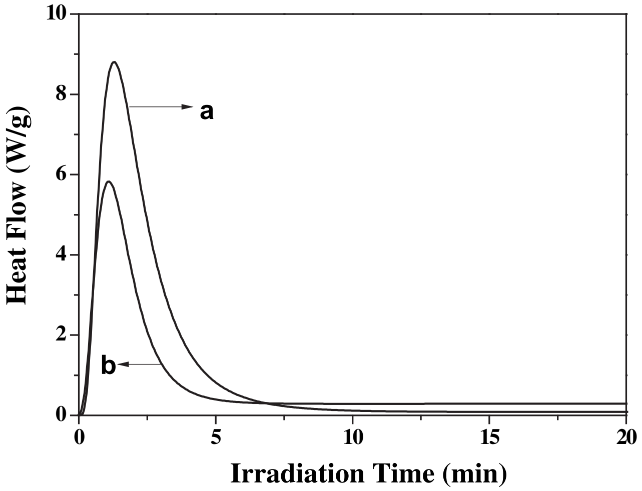

Fig. 3. Photo-DSC exotherms of (a) multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures (50 mol% ene and 50 mol% thiol based on functional groups) and (b) Bayhydrol® UV VP LS 2282 based PU aqueous dispersions with 1.5 wt% Irgacure®2959 using unfiltered UV light source in air conditions. Light intensity is 14 mW/cm^2 with 365 nm light.

3.2. *Mechanical properties of UV-curable PU coatings based on multifunctional thiol- and ene-terminated PU aqueous dispersions*

The cured PU films are analyzed by dynamic mechanical thermal analysis (DMA) in order to gain more insight into their mechanical properties and network structure [13,14]. Fig. 4 shows a comparison between the storage modulus and tan (δ) of cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixture (50 mol% thiol and 50 mol% ene based on functional groups) film and Bayhydrol® UV VP LS 2282 based UV-curable PU film. The glass transition temperature (as defined by the tan (δ) maximum) is 68 °C for urethane-acrylate based UV-curable PU films. For a system of cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixture (50 mol% thiol and 50 mol% ene based on functional groups), its glass transition temperature is 103 °C. The T_g enhancement upon cured PU films results from higher degree of cross-linking reaction. It is also interesting to compare the storage modulus in the rubbery plateau region for above two cured PU films. As expected, cured PU films for multifunctional thiol- and ene-terminated PU aqueous dispersions mixture at 50 mol% thiol/50 mol% ene groups molar ratio give a high modulus films, their rubbery elastic modulus value is 1515 MPa at 25 °C, which is higher than 1145 MPa for urethane-acrylate based PU films. Compared with Bayhydrol® UV VP LS 2282 based PU film, cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixture film can show enhanced storage modulus and higher T_g. This experimental evidence indicates the incorporation of thiol-ene chemistry in the polyurethane dispersion coatings enhances the mechanical properties of cured PU films to produce a higher degree of cross-linking network structure.

Further information regarding the network structures can be obtained from the shape of the tan (δ) as a function of temperature (Fig. 4) [27,28]. An important observation of the results in Fig. 4 is the relative narrow tan (δ) peaks for cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixture coatings. The tan (δ) vs temperature plot of Bayhydrol® UV VP LS 2282 based UV-curable PU films has a full width at half maximum (FWHM) value of 38–96 °C (Fig. 4b). For cured systems of multifunctional thiol- and ene-terminated PU aqueous dispersions mixture coatings with the same radiant exposure, the tan (δ) peak has a FWHM value of 74–122 °C (Fig. 4a). The narrowed FWHMs (from 58 to 48 °C) indicate uniform thiol-ene PU molecular networks resulted from the free-radical polymerization of thiol-ene chemistry [28–30].

The increase in the mechanical properties of the resulting multifunctional thiol- and ene-terminated PU mixtures coatings has been confirmed by tensile tests measurements. Fig. 5 shows the stress-strain curves for cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixture (50 mol% thiol and 50 mol% ene based on functional groups) film and Bayhydrol® UV VP LS 2282 based PU film. The physical properties changed markedly as evidenced by tensile strength at break increasing by 25%, from 19.2 MPa for the Bayhydrol® UV VP LS 2282 based UV-curable PU films up to 23.8 MPa for the samples containing 50 mol% thiol/50 mol% ene groups multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures. From these results, it is concluded that the mechanical properties of cured PU films should be related to introduction of thiol-ene chemistry. The increase of tensile strength at break is due to the increased amount of thiol-ene cross-linkage

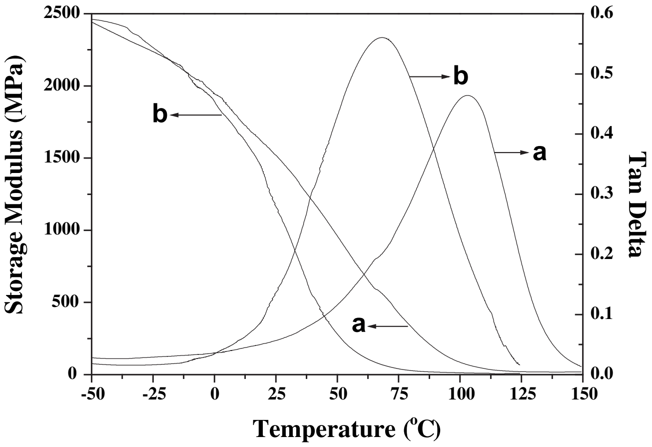

Fig. 4. Tensile storage modulus E′ and tan δ (loss factor) vs temperature plots for UV-cured 4 mm thick plates formed from (a) multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures (50 mol% ene and 50 mol% thiol based on functional groups) and (b) Bayhydrol® UV VP LS 2282 based PU aqueous dispersions. DMA first scan plots obtained with scan rate 2 °C/min and frequency 1 Hz.

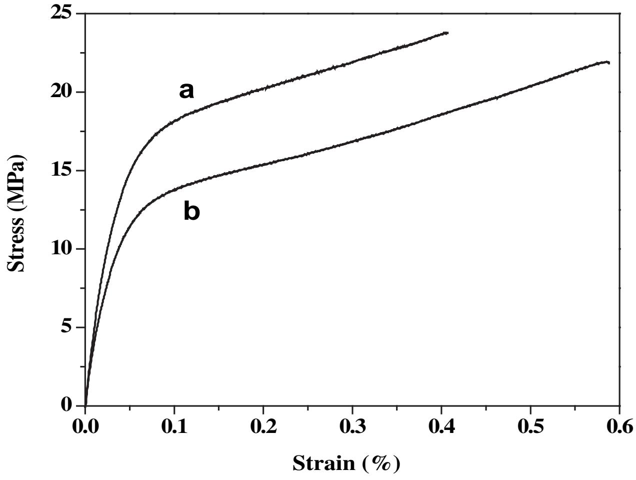

Fig. 5. Tensile stress vs strain curves for UV-cured films formed from (a) multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures (50 mol% ene and 50 mol% thiol based on functional groups) and (b) Bayhydrol® UV VP LS 2282 based PU aqueous dispersions.

Table 2
Mechanical properties in UV-cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures (50 mol% ene and 50 mol% thiol based on functional groups) films.[a]

Sample component[b]	Yang's modulus	Tensile strength at break (MPa)	Strain at break (%)	Energy to break (N mm/mm^3)
PUD-1	505.4	23.8	40.5	224.5
PUD-2	404.1	21.9	58.6	340.9

[a] Samples are cured under 600 mW/cm^2 UV light at a speed of 10 m/min.
[b] PUD-1: Multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures, PUD-2: Bayhydrol® UV VP LS 2282 based PU aqueous dispersions.

[29,30]. It corroborates the hypothesis the degree of cross-linking for multifunctional thiol- and ene-terminated PU aqueous dispersions mixture systems is higher than that of urethane-acrylate based UV-curable PU aqueous dispersions systems.

Table 2 summarizes the Young's modulus, tensile strength at break, strain at break and energy to break values for cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures (50 mol% thiol and 50 mol% ene based on functional groups) film and Bayhydrol® UV VP LS 2282 based UV-curable PU film. For systems of cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures have tensile strength at break and Young's modulus values of 23.8 MPa and 505.4, respectively, whereas their strain and energy to break values are 0.41 and 224.5 (N mm/mm^3), respectively. For systems of cured Bayhydrol® UV VP LS 2282 based UV-curable PU film, their Young's modulus, tensile strength at break, strain at break and energy to break values are 404.1, 21.9 MPa, 0.59 and 340.9 (N mm/mm^3), respectively. The tensile strength at break and Young's modulus for cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures system are both much higher than those of urethane-acrylate based PU films, whereas their tensile stress and elongation values at break are both decreased, indicating extensive thiol-ene cross-linking occurs. Incorporation of the thiol-ene chemistry into the PU dispersion coatings has a major impact on the cured PU coatings film as evidenced by the large change in mechanical properties reported in Table 2.

The mechanical properties and crosslink extend of cured polyurethane films can be conveniently followed through pendulum and pencil hardness measurements, which are correlated with the elastic modulus and T_g of the crosslinked polymer [31,32]. Table 3 shows the pendulum and pencil hardness value of the cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixture (50 mol% thiol and 50 mol% ene based on functional groups) film and Bayhydrol® UV VP LS 2282 based UV-curable PU film. From Table 3, the pendulum hardness value of resulting cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixture increases to a high value of 205 s from 174 s for the sample of urethane-acrylate based PU films, while their pencil hardness also correspondingly increases to 7H from 5H. The results of pendulum and pencil hardness tests are in accordance with above stress-strain and DMA results, probably because the newly PU coatings is highly crosslinked.

Table 3
Persoz and pencil hardness of UV-cured multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures (50 mol% ene and 50 mol% thiol based on functional groups).[a]

Sample component[b]	Pencil hardness	Persoz hardness (s)
PUD-1	7H	205
PUD-2	4H	174

[a] Samples were cured under 600 mW/cm^2 UV light at a speed of 10 m/min and annealed at 85 °C for 2 h.
[b] PUD-1: Multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures, PUD2: Bayhydrol® UV VP LS 2282 based PU aqueous dispersions.

4. Conclusions

The photopolymerization and mechanical behaviors of polyurethane dispersion coatings can be changed greatly by incorporation of thiol-ene chemistry. A significant increase in the polymerization rate and final double bond and thiol groups conversion are observed. For samples containing multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures (50 mol% ene and 50 mol% thiol based on functional groups), the value of Young's modulus and tensile strength at break increases by 25% and 10%, respectively as compared to urethane-acrylate based UV-curable polyurethane dispersion system. The relative narrow tan (δ) peaks in the rubbery state also confirm the existence of higher degree of cross-linking reaction in newly UV-curable polyurethane dispersion coatings. These experiment facts suggest that the incorporation of thiol-ene chemistry to the polyurethane dispersion coatings increase their polymerization rate, producing a high degree of cross-linking as confirmed by the photo-DSC, Real-time FTIR, DMA, tensile tests and basic mechanical measurements. The increasing in the photopolymerization and mechanical properties of polyurethane dispersion coatings are attributed to the rapid reaction between the multifunctional thiol groups and ene groups of newly polyurethane dispersion coatings as confirmed by the increase in the storage modulus, T_g, pendulum and pencil hardness. The multifunctional thiol- and ene-terminated PU dispersions coatings systems facilitate development of a UV-curable polyurethane dispersions system having excellent photopolymerization and mechanical properties than current UV-curable urethane-acrylate based systems.

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