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# Newly UV-curable polyurethane coatings prepared by multifunctional thiol- and ene-terminated polyurethane aqueous dispersions mixtures: Preparation and characterization

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ABSTRACT

A series of newly developed UV-curable polyurethane coatings were prepared by blending multifunctional thiol- and ene-terminated polyurethane aqueous dispersions. The composition, structure, solution stability and mechanical properties of the title coatings were characterized in detail by FT-IR, photo-DSC and DMA measurements. It was found that the resulting polyurethane coatings showed good solution stability and high photopolymerization activity even after a long time (i.e. 1 month). The incorporation of a waterborne polyurethane chain into the both multifunctional thiols and ene monomers promoted their solution stability and avoided any reaction between thiols and ene groups as a result of their high reacting activity in non-aqueous systems. UV-cured films prepared by this method were found to exhibit excellent physical properties with improvements over what can be attained directly with current UV-curable urethane–acrylate based systems. This method allows for the preparation of high performance UV-curable polyurethane aqueous coatings based on thiol-ene chemistry 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 [1–11]. UV-curable polyurethane (PU) aqueous coatings have been most extensively studied in recent years because of their versatility, environmental friendliness and excellent mechanical performance [12–14]. However, current urethane–acrylate based UV-curable PU dispersions coatings have such major limitations as oxygen inhibition, non-uniform crosslinking, wide mechanical transition ranges and high internal stress levels [15,16]. 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 [17,18]. Recently, novel waterborne thiol-ene PU dispersions using water dispersable enes were synthesized by Urban et al. to explore their possible applications as UV-curable coatings [19]. It might 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. This, however, would provide little control over solution stability of multifunctional thiol-enes PU dispersions coatings systems and produce polymer dispersions that would slowly react even in the absence of UV irradiation during synthesis and storage of thiol-ene PU dispersions. 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.

The present paper describes for the first time the preparation and identification of UV-curable PU coatings based on multifunctional thiol- and multifunctional ene-terminated PU aqueous dispersion mixtures. We also report the solution stability and photopolymerization behavior of the resulting PU coatings. The composition, structure, solution stability and mechanical properties of

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resulting PU coatings are characterized by FT-IR, photo-DSC and DMA measurements. The effect of storage time and irradiation time on the solution stability and mechanical behavior of the resulting cured PU coatings is discussed in detail.

## 2. Experimental

### 2.1. Materials

Polyester polyol (Desmophen 1019–55) and 2-isocyanato-1-(isocyanatomethyl)-1,5,5-trimethyl-cyclohexane (Desmodur-I) were used as a principal polyol and polyisocyante for PU aqueous dispersions and were supplied by Bayer Material Science, Pittsburgh, PA. Photoinitiator of 2-hydroxy-4-(-2-hydroxyethoxy)-2-methylpropion-phenone (Irgacure®2959) was from Ciba Chemical Co. 2,2-bis(3-sulfanylpropanoyloxymethyl)butyl-3-sulfanylpropanoate (TriSH), 2,2-bis(prop-2-enoxymethyl)butan-1-ol (DiAE), 3-hydroxy-2-(hydroxymethyl)-2-methyl-propanoic acid (DMPA), dibutyltin dilaurate (DBTDL), and triethylamine (TEA) were received from Aldrich Chemical Co. Acetone (99.5%), toluene (99.5%) and propan-2-ol (99%) were received from Fluka. All materials were used as-received.

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

Thiol-terminated and ene-terminated PU prepolymers were prepared by a procedure described in the literature [12–14,20]. The formulations used to prepare multifunctional thiol- and ene-terminated PU dispersions are also listed in Table 1. Under nitrogen atmosphere, Desmophen 1019–55 (76.9 g, 0.075 equiv), DMPA (3.42 g, 0.05 equiv), Desmodur-I (22.68 g, 0.2 equiv), DBTL and acetone (85.6 g, 20.8 wt.% based on total dispersion) were added and stirring was 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 or DiAE for 4–12 h at 30 °C. In the final chain terminated step the ratio of thiol groups (from TriSH) to isocyanate groups was 2.0/1.0, 2.5/1.0, and 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 triethylamine (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 40 wt.%. At the end, a defoamer (Foamstar-I) was added, and stirring continued for 15 min at a speed of 250 rpm.

**Table 1**
Compositions used to synthesize various multifunctional thiol- and ene-terminated PU dispersions.[a]

| Samples and reagent | Ene-PU1 | SH-PU1 | SH-PU2 | SH-PU3 |
|---|---|---|---|---|
| DMPA wt (equiv) | 3.42 (0.025) | 3.42 (0.025) | 3.42 (0.025) | 3.42 (0.025) |
| Polyester diol wt | 76.92 (0.0375) | 76.92 (0.0375) | 76.92 (0.0375) | 76.92 (0.0375) |
| IPDI wt (equiv) | 22.68 (0.1) | 22.68 (0.1) | 22.68 (0.1) | 22.68 (0.1) |
| DiAE wt (equiv) | 17.86 (0.075) | – | – | – |
| TriSH wt (equiv) | – | 20.76 (0.05) | 25.95 (0.0625) | 31.14 (0.075) |
| TEA wt(equiv) | 2.54 (0.025) | 2.54 (0.025) | 2.54 (0.025) | 2.54 (0.025) |
| Acetone wt | 85.6 | 85.6 | 85.6 | 85.6 |
| Water wt | 183 | 187 | 195 | 203 |

[a] SH-PU1–SH-PU3: thiol-terminated PU dispersions, Ene-PU1: ene-terminated PU dispersions; Catalyst: 0.12 wt.% dibutyltin dilaurate (DBTDL) based on total charge; solid content: 40%.

The multifunctional thiol- and ene-terminated PU dispersions were mixed at various thiol/ene molar ratios with the photoinitiator 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 (80 W/cm, 600 mW/cm$^2$) at a speed of 10–20 m/min. The polymerization of the carbon 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).

### 2.3. Characterization

FTIR spectra were recorded on a Bruker Tensor 37 FTIR spectrometer. Particle sizes were determined using a Microtrac UPA 250 light scattering ultrafine particle analyzer. The sample was diluted to the required concentration with distilled water before measurement. The viscosity ($\eta$) measurements of the dispersions were performed using a Brookfield viscometer (Model LVTDV-II) at a shear rate of 100 s$^{-1}$ at 25 °C. Surface tension was measured with a Kruss processor tension meter (K12), using a vertical plate to measure the wetting force. Each reported value represents the average of three measurements. 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 [17,18]. The samples were measured in air. A dynamic mechanical thermal analysis (DMA) measurements of these films were performed using a TA Instruments DMA 2980 at 1 Hz scanning with a 5 μm amplitude over the temperature range of −50 to 200 °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 × W × H). $T_g$ was taken as the temperature at the peak of the tan $\delta$ curve in the glass transition region.

## 3. Results and discussion

### 3.1. Synthesis and structure analysis of UV-curable PU coatings based on multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures

The preparation procedure of multifunctional thiol- and ene-terminated PU dispersions is shown in Fig. 1(A). Isocyanate terminated PU prepolymer is first synthesized by polycondensation of Desmophen 1019–55, Desmodur-I and DMPA in acetone at 60 °C. Upon reaching the theoretical –NCO value, the PU prepolymer is chain terminated by 2,2-bis(3-sulfanylpropanoyloxymethyl)butyl-3-sulfanylpropanoate (TriSH) or 2,2-bis(prop-2-enoxymethyl)-butan-1-ol (DiAE) to obtain multifunctional thiol- and ene-terminated PU prepolymers. The molar ratio of S–H groups to –NCO groups is varied from 2.0:1.0 to 3.0:1.0 in a chain extension step (designated as SH-PU1, SH-PU2 and SH-PU3, respectively), while the DiAE is used as a chain terminator, with a ratio of C═C groups to isocyanate groups of 2.0/1.0 (designated as Ene-PU). The obtained PU prepolymers are neutralized by triethylamine (DMPA equiv.) and finally dispersed in water. Therefore, multifunctional thiol- and ene-terminated PU dispersions are thus prepared. A series of UV-curable PU coatings are prepared by

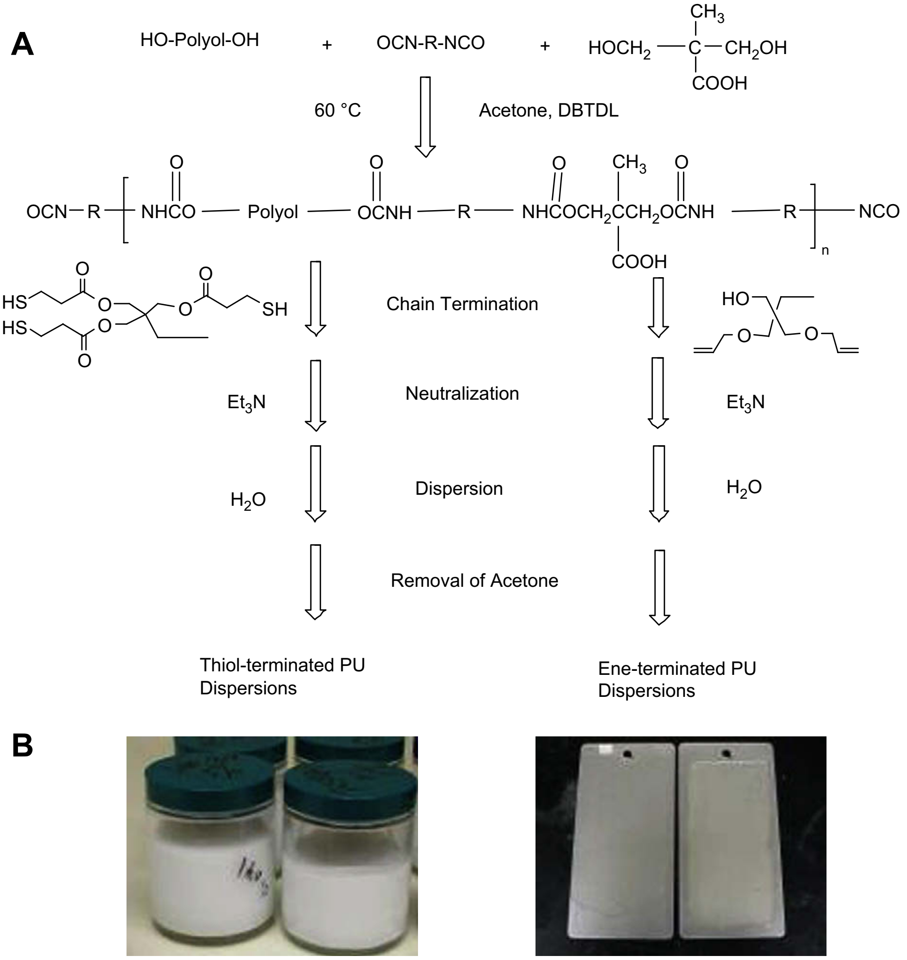

**Fig. 1.** (A). Elementary steps for the synthesis of multifunctional thiol- and ene-terminated PU dispersions. (B) Pictures of thiol- and ene-terminated PU dispersions.

mixing the multifunctional thiol- and ene-terminated PU dispersions in various thiol/ene ratios together with Irgacure®2959 (1.5 wt.% PU coatings) and films are formed by casting onto an aluminium plate. Fig. 1(B) provides pictures of multifunctional thiol- and ene-terminated PU dispersions and their films forming. It is clear that the resulting PU dispersions are very stable. The films formed have good appearance and there is no odor and yellow by-product. Other details concerning multifunctional thiol- and multifunctional ene-terminated PU dispersions in this study are given in Table 2. It is shown that the average particle size of the multifunctional thiol- and multifunctional ene-terminated PU dispersions are from 100 nm to 200 nm. The particle size of the thiol-terminated PU dispersions decrease from 200 to 106 nm with a corresponding decrease in surface tension from 38.6 mN/m to 31.9 mN/m as the molar ratio of –SH groups to –NCO groups is increased from 2.0/1.0 to 3.0/1.0. As the –SH/–NCO molar ratio increases, the molecular weight of PU prepolymer decreases. Thus, the viscosity of the bulk prepolymer decreases. Because the energy cost for dispersing a lower viscosity prepolymer is less than that for high viscosity systems, a PU dispersion with smaller particle size is expected (as the –SH/–NCO molar ratio increases). At the same solid content, the PU dispersion with smaller particle size will have a larger 'effective' volume of the dispersed phase [21]. Thus, according to the Money equation, the viscosity of the PU dispersion with smaller particle size will be larger. The decrease in surface tension with decrease in particle size could be related to a relationship [21] that governs the surface tension of mixtures. For the dispersion with a smaller particle size and the same solid content, the surface area of the particles (per unit volume) will be larger [21]. Thus, the concentration of the surfactant (i.e. the –COOH/$Et_3N$ pair here) will be larger, and the surface tension of a surfactant/water mixture decreases as the concentration of the surfactant increases (as the SH/NCO molar ratio increases). The S–H concentrations of the resulting thiol-terminated PU dispersions are $\sim 2.39 \times 10^{-5} - 4.43 \times 10^{-4}$ mol/g, while the C=C concentrations of the ene-terminated PU dispersions are $\sim 6.91 \times 10^{-4}$ mol/g.

UV-curable PU dispersions coatings based on the above multifunctional thiol- and ene-terminated PU dispersions mixtures have been prepared and investigated. As a reference, comparable non-

**Table 2**
The multifunctional thiol- and ene-terminated PU dispersions.

| Sample[a] | SH/NCO (or C=C/NCO)[b] | S–H (or C=C) number[c] (mol/g) | Average particle size (nm) | Rotating viscosity (mPas) | Surface tension (mN/m) |
|---|---|---|---|---|---|
| SH-PU3 | 3.0/1.0 | $4.43 \times 10^{-4}$ | 106 | 50.7 | 31.9 |
| SH-PU2 | 2.5/1.0 | $3.46 \times 10^{-5}$ | 120 | 48.4 | 33.4 |
| SH-PU1 | 2.0/1.0 | $2.39 \times 10^{-5}$ | 200 | 44.8 | 38.6 |
| Ene-PU | 2.0/1.0 | $6.91 \times 10^{-4}$ | 189 | 57.6 | 42.6 |

[a] SH-PU1–SH-PU3: thiol-terminated PUDs, Ene-PU: ene-terminated PUDs.

[b] SH/NCO and C=C/NCO: the ratio of SH or C=C groups to isocyanate groups in chain termination step.

[c] S–H (C=C) Number: free [SH] or [C=C]/gram of dispersion; Solid content: 40%.

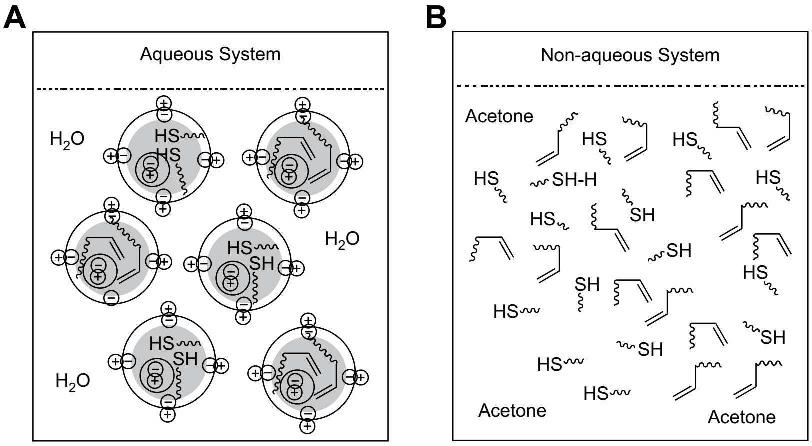

**Fig. 2.** (A) UV-curable PU coatings based on thiol- and ene-terminated PU dispersions mixtures in water and (B) non-aqueous system based on thiol- and ene-terminated PU prepolymer mixtures in acetone.

aqueous PU systems based on multifunctional thiol- and ene-terminated PU prepolymer mixtures in non-aqueous systems (i.e. acetone) were also prepared and examined. As illustrated in Fig. 2, it should be possible to prepare a reactive aqueous PU dispersion mixture in which their thiol and ene groups are present in separate dispersion particles and interact until coalescence due to electrostatic repulsion effects in aqueous phase. In stark contrast to non-aqueous systems or dispersions which have both reactive groups in the same dispersion particles, there will be no possibility of reaction before application in such systems [17,18].

Fig. 3, which depicts FTIR absorbance changes for the thiol and ene groups before and after UV-curing, indicates that photo-polymerization occurs for the resulting thiol- and ene-terminated PU dispersions mixtures. As shown in Fig. 3(A), ene-terminated PU dispersions show absorption peaks at 927 $cm^{-1}$, associated with the $–CH{=}CH_2$ stretching band and a absorption peak at approximately 1730 $cm^{-1}$ associated with urethane C=O groups. The thiol-terminated PU dispersions display strong bands due to urethane C=O groups at approximately 1730 $cm^{-1}$, accompanied by a broad peak centered at 2570 $cm^{-1}$, attributed to the S–H functional groups (Fig. 3(B)). As shown in Fig. 3(C), the films of thiol- and ene-terminated PU dispersions mixtures before UV curing show strong absorption bands at 2570 and 927 $cm^{-1}$, while their absorption bands at 2570 and 927 $cm^{-1}$ disappear after UV curing due to thiol-ene photopolymerization later (Fig. 3(D)).

### 3.2. Solution stability study of UV-curable PU coatings based on multifunctional thiol- and ene-terminated PU aqueous dispersions mixtures

Photo–DSC exotherms, which clearly depict the solution stability of multifunctional thiol- and ene-terminated PU dispersions mixtures systems in air, are shown in Fig. 4. The fact that the maximum polymerization rate of the resulting thiol- and ene-terminated PU dispersions upon storage times of 7–28 days at room temperature are almost the same which suggests that their solution stabilities are rather good. It is seen from Fig. 4 that, the ene-terminated PU dispersion system exhibits a minimal exotherm while bulk thiol-terminated PU dispersions systems show no exotherms. It is concluded that, the resulting thiol- and ene-terminated PU dispersion mixtures have high photopolymerization activity even after a storage time of 1 month.

On the contrary, the solution stability study of the thiol- and ene-terminated PU prepolymer mixtures coatings systems in non-aqueous systems (i.e. acetone) with 1 wt.% Irgacure®2959 are shown in Fig. 5. The results clearly show that thiol- and ene-terminated PU mixtures in acetone exhibit poor polymerization

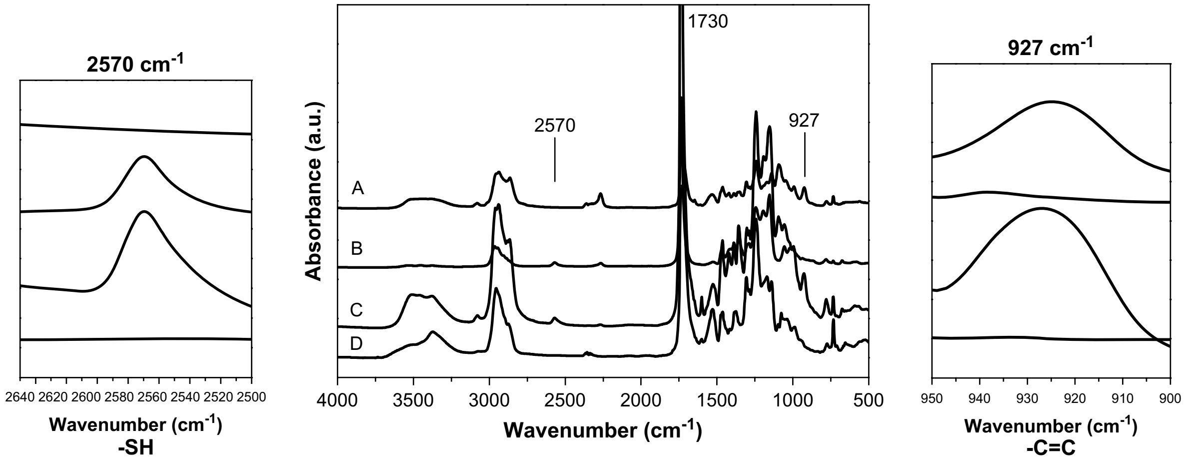

**Fig. 3.** FTIR spectra of (A) ene-terminated PU dispersions, (B) thiol-terminated PU dispersions, (C) thiol- and ene-terminated PU dispersions mixtures before UV curing, and (D) thiol- and ene-terminated PU dispersions mixtures after UV curing.

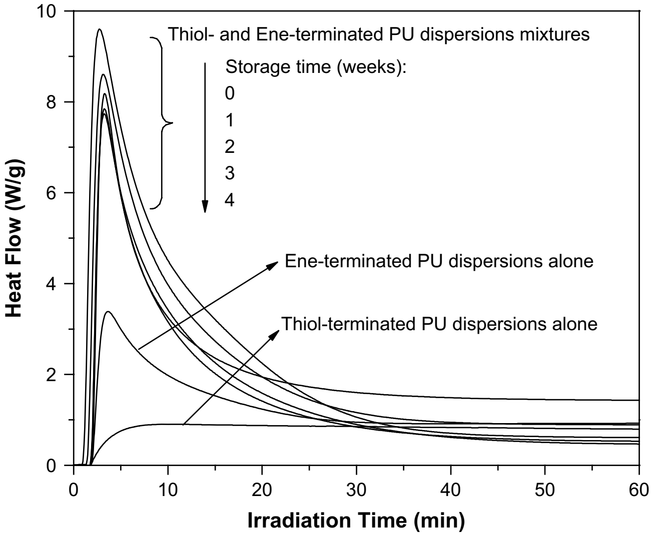

**Fig. 4.** Photo-DSC exotherms for thiol- and ene-terminated PU dispersions mixtures with 1 wt.% Irgacure®2959 in air versus time. The functionality molar ratio of thiol/ene groups is 1:1, and the light intensity is 9.98 mW/cm$^2$ at 365 nm.

rates. With storage time increase from 0 to 5 min, their polymerization rate upon exposure to UV light decreases dramatically, i.e., they have already reacted thermally. The photo-DSC exotherms of thiol- and ene-terminated PU prepolymer mixtures is near zero after 5 min. These results are not unexpected since it is well known that multifunctional thiol-ene systems react rapidly via a radical process and can exhibit poor shelf-life stability [17,22]. It is obvious that non-aqueous thiol- and ene-terminated PU prepolymer mixtures can exhibit poor shelf life stability under certain conditions.

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

Dynamic mechanical thermal analysis is utilized to investigate the mechanical properties of multifunctional thiol- and ene-terminated PU dispersions mixtures having different functionality molar ratios of thiol/ene groups in an effort to understand the structure/property relationships of these UV-cured PU dispersions coatings films. The storage modulus $E'$ is a measurement of materials stiffness and can be used to provide information regarding cross-link density [23,24]. The temperature associated with the peak magnitude of the tan ($\delta$) plot is defined as the glass transition temperature ($T_g$). As shown in Fig. 6, the storage modulus above $T_g$ of UV-cured films of multifunctional thiol- and ene-terminated PU dispersions mixtures increase with increasing the functionality molar ratios of thiol/ene groups. At 125 °C (rubbery state), for the systems with –SH/–C=C molar ratios of 0/1, 0.6/1 and 1/1, respectively, the $E'$ values are 1.61, 17.02 and 24.69 MPa, respectively, with the corresponding $T_g$ values of 68, 94 and 103 °C, respectively. The increase of storage modulus and $T_g$ can be explained by an increase in the crosslink density as the ratio of thiol to ene functional groups approaches 1/1. To obtain the best physical and mechanical properties of the UV-cured thiol-ene system, the molar ratios of thiol/ene groups under which the film is formed must be considered.

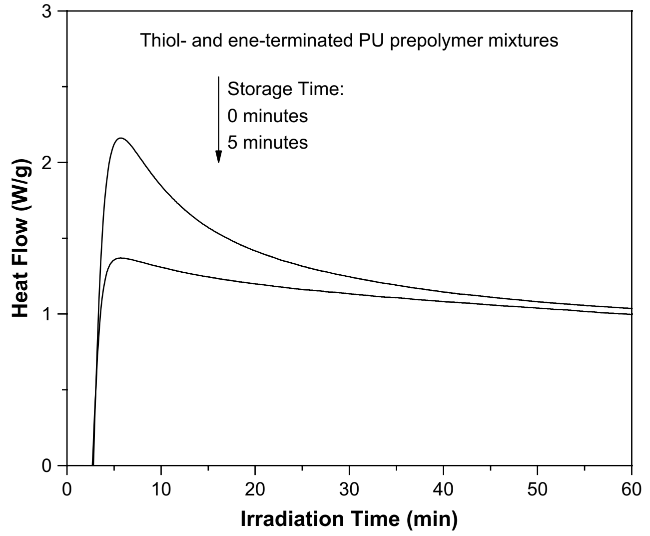

**Fig. 5.** Photo-DSC exotherms for thiol- and ene-terminated PU prepolymers mixtures with 1 wt.% Irgacure®2959 in air versus time. The functionality molar ratio of thiol/ene groups is 1:1, and the light intensity is 9.98 mW/cm$^2$ at 365 nm.

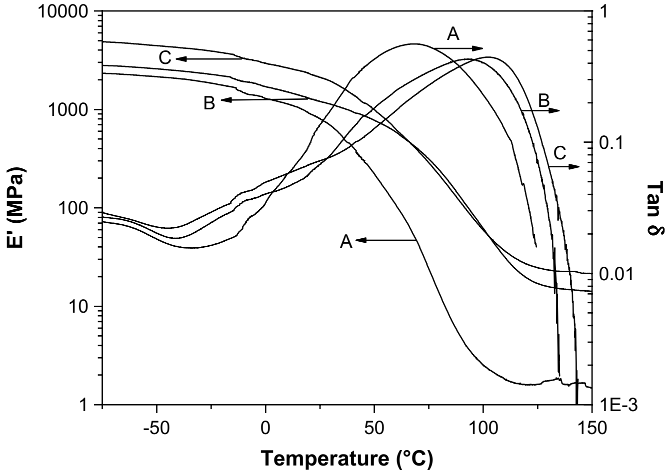

**Fig. 6.** The tensile storage modulus E′ and tan $\delta$ of UV-cured films of thiol- and ene-terminated PU dispersions mixtures versus temperature. Their functionality molar ratio of thiol/ene groups is (A) 0/1, (B) 0.6:1 and (C) 1/1, respectively.

## 4. Conclusions

In this paper, multifunctional thiol- and ene-terminated PU dispersions mixtures were successfully prepared and characterized by means of FT-IR, photo-DSC and DMA measurements. The UV-curable PU dispersions coatings based on multifunctional thiol- and ene-terminated PU dispersions mixtures showed good solution stability and high reacting activity even after a long storage time (i.e. 1 month). The incorporation of PU aqueous dispersions into the multifunctional thiol-ends systems was effective in promoting good storage stability. UV-cured films prepared by this method were found to exhibit excellent physical properties. The route offers advantages in comparison with comparable non-aqueous systems and traditional urethane–acrylate based systems. The UV-curable PU dispersions mixtures can be used to facilitate the development of UV-curable PU dispersion systems with low oxygen inhibition and high performance.

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