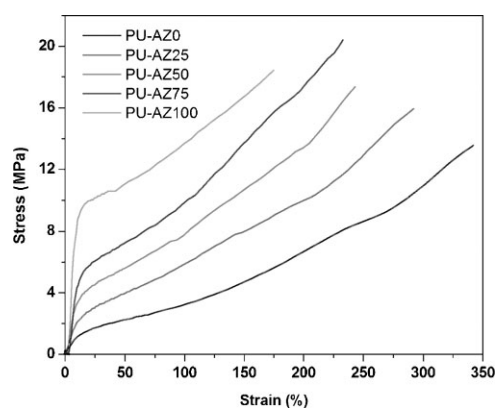


Castor-Oil-Based Waterborne Polyurethane Dispersions Cured with an Aziridine-Based Crosslinker

Ying Xia, Richard C. Larock*

Castor-oil-based anionic PU dispersions are post-cured using a multi-aziridine-based crosslinker CX-100. Thermal and mechanical properties of the resulting films are studied by DMA, DSC, TGA, and tensile tests. Mechanical properties are dramatically improved by the crosslinker. For example, the Young's modulus and tensile strength increase from 14.5 to 125 MPa and 13.1 to 18.1 MPa, respectively, when the aziridine fraction increases from 0 to 100%. The onset decomposition temperature of the films, T_5 , increases from 162 to 209 °C, indicating a significant increase in the thermal stability as the amount of aziridine is increased. This work provides an effective way of curing biorenewable anionic PU dispersions to prepare high performance, environmentally friendly coatings.



Introduction

Biorenewable vegetable-oil-based polymeric materials have received much attention during the last decade, due to environmental concerns and finite petroleum resources.^[1,2] A variety of polymerization methods, including free radical,^[3] cationic,^[4] olefin metathesis,^[5] and condensation polymerization,^[6] have been employed to prepare these polymers. Vegetable oil-based polyols have been used to prepare polyurethanes (PUs) with a wide range of thermal and mechanical properties, which appear promising as replacements for petroleum-based PUs.^[7] Vegetable oil-based diisocyanates have also been prepared as possible replacements for petroleum-based diisocyanates in PUs.^[8,9] Waterborne anionic and cationic poly-

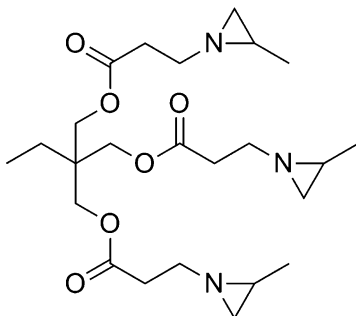
urethane dispersions (PUDs) have been prepared with a wide range of applications, including adhesives,^[10] coatings,^[11] and paints.^[12] They exhibit excellent adhesion properties and possess low film-forming temperatures. Compared to conventional solvent-based PUs, waterborne PUDs are environmentally-friendly with low volatile organic chemicals (VOCs) and low hazardous air pollutants (HAPs).^[13] Vegetable oil-based anionic and cationic PUDs have been successfully prepared in our group by incorporating dimethylolpropionic acid (DMPA)^[14,15] and *N*-methyl-diethanolamine (MDEA),^[16,17] respectively. The PU films obtained range from elastomeric polymers to ductile plastics, depending on the hydroxyl content of the vegetable oil-based polyols and their hard segment content. These materials should find wide applications as high performance coatings.

For anionic PUDs prepared with DMPA, the carboxylate groups in the PU provide surface charged PU particles, which stabilize the PU dispersion in the water phase. These aqueous PUDs have a disadvantage in that the PU films

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■ Scheme 1. Structure of CX-100.

exhibit high hydrophilic properties due to the presence of the hydrophilic carboxylate groups, resulting in poor water or solvent resistance.^[18] Therefore, post-curing reactions^[19–23] and polymer hybridization^[15] have been used to improve the molecular weight and the crosslink density. Among these solutions, reacting the carboxylate groups in the PUDs with an aziridinyl curing agent, when the pH drops below 6.0, or air drying^[24] represent perhaps the most convenient solutions. These aziridinyl-cured PU films demonstrate dramatically improved thermal and mechanical properties.^[21]

Herein, a triaziridinyl curing agent CX-100 (Scheme 1) has been blended with castor-oil-based anionic PUDs to obtain self-curable PU dispersions. The aziridine groups react with the carboxylate groups present in the PU at ambient temperature to eliminate the hydrophilic carboxylate groups and further crosslink the PU network. In this way, solvent resistance, and the thermal and mechanical properties of the castor-oil-based PU films are increased significantly. This work provides a new way to prepare biorenewable, high performance coating materials.

Experimental Part

Materials

Castor oil, isophorone diisocyanate (IPDI), DMPA, and dibutyltin dilaurate (DBTDL) were purchased from Aldrich Chemical Company (Milwaukee, WI). Triethylamine (TEA) and methyl ethyl ketone (MEK) were purchased from Fisher Scientific Company (Fair Lawn, NJ). The aziridine-based crosslinker CX-100 [trimethylolpropane-tris[1-(2-methyl)aziridino]propionate] (Scheme 1) was obtained from DSM NeoResins (Waalwijk, The Netherlands). All materials were used as received without further purification.

Synthesis of Castor-Oil-Based PUDs

Scheme 2 shows the approach used to prepare the castor-oil-based PUDs. The castor oil (20.00 g), IPDI (12.46 g), DMPA (3.72 g), and 1 drop of DBTDL as catalyst were added to a four-necked flask equipped with a mechanical stirrer, nitrogen inlet, condenser, and thermometer. The molar ratio between the NCO groups of the IPDI,

the OH groups of the castor oil, and the OH groups of the DMPA was 2.0:1.0:0.99. The reaction was carried out at 78 °C for 1 h and then 100 mL of MEK was added to reduce the viscosity and prevent gelation. The reaction was kept for another 2 h at 78 °C. After cooling down to room temperature, the PU solution was neutralized by TEA (1.2 equiv. per DMPA) and stirred for 30 min. Then water (300 mL) was added, followed by 30 min of vigorous stirring to effect dispersion. After removal of the MEK under vacuum, castor-oil-based PUDs were obtained with a solid content of ≈10 wt.-%.

Preparation of the CX-100-Cured PU Films

The desired amount of CX-100 was added dropwise to the castor-oil-based PUDs, followed by stirring for 30 min. Then the dispersion was poured into a glass mold to dry at ambient temperature. The films were further cured at 50 °C for 24 h and conditioned at 25% humidity before testing. The amounts of CX-100 used [0, 2.8, 5.6, 8.4, and 11.2 parts per hundred rubber (phr)] are summarized in Table 1, where the CX-100 has reacted with 0, 25, 50, 75, and 100% of the carboxylates in the castor-oil-based PU, respectively. The nomenclature for the resulting samples is as follows: a CX-100-cured PU film, where the percent of the aziridine to the carboxylic acid groups is 75%, is designated as PU-AZ75.

Characterization

Ethanol uptake and ethanol absorption have been measured as follows.^[22] Dry PU films of 20 × 20 mm² were conditioned by drying at 50 °C for 24 h, cooled in a desiccator and weighed (W_0). The films were then immersed in a 95% ethanol bath for 48 h. The towel-dried sample weight (W_1) and reconditioned sample (dried at 50 °C for 24 h and cooled in a desiccator) weight (W_2) were obtained. The percentage of ethanol absorption (W_a) and weight loss of the polymer films in ethanol (W_d) have been calculated according to the following equations:

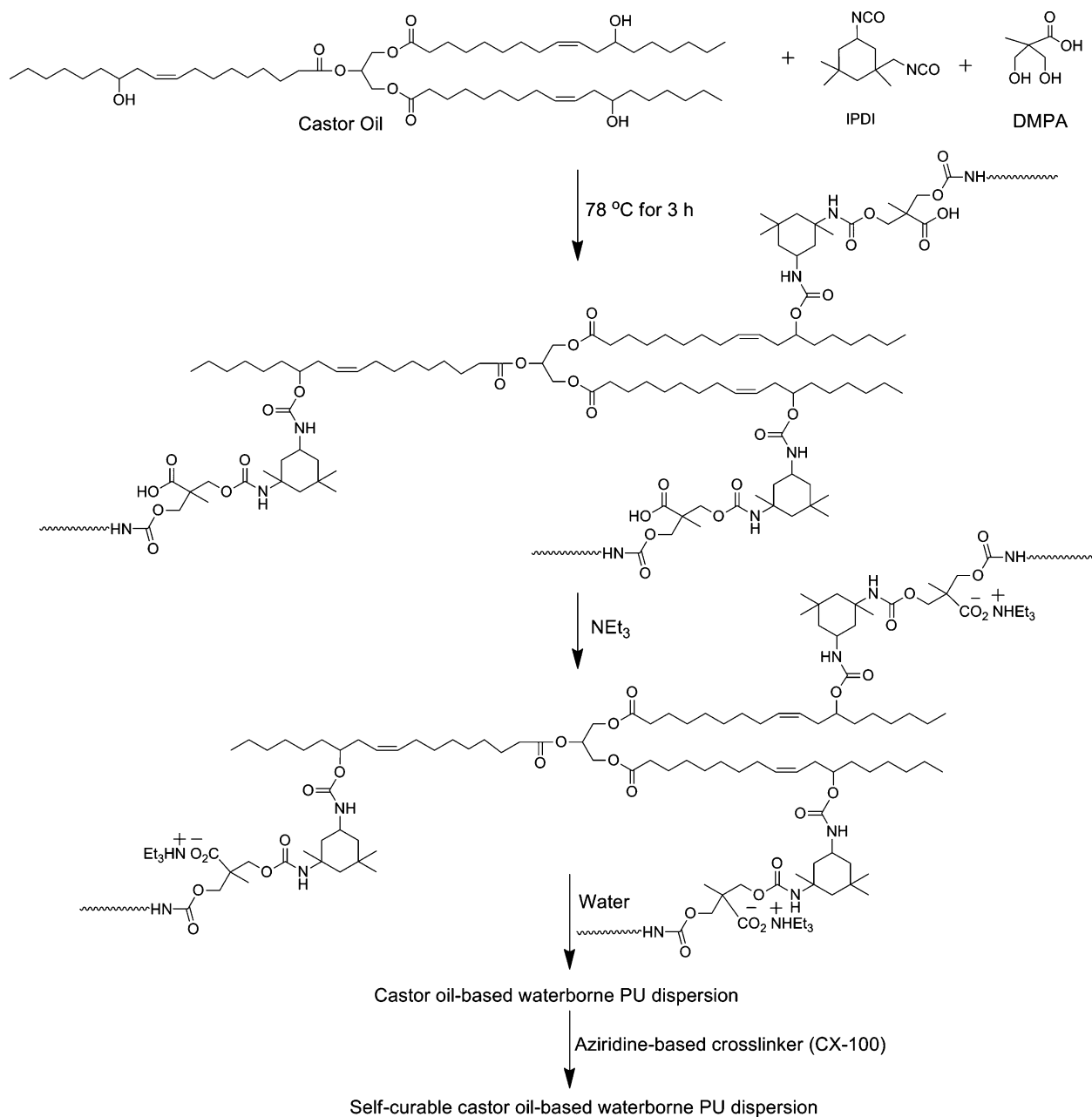
$$W_a\% = \frac{W_1 - W_2}{W_2} \times 100\%$$

$$W_d\% = \frac{W_0 - W_2}{W_0} \times 100\%$$

where W_a and W_d are the amount of ethanol absorbed by the PU film and the amount of PU film dissolved in ethanol, respectively.

The dynamic mechanical properties of the films were determined using a TA Instruments DMA Q800 dynamic mechanical analyzer with a film-tension mode of 1 Hz. Rectangular samples 0.5 mm thick and 8 mm wide were used for the analysis. The samples were cooled and held isothermally for 3 min at −80 °C before the temperature was increased at 5 °C · min^{−1} to 150 °C. The glass transition temperatures (T_g s) of the samples were obtained from the peaks of the tan δ curves.

DSC was performed on a thermal analyzer (TA instrument Q2000). The samples were heated at a rate of 20 °C · min^{−1} from 25 to 100 °C to erase the thermal history, equilibrated at −70 °C and then heated to 150 °C at a heating rate of 20 °C · min^{−1}. The T_g s of the samples were determined from the midpoint temperature in the



Scheme 2. Synthesis of the castor-oil-based PU dispersions cured by CX-100.

heat capacity change of the second DSC scan. Samples of ≈ 5 mg were cut from the films and used for analysis. TGA of the films was carried out on a TA instrument Q50 (New Castle, DE). The samples were heated from 50 to 650 °C at a heating rate of 20 °C · min⁻¹ in air. Generally, ≈ 10 mg samples were used for the TGA.

The tensile properties of the PU films were determined using an Instron universal testing machine (model 4502) with a crosshead speed of 100 mm · min⁻¹. Rectangular specimens of 80 × 10 mm² (length × width) were used. An average value of at least four replicates of each sample was taken. The toughness of the polymer, which is the fracture energy per unit volume of the sample, was obtained from the area under the corresponding tensile stress/strain curves.

Results and Discussion

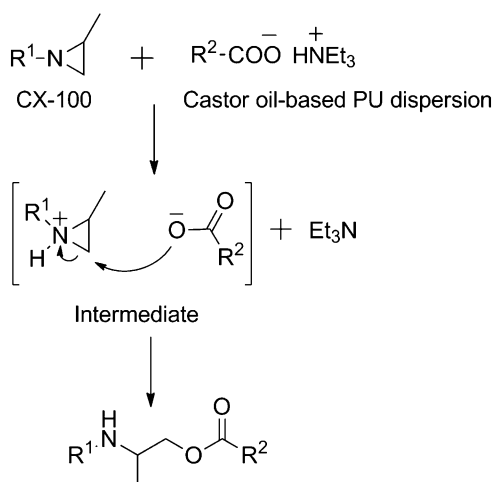
Structure and Ethanol Uptake

The castor-oil-based anionic PU dispersions contain carboxylate groups, which act as an internal emulsifier to stabilize the dispersions. These carboxylate groups can react with aziridine groups very quickly to open the aziridine ring and form an ester group and a secondary amine (Scheme 3). The crosslinking reaction between the aziridine and the carboxylate can occur at ambient conditions with a reasonable rate, and no heat or catalyst is needed to complete the cure process.^[25] Thus, the multiaziridine rings

Table 1. DMA, DSC, and TGA data for the PU-AZ films.

Polymer	AZ/COOH	CX-100 amount [phr]	Gel content	T_g^a	T_g^b	TGA data [°C]		
			[wt.-%]	[°C]	[°C]	T_5^c	T_{50}^d	T_{max}^e
PU-AZ0	0	0	84	41.3	13.3	162	333	314
PU-AZ25	0.25	2.8	86	44.7	16.5	183	337	318
PU-AZ50	0.50	5.6	87	47.7	17.0	189	332	317
PU-AZ75	0.75	8.4	88	51.8	16.2	198	327	318
PU-AZ100	1.00	11.2	89	51.7	16.4	209	337	342

^a) Glass transition temperature obtained from DMA; ^b) glass transition temperature obtained from DSC; ^c) temperature of 5% weight loss; ^d) temperature of 50% weight loss; ^e) temperature of maximum thermal degradation.



Scheme 3. Reaction between the PU dispersion and CX-100.

in the crosslinker CX-100 can react with the carboxylate groups in the PU to form a more highly crosslinked network, providing a very efficient way to crosslink the castor-oil-based anionic PU dispersions, and improve the thermal and mechanical properties of the films.

The amount of ethanol swelling and the gel content indicate the degree of crosslinking of a polymer. Figure 1 shows the ethanol uptake results. The amounts of ethanol absorbed and the amounts of film dissolved in ethanol decrease from 155.9 to 73.9% and 16.3 to 10.8%, respectively, when the percent aziridine is increased from 0 to 100%, which indicates that post-cure between the CX-100 and the anionic PU dispersions has occurred and the crosslink densities of the films have increased. Similar results have been reported by Lai et al.^[22] The amount of crosslinked polymer formed (gel content) increases from 84 to 89 wt.-% (Table 1), as a result of the increased crosslink density.

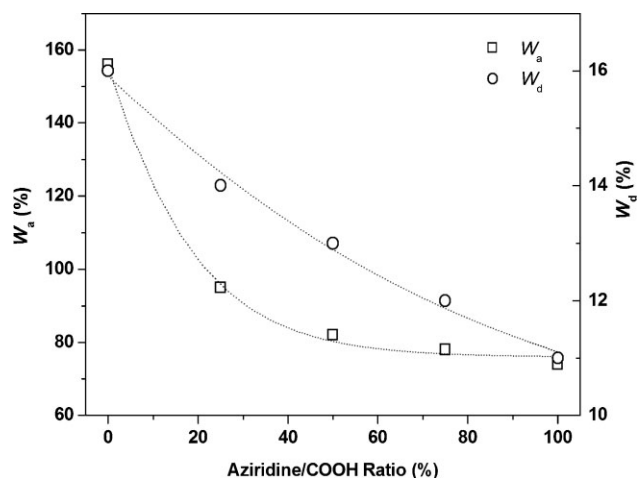


Figure 1. Ethanol uptake results for the films: the amount of ethanol absorbed by the film (W_a) and the amount of film dissolved in ethanol (W_d).

Thermal Properties

The storage modulus (E') and $\tan \delta$ curves as a function of temperature for films with different CX-100 loadings are shown in Figure 2. All of the films are in the glassy state below room temperature and E' decreases slightly with an increase in temperature. Then a rapid decrease in E' occurs above 25 °C for all of the films and a peak maximum is observed in the $\tan \delta$ versus T curves (α relaxation), which is taken as the glass transition temperature (T_g). All of the films show only one $\tan \delta$ peak, indicating the homogeneous nature of the aziridine-cured PU system. Both the storage moduli at room temperature and high temperature are enhanced, which is evidence that the aziridine curing process increases the crosslink densities and improves the mechanical properties. Moreover, a rubbery storage modulus plateau is observed for PU-AZ100 at high temperatures,

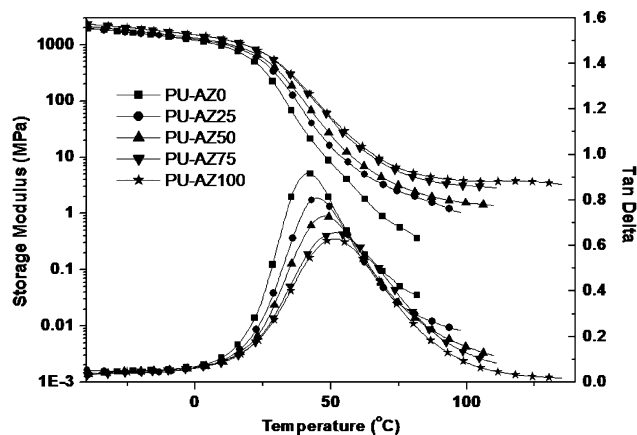


Figure 2. The storage modulus and loss factor ($\tan \delta$) as a function of temperature for the PU-AZ films.

indicating the enhanced crosslinking for the PUs with CX-100. Furthermore, the decreased height of the $\tan \delta$ peak with higher amounts of CX-100 indicates increased crosslink densities for the films.^[26] The T_g s obtained from DMA are summarized in Table 1. The T_g s increase from 41.3 to 51.7 °C, when the percent aziridine increases from 0 to 100%. This can be explained by the polymer chain motion being restricted at higher crosslink densities. The DSC thermograms of the PU films are depicted in Figure 3. All of the curves show one glass transition with no melting or crystallization transition, indicating the amorphous nature of these PUs. The T_g values are summarized in Table 1. Compared to the neat PU film, PU films cured with CX-100 have higher glass transition temperatures, which result from the increased crosslink densities. However, the PU films with a variety of CX-100 loadings have pretty similar T_g s, presumably because the soft chains from the CX-100 compensate for the increased crosslink densities. A similar

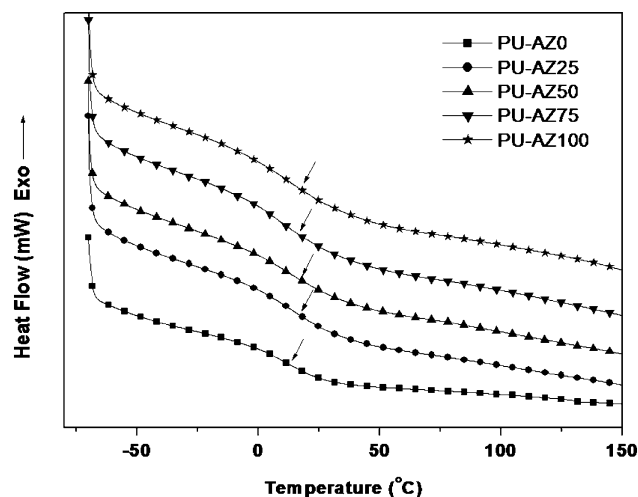


Figure 3. DSC scans for the PU-AZ films.

phenomenon has been observed in the DMA results from PU-AZ75 and PU-AZ100. The T_g s obtained from DMA are ≈ 30 °C higher than the T_g s obtained from DSC. This results from the different nature of these two methods. DMA measures the change in the mechanical response of the polymer chains, while DSC measures the change in heat capacity from frozen to unfrozen chains.^[14]

The TGA curves for all of the PU-AZ films with different CX-100 loadings are shown in Figure 4, and the T_5 , T_{50} , and T_{max} data are summarized in Table 1. PUs are generally thought to have a relatively low thermal stability, due to the labile urethane bonds, which usually decompose below 300 °C through dissociation of the urethane bonds to form isocyanates, alcohols, primary amines, secondary amines, olefins, and carbon dioxide.^[27] According to Figure 4, three thermal degradation processes for the PU films are observed. Degradation in the range 150–300 °C is attributed to decomposition of the urethane bonds. The fastest degradation process between 300 and 450 °C results from chain scission of the castor oil. The last degradation step

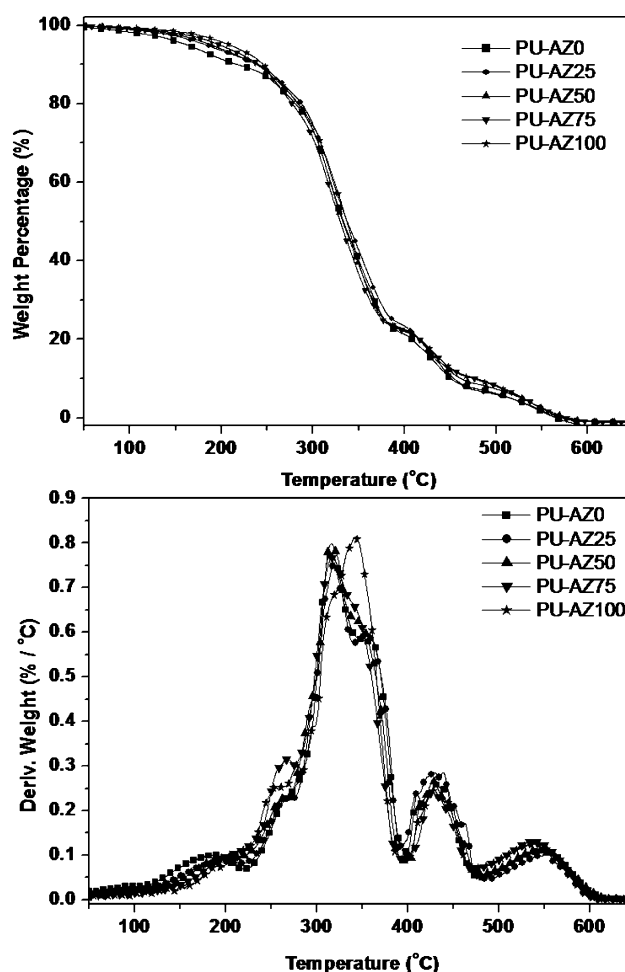


Figure 4. TGA curves and their derivative curves for the PU-AZ films.

above 450 °C corresponds to further thermo-oxidation of the PU films in air. The onset decomposition temperatures of the PU films are recorded as T_5 , where 5 wt.-% mass of the films is lost. As summarized in Table 1, T_5 increases from 162 to 209 °C as the CX-100 amount increases from 0 to 11.2 phr. This significantly increased thermal stability of the PU films can be ascribed to the increased crosslink density imparted by the aziridine-based crosslinker CX-100. However, T_{50} , the temperature at which the PU films lose 50 wt.-% of their mass, does not change that much as the CX-100 amount increases, which can perhaps be explained by the fact that the secondary amines formed by reacting the carboxylate groups with the aziridine decompose together with the amines formed from dissociation of the urethane groups. The maximum degradation temperatures ($T_{\max}$) can be obtained from the TGA derivative curves and are summarized in Table 1. Increased crosslink densities increase the $T_{\max}$ and PU-AZ100, which has all of the carboxylate groups reacted with aziridine groups, has a much higher $T_{\max}$ compared to PU-AZ0. This is in good agreement with the thermal stabilities of the PU-AZ films, which are significantly improved with the increased crosslink densities.

Mechanical Properties

Figure 5 shows the tensile stress/strain behavior of all of the PU-AZ films with CX-100 amounts ranging from 0 to 11.2 phr, and Table 2 summarizes the Young's moduli, tensile strengths, elongation at break values, and toughness of the PU-AZ films. All of the PU-AZ films show characteristics of ductile polymers. With an increase in the percent aziridine from 0 to 100%, the Young's moduli and tensile strengths dramatically increase from 14.5 to 125 MPa, and 13.1 to 18.1 MPa, respectively, due to the multiaziridine-containing crosslinker CX-100 crosslinking the PU chains more effectively. On the other hand, the elongation at break values decrease from 336.1 to 173.1% with the increase in crosslink density, as expected.

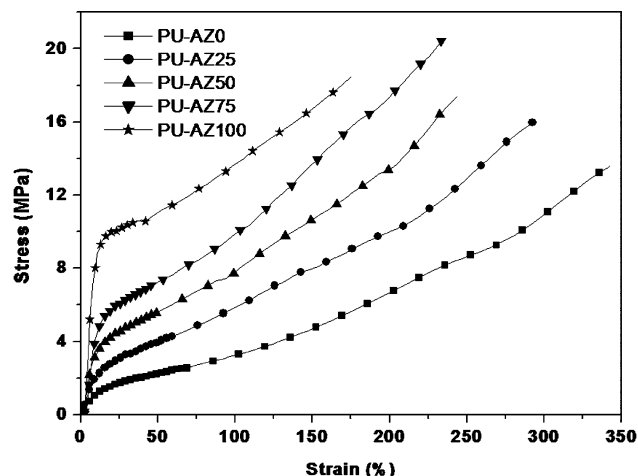


Figure 5. Stress/strain curves for the PU-AZ films.

Besides the Young's modulus and strength, the toughness, which is a material's resistance to fracture when stressed, is also obtained from Figure 5 by integrating the area below the stress/strain curve. Ductile materials are tough, while brittle materials have low toughness.^[28] Both the tensile strength and the elongation at break contribute to the overall toughness value. As seen in Table 2, the toughness first increases from 20.7 to 29.2 MPa with an increase in the percent of aziridine from 0 to 75%, and then the toughness drops to 21.7 MPa with a 100% aziridine. Generally, an increased crosslink density increases the tensile strength, but lowers the elongation at break.^[28] This results in a change in the toughness for these PU-AZ films. Compared to the previously prepared methoxylated soybean oil polyols (MSOLs),^[14,16] the homogeneous distribution of hydroxyl groups in castor oil results in PU films with higher toughness, which mainly results from the high elongation at break values.

Table 2. Tensile properties for the PU-AZ films.

Polymer	Mechanical properties ^{a)}			
	E	σ_b	ε_b	Toughness
	[MPa]	[MPa]	[%]	[MPa]
PU-AZ0	14.5 ± 2.4	13.1 ± 0.7	336.1 ± 6.5	20.7 ± 0.5
PU-AZ25	21.9 ± 5.6	16.3 ± 0.5	278.2 ± 15.1	22.9 ± 1.0
PU-AZ50	43.5 ± 5.3	17.7 ± 0.5	246.2 ± 2.3	23.6 ± 1.2
PU-AZ75	48.4 ± 7.1	21.7 ± 1.2	241.4 ± 11.2	29.2 ± 2.4
PU-AZ100	125.0 ± 20.3	18.1 ± 0.5	173.1 ± 4.2	21.7 ± 1.3

^{a)} E = Young's modulus, σ_b = tensile strength, and ε_b = elongation at break.

Conclusion

Castor-oil-based anionic PU dispersions have been post-cured by a multiaziridine-based crosslinker CX-100 to prepare coatings with higher thermal and mechanical properties. The crosslink densities of the resulting films increase with more CX-100, which is evidenced by their ethanol uptake. The T_g s of the resulting films increase with an increase in the amount of the crosslinker, but do not change a lot at higher CX-100 loadings, which results from the flexible CX-100 chains compensating for the increased crosslink density. The mechanical properties are dramatically improved with the crosslinker CX-100. For example, the Young's modulus and tensile strength increase from 14.5 to 125 and from 13.1 to 18.1 MPa, respectively, when the percent aziridine increases from 0 to 100%. The onset decomposition temperatures of the resulting films, T_5 , increase from 162 to 209 °C, indicating a significantly increase in the thermal stability of the resulting films. This work provides an effective and promising way of curing biorenewable anionic PU dispersions for environmentally-friendly, high performance coatings. Moreover, additional work on using fatty-acid-derived aziridine crosslinkers^[29] is under consideration.

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