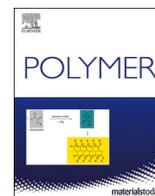




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Spectroscopic study of the morphology development of closed-cell polyurethane foam using bio-based malonic acid as chain extender

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ABSTRACT

In this study the advantages of using bio-based multi-functional malonic acid salt as chain extender in preparing closed cell polyurethane foams is demonstrated. We found that the presence of malonic acid salt can alter the reaction kinetics, segmental mobility and hence the relative kinetics of polyurethane and polyurea formation. By analyzing the infrared active vibrations, it is demonstrated that the formation of urethane and urea linkages is accelerated at the initial stage of reaction, resulting in enhanced viscosity build-up attributed to the catalytic activity of the triethylamine complexed with malonic acid. The relative kinetics in formation of different morphological features thus can be used to control the cell opening process. These results, combining information on polymerization kinetics, gas evolution and phase separation, illustrate the capability of using malonic acid salt as the chain extender to manipulate polyurethane foam morphology and its potential application in polyurethane closed cell foam systems.

1. Introduction

Polyurethane (PU) foam is a well-studied subject over the last few decades. Its commercial success is amply demonstrated in the substantial number of products all around us. Most PU foams are open-cell foams used extensively in various cushioning applications [1,2]. Closed-cell foams are generally used as insulation or for structural purposes [2]. The open-cell foams are most conveniently formed using a one-step reaction involving the production of carbon dioxide (CO₂) when isocyanate reacts with water used in the formulation. In contrast, closed cell foams are usually formed using physical blowing agents [2]. In this study, we explored the possibility for using the water-activated one-step reaction to form closed-cell foams. In such fashion, it is then possible to obtain the superior mechanical property relative to the sample density of the closed-cell foam yet retain the simplicity of the one-step reaction generally associated with open-cell foam.

The physical aspect in formation of a foam can be reduced to understanding the nucleation of individual cells containing CO₂ gas created when isocyanate reacts with water molecules and the subsequent coarsening process [1,3]. The migration of mass from the membrane (cell wall) to form the struts (cell-cell boundary) is strongly

dependent on the molecular weight of the polymers being formed. In addition, this migration also strongly depends on the surface energy of the cell membrane [3]. The balance of the two competing processes determines the relative degree for the final foam to be open (ruptured cells) or closed.

The underlying chemistry in forming a PU foam is quite intriguing. The “one-shot” reaction to form PU foam consists of a liquid polyol, isocyanate and water along with additives such as chain extenders, surfactant, catalysts and others [1]. The formation of urethanes involves reaction between the hydroxyl units of the polyol or chain extender and isocyanate. The polyureas are formed concurrently when isocyanates react with water molecules. These two reactions form the copolymers generally referred to as polyurethanes [1]. The molecular weight of the copolymers formed can thus increase significantly during the reaction. In addition, polyureas, usually referred to as hard segments, can phase separate and form hydrogen-bonded domains that act as physical crosslinks connecting the elastic polyols to produce much of the elasticity associated with PU foams. The development of the phase separated morphology depends on the relative rates at which these two reactions proceed. Phase separation may be effectively intercepted and arrested by the vitrification of the phase [2,4]. Therefore, the process forming a

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PU foam is multifaceted involving a combination of gas evolution, polymerization and phase separation. The resultant morphological features, extending over several length scales, may vary greatly depending upon the kinetic competition between the chemical and physical processes.

In addition to the morphological features within structural elements, the physical properties of PU foams also depend on their macroscopic cellular structure, such as closed vs. open cell content. Generally speaking, most foams contain a combination of open and closed cells [2, 4]. In PU foams, a large fraction of closed cells will inherently alter the foam physical properties, especially stiffness [5]. As described above, the open/closed cell content ratio of a foam is determined by the interplay of various physical and chemical forces during the foaming process [3,6]. In PU foams a silicone surfactant can be added to establish the surface tension gradient along the cell window and thus provide foam stability to control the open/closed cell content [4]. The proper balance on the rates of both gas evolution and viscosity increase is a must to manipulate the structural features. Faster molecular weight build-up stabilizes the cell walls providing a polymer resistant to membrane rupture and thus results in formation of a higher degree of closed cell foam [4].

In this study, we focus on the role of the chain extender in determining PU foams. Chain extenders are typically low molecular weight diols used to not only increase the molecular weight of the PUs but also to control morphological and physical properties [2,7–20]. Although important this subject has not been comprehensively studied. Our previous study demonstrated that even a relatively small change in the structure of chain extender can significantly alter the morphological development thus physical properties [7]. Additional chemical cross-links can also be introduced when using multi-functional chain extender as the crosslinking agent. It has been reported that the addition of chain extender results in significant modifications of the viscoelasticity and composition of the hydrogen-bonded species, thus alter the phase evolution of the foaming reaction [21–24]. Therefore, changes in the chemical structure and amount of added chain extender will strongly influence foam morphology development and resultant physical properties.

The emphasis of the current study is to employ malonic acid as the chain extender to form PU foams. Malonic acid is of interest for several reasons. Concerning its chemistry, the overall structural features of malonic acid contain two active carboxyl groups and one active methylene group. On one hand, the condensation reaction between carboxylic acids and isocyanates results in formation of amides as well as CO₂ for foaming. On the other hand, the active methylene groups also react with isocyanates to form amide linkages [25,26]. In this case, malonic acid can be considered as a crosslinker as will be demonstrated in the following discussion. In addition to its unique features, another attractive advantage of malonic acid is the means by which it is generated. In practice, malonic acid has been commercially produced through a microbial process utilizing sugar and water instead of the conventional petrochemical route. The production process can be completed at relatively low cost [27]. Therefore, utilization of this bio-based chain extender is attractive from both fundamental and applied perspectives.

Here, we provide a detailed analysis of the evolution of PU foams with varying content of malonic acid salt, prepared from bio-based malonic acid and triethylamine. The multi-functionality of the malonic acid salt proved to be crucial in forming and controlling the foam reactions. PU foams with the traditional 1,4-butane diol (1,4-BDO) as chain extender were also studied for comparison. In our reactions, no surfactant was used in order to investigate only chain extender effects on the morphology development without any other additives. Infrared spectroscopy and viscosity measurements, in conjunction with electron microscopic examination of the cellular structure, gave a clear description of how malonic acid salt affects the polyurethane foaming reaction and morphology development. To the best of our knowledge, this work represents the first time that malonic acid has been applied to

PU foams and studied in this detail. Our results are reported herein.

2. Experimental

2.1. Materials

The polyol (Voranol 8136) used in this study was provided by Dow Chemical. It is a random copolymer consisting of poly(propylene oxide) polyether with ethylene oxide (<20 wt %) and terminated with secondary hydroxyl groups. It has an equivalent weight of 1029 g/mol and an average functionality of 3.01. The diisocyanate employed was an 80:20 mixture of 2,4- and 2,6-toluene diisocyanate (T80, Sigma Aldrich). The catalyst package used was a mixture of Dabco BL-11, Dabco 33-LV and Dabco T9 (Air products and Chemicals Inc.). The chain extenders employed were 1,4-butane diol (1,4-BDO, Sigma Aldrich) and malonic acid (Lygos). Triethylamine (Sigma Aldrich) was used to react with malonic acid, forming a malonic acid salt. Water purchased from Fisher Scientific was used as a chemical blowing agent. All chemicals were used as received.

Malonic acid and its ester derivatives have primarily been used in pharmaceutical applications (60%) with the remainder used in electronics, agricultural industries and flavors/fragrances. The existing petrochemical process is characterized by high raw materials costs, significant waste disposal cost and increasing concern related to environmental and safety impacts all limiting the growth potential of malonates. These concerns have been remediated by the development of a fermentation route using low cost sugars in a sustainable and environmentally benign process. The malonic acid used in this study comes from such a source (Lygos).

2.2. Foam preparation

The reaction of carboxylic acids and isocyanates proceeds at a rather slow rate under typical conditions. In order to accelerate reaction, a malonic acid salt was prepared by reacting 1 mol of malonic acid and 2 mol of triethylamine. In our foam study, the malonic acid salt readily reacts with isocyanates to liberate carbon dioxide necessary for the foaming as well as tertiary amine, also serving to catalyze the reaction of isocyanates with compounds containing reactive hydrogen atoms, such as the polyol to form urethane linkages [28].

Foams were prepared using the mixtures as shown in Table 1. Consistent with most commercial formulations, an isocyanate index of 105 and a water concentration of 4 g per 100 g polyol were maintained in this study [4]. The polyol, chain extender (malonic acid salt or 1,4-BDO), water, BL-11 and 33-LV catalysts were first well mixed in a plastic beaker with a glass rod for 1 min. T-9 catalyst was then added and mixed for an additional 30 s. Next, specific TDI was added and the mixture was stirred vigorously for 4 s. The reactants were then transferred to appropriate reaction vessels.

Table 1

Polyurethane Foam Formulations Used in This Study. All formulations are based on 100 parts by weight of polyol.

Component (part by weight)	Malonic acid salt ^a				1,4-BDO
	0%	1.5%	3%	6%	
Voranol 8136	100	100	100	100	100
Chain extender		1.50	3.00	6.00	0.87
Water	4.00	4.00	4.00	4.00	4.00
Dabco BL-11	0.20	0.20	0.20	0.20	0.20
Dabco 33-LV	0.40	0.40	0.40	0.40	0.40
Dabco T-9	0.14	0.14	0.14	0.14	0.14
T80	49.53	50.42	51.32	53.12	51.32

^a The malonic acid salt was prepared from 1 mol of malonic acid with 2 mol of triethylamine. Therefore, the content of malonic acid relative to polyol used in these formulations varies from 0% to 2%.

2.3. Characterization

2.3.1. Infrared spectroscopy

Infrared spectra were obtained using a PerkinElmer Frontier spectrometer equipped with an attenuated total reflectance (ATR) cell (Harrick Scientific FastIR™). Infrared spectral collection began just as the mixed formulation was poured onto the crystal. 16 scans of 4 cm^{-1} resolution were signal averaged to provide a temporal resolution of 13 s. After the first 10 min, spectra were collected at 1 min intervals for 30 min following reaction initiation. It should be emphasized that the reaction kinetics are carried out at a constant temperature ($23\text{ }^\circ\text{C}$), thus removing many temperature induced effects. By performing all experiments at the same temperature, it is possible to illustrate the differences in the reaction kinetics under identical experimental conditions.

Analysis of the spectra was performed as described previously [29]. A combination of Gaussian and Lorentzian function was fitted to the carbonyl vibrations ($1760\text{--}1590\text{ cm}^{-1}$). Band area data were normalized using the CH stretch ($3025\text{--}2800\text{ cm}^{-1}$) to compensate for any spectral differences due to the degree of contact with the crystal. Chemical conversion was obtained by monitoring the change in the integrated absorbance of NCO stretch ($2320\text{--}2250\text{ cm}^{-1}$), as defined below:

$$P_{NCO_t} = \frac{[\text{NCO}]_0 - [\text{NCO}]_t}{[\text{NCO}]_0} \quad (1)$$

where $[\text{NCO}]_0$ is initial integrated intensity of the NCO stretch estimated by extrapolating the initial set of data points to $t = 0$.

2.3.2. Viscosity measurement

The viscosity of the foam during the reaction was determined by a Brookfield viscometer (DV3T). The viscosity was specified with the Brookfield spindle SC4-27.

2.3.3. Scanning electron microscopy (SEM)

The cellular structure of the prepared foams was observed with a field emission scanning electron microscope (FEI Magellan 400) operated at 1 kV. Cross-sections of the samples were carefully cut perpendicular to the foaming direction. The fracture surface was gold coated before scanning.

2.3.4. Validation of malonic acid as crosslinker

Infrared spectroscopy was used to monitor the reaction between malonic acid salt and isocyanate over time. The IR spectral collection was started just as the mixed formulation ($\sim 0.30\text{ g}$ malonic acid salt and $\sim 0.18\text{ g}$ T80) was poured onto the crystal. 6 scans per spectrum were co-added to give a time resolution of 6 s. Measurements were performed using 4 cm^{-1} spectral resolution.

To verify the reaction between the active methylene group of malonic acid and isocyanate, a model system was made by reacting dimethyl malonate, triethylamine and phenyl isocyanate. The reaction progress was characterized by infrared spectroscopy.

3. Results and discussion

3.1. Foam reaction kinetics

Foam reaction kinetics were studied in order to understand the effect of adding malonic acid salt. Fig. 1 presents the isocyanate conversion vs reaction time for various foaming systems. The isocyanate conversion (P_{NCO_t}) rate, taken as the slope of the curves at the early stage of reaction (Fig. 1, inset), increases as a function of malonic acid salt used. The same trend is also found for the P_{NCO_t} consumed as a function of time. As expected, the addition of salt accelerates the rate of reaction since the triethylamine complexed with malonic acid is available as a catalyst.

The decrease in isocyanate absorbance as a function of reaction time is related to their reactions with active hydrogen-containing

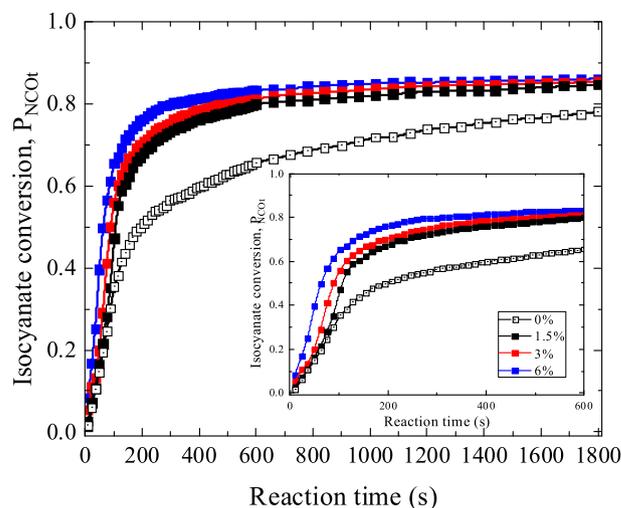


Fig. 1. Isocyanate conversion P_{NCO_t} vs reaction time for the foaming systems studied.

compounds, such as polyol, water and chain extender. During this polymerization process, it is also expected that the viscosity profile differs significantly due to the presence of malonic acid salt. Fig. 2 shows viscosity variation of the PU foams synthesized with different amounts of malonic acid salt. As shown in Fig. 2, the viscosity increases as a function of reaction time with the increase more pronounced with increasing amount of malonic acid salt. In PU foams, the viscosity build during reaction is a critical component in developing their morphology and thus final properties [4]. The multi-functional malonic acid salt enables its use as chain extender to manipulate the development of phase-separated morphology and the final cellular structure of the foams, as discussed below.

3.2. Formation kinetics of the phase-separated morphology

Time-resolved infrared spectroscopy has been found particularly useful in following structural formation during foaming [21,24,29–33]. The carbonyl region of the infrared spectrum ($1760\text{--}1620\text{ cm}^{-1}$) is indicative of several changes in the morphological features associated with PU foams. Four different C=O stretching vibrations related to urethane and urea groups should be considered. The band at 1730 cm^{-1} is assigned to the free urethane group. Vibrations at 1715 , $1700\text{--}1650$ and 1640 cm^{-1} are attributed to free, monodentate (disordered hydrogen bonded), and bidentate (ordered hydrogen bonded) ureas, respectively. The relative intensity of these bands depends strongly on

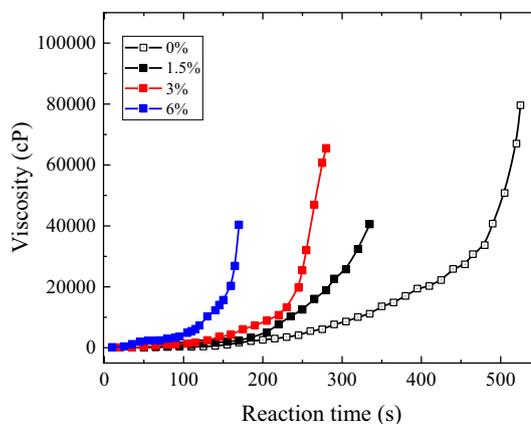


Fig. 2. Viscosity data over reaction time for the foaming systems studied. Various amount of malonic acid was used as indicated.

changes in the hydrogen bonding characteristics frequently used to characterize the degree of phase separation.

The carbonyl region for the foaming systems studied is presented in Fig. 3. Fig. 3(a) shows the time evolution of the infrared spectra for foam with no chain extender. In this case, free urethane occurs as a shoulder of the strong absorbance of free urea. These two bands grow with time and the rate of the free urea intensity increase is significantly faster than that of the free urethane. Meanwhile, a broad band near 1670 cm^{-1} , attributed to a loosely ordered urea phase, also increases intensity. At approximately 4 min, the intensity of free urea begins to decrease as a function of time. Subsequently, a bidentate urea band at 1640 cm^{-1} is observed and grows strongly in intensity as foaming proceeds. This band is indicative of the ordered hydrogen bonds associated with phase-separated structure. The formation of bidentate urea seems to occur at the expense of free urea by hydrogen bonding [29,34].

Fig. 3(b)–(d) exhibit the development of the absorbance in the carbonyl region for foams with various contents of malonic acid salt. An analogous reaction sequence detailed above is observed for foam systems with the chain extender. However, several notable differences from the foam with no chain extender have been observed. Adding chain extenders to the formulations significantly alters the formation of urethane as well as urea hydrogen bonds. In order to follow evolution of phase separated morphology more clearly, we deconvoluted the various components in the carbonyl stretching region. Although the inherent extinction coefficient of various components may vary [30,31], the deconvolution procedure presents the possibility to obtain a qualitative description of the structural evolution as a function of time [29].

The evolution of free urethane, monodentate urea and bidentate urea as a function of reaction time is shown in Fig. 4(a)–(c), respectively. At the beginning of the foaming reaction with the addition of the malonic

acid salt, the development of free urethane is faster than the foam with no chain extender (Fig. 4(a)). This is related to the rapid increase in molecular weight build-up as shown in Fig. 2. The reduction in segmental mobility limits the formation of urethane linkages. The intensity of this band thus decreases inversely to the chain extender content: $6\% > 3\% > 0\% > 1.5\%$, for the latter part of the reaction. The intensity of monodentate urea (Fig. 4(b)) grows faster with increased chain extender content, consistent with the previous study on the reaction between isocyanate with carboxylic acid [35]. It should also be noted that amides may form (bands in the $1700\text{--}1650\text{ cm}^{-1}$ region) in the reaction of malonic acid with isocyanates [35]. The intensity of monodentate urea may contain the contribution from hard segments created by the chain extender. In contrast, as shown in Fig. 4(c), the development of bidentate urea is observed to decrease with increased malonic acid chain extender content. This suggests lower concentrations of well-ordered hard segment domains are present in the foam system with a higher amount of the chain extender based on malonic acid.

As shown in Fig. 4, the addition of chain extender to the formulations is shown to not only change the number of highly ordered urea domain but also dramatically alter its formation kinetics. In this analysis, the onset of phase separation is taken as the point where the 1640 cm^{-1} band first appears. In Fig. 4(c), the onset of phase separation appears earlier in time with increased chain extender content. The intensity of bidentate urea absorbance is then replotted against the isocyanate conversion to remove the concentration effects in the reacting foams. This procedure is undertaken because the carbonyl concentration is directly proportional to the isocyanate conversion. The result is shown in Fig. 4(d). The chain extender produces a clear shift of the onset of phase separation towards a higher value of isocyanate conversion. This is understandable as a considerable amount of urethane and urea

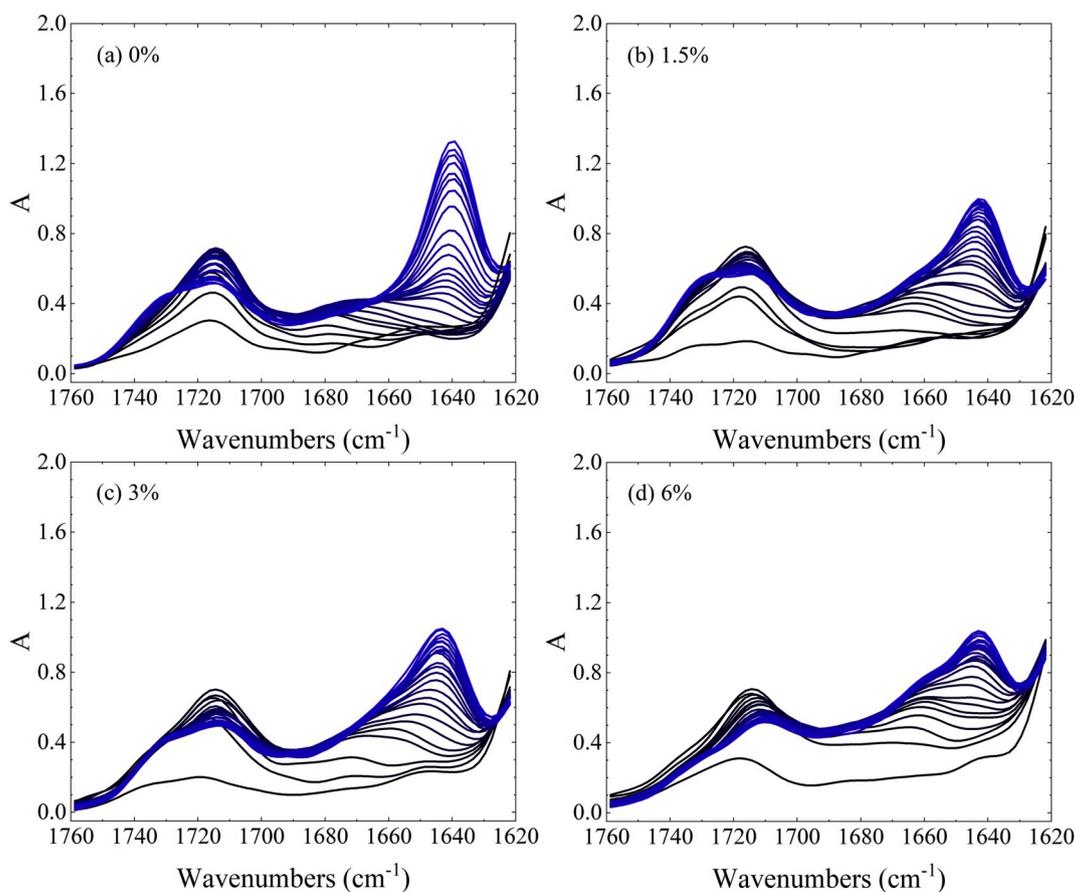


Fig. 3. Infrared spectra collected in the carbonyl region during reaction for the foaming systems studied. Reaction time increases going from black to blue traces. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

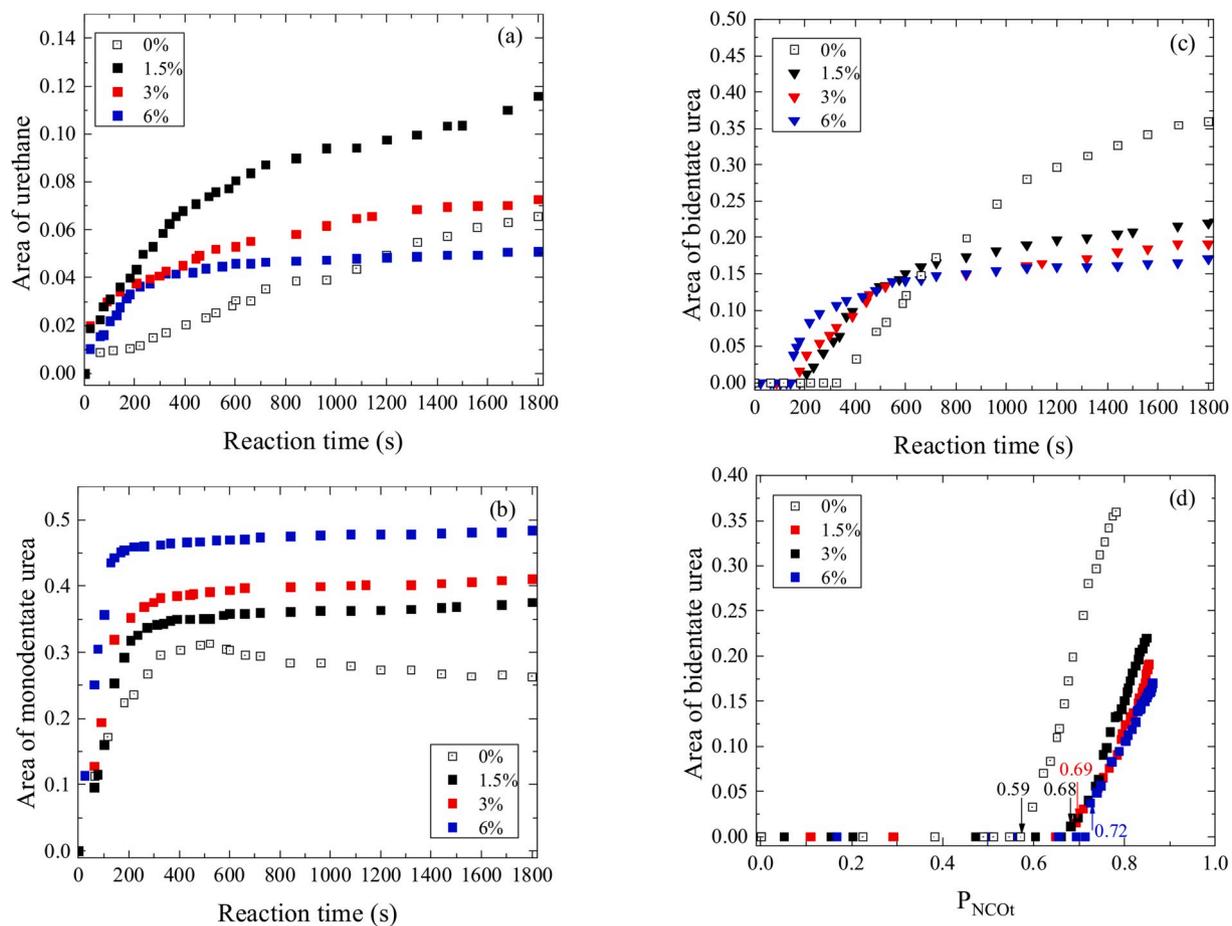


Fig. 4. Changes in hydrogen bonding with time during reaction as determined by band deconvolution: evolution of free urethane (a), monodentate urea (b) and bidentate urea (c) as a function of reaction time; evolution of bidentate urea (d) as a function of isocyanate conversion.

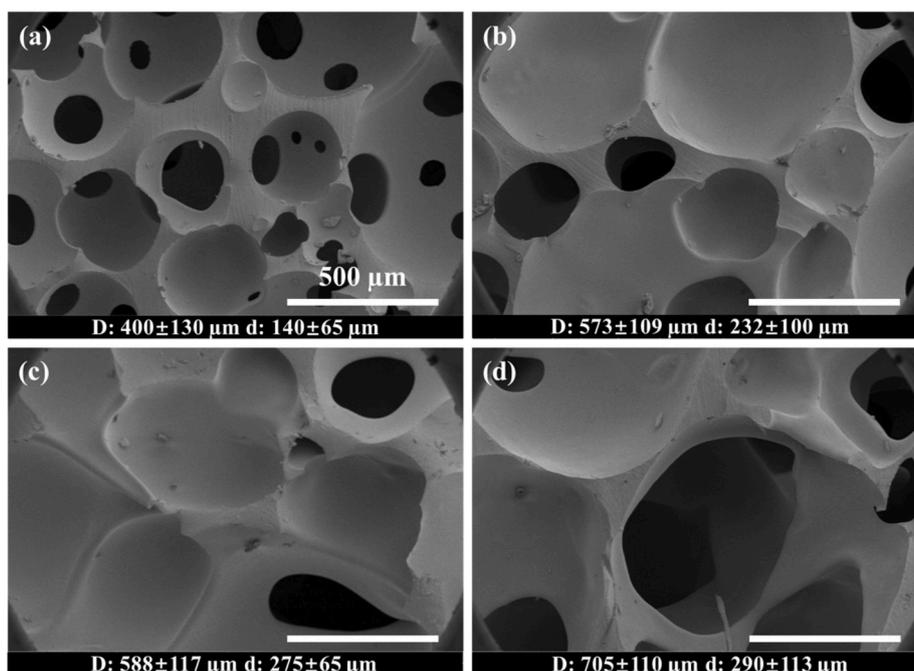


Fig. 5. Scanning electron micrographs images of polyurethane foams prepared with malonic acid salt of (a) 0%, density 0.193 ± 0.007 (b) 1.5%, density 0.108 ± 0.008 (c) 3%, density 0.128 ± 0.005 and (d) 6%, density 0.182 ± 0.009 . D: average cell diameter (μm), d: average pore diameter (μm).

polymerization was formed in the early stage of the reaction. The mobility of urea oligomers during the morphology development depends on local constraints thus the reduction in phase separation is more likely to be associated with changes in reaction kinetics that reduce organized hydrogen bonded polyureas in a timely manner [32,34].

3.3. Cellular morphology

Scanning electron microscopy (SEM) was used to examine the cellular structure of PU foams as a means to connect the morphological features produced and reaction kinetics. Fig. 5 presents SEM micrographs of PU foams made with different amounts of malonic acid salt. As observed from Fig. 5(a), the foam with no chain extender has an open cell structure with virtually no closed cells. By comparison to the PU foams prepared with chain extender, shown in Fig. 5(b) and (c), it can be seen that these foams have a higher closed cell content. As previously suggested, the reduction of the hydrogen bonded urea aggregation can suppress the cell-opening process [21]. As discussed above, the addition of the chain extender accelerates the molecular weight build-up in the reacting system and thus increase viscosity, decreasing the tendency of cells to rupture. In addition to viscosity, the rate of gas evolution is also important in determining final cellular structure of the system. As displayed in Fig. 5(d), perhaps caused by the catalytic effect of malonic acid salt [36], in samples with 6% chain extender the cell size increases with increasing the amount of salt used.

3.4. Attributes of malonic acid salt as chain extender

3.4.1. Provide CO₂ for foaming

Previous studies have shown that the condensation reaction between isocyanates and carboxylic acids results in the initial formation of an intermediate, mixed carbamic-carboxylic anhydride which in most cases is not stable [35]. The subsequent decomposition of the intermediate can proceed via two paths, both involving production of CO₂. The first path generates an amide, while the second path gives a symmetrical urea and the anhydride of the acid [35]. Fig. 6 shows the infrared spectra of the reaction between malonic acid salt and T80 isocyanate. As illustrated in Fig. 6(a), it is clear that the reaction between malonic acid and T80 isocyanate follows the first mechanism since the bands attributed to stretching of the carbonyl group of the anhydride (1840–1800 cm⁻¹ and 1780–1740 cm⁻¹) are not observed. Similarly, none of the bands assignable to anhydride are found in the formation process of our PU foams. The appearance of the amide bands (1700–1650 cm⁻¹) also confirms the occurrence of this reaction. In addition to the amide formed from carboxylic acids reacting with isocyanates, this region contains the absorbance of amide formed by the active methylene groups with isocyanates (as discussed below) [37].

Fig. 6(b) presents the spectra in the region containing characteristic vibration of the isocyanate group. The intensity of the band decreases with time as a result of the reaction. The reaction between carboxylic acids and isocyanates is also clearly evidenced by the peak at 2400–2320 cm⁻¹, attributed to CO₂, which is one of the products generated during the reaction. It is clearly seen that the mixture of malonic acid salt and T80 is blown to produce a foamed structure during the reaction. Therefore, in the formation of PU foams, the addition of malonic acid can provide additional foaming capability besides the isocyanate-water reaction.

3.4.2. Malonic acid as a crosslinker

PU foams have also been prepared using a difunctional polyol previously studied [7]. We found that the foam with malonic acid salt as chain extender is not soluble but can be swollen in DMF. However, samples with no chain extender, or incorporating 1,4-BDO as the chain extender, are readily soluble under the same reaction condition. Therefore, it is hypothesized that malonic acid can also act as a crosslinker in formation of PU foams. In addition to the two reactive

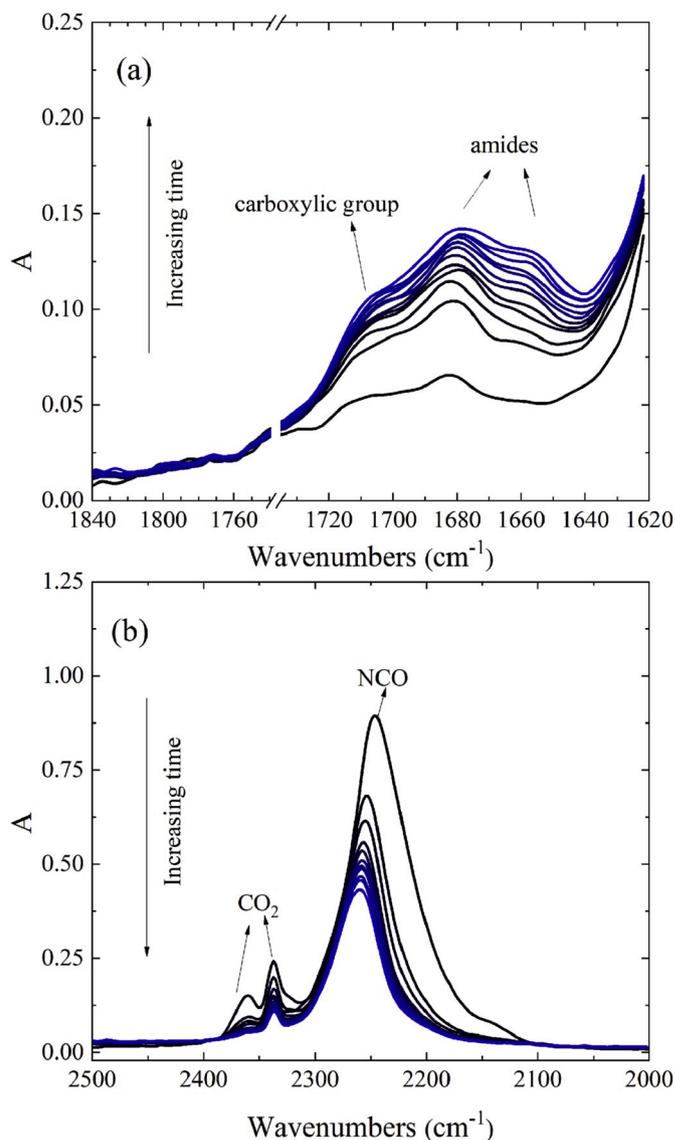


Fig. 6. Infrared spectra collected during reaction between malonic acid salt and T80 isocyanate in the carbonyl region (a) and isocyanate region (b).

carboxylic acid groups in malonic acid, it is also necessary to consider the active methylene group on the chain due to the two strong electron withdrawing groups, i.e., carbonyl groups, on either side of the methylene unit [26]. To investigate this potential, we utilized a model system comprised of dimethyl malonate, triethylamine and phenyl isocyanate. Dimethyl malonate was used to mimic the structure of malonic acid but remove the effects of the two reactive groups on the end. Fig. 7 shows the infrared spectra of the model system collected during the reaction. A new peak around 1670 cm⁻¹ is attributed to the amide carbonyl stretching [26], arising from the reaction of active methylene groups with isocyanates (Fig. 7(a)). As expected, the intensity of an isocyanate group at around 2257 cm⁻¹ decreases with time (Fig. 7(b)). In that figure, a negligible absorption of CO₂ was observed and may even be caused by the CO₂ in the background atmosphere. The infrared spectra of pure phenyl isocyanate over time excludes the possibility of the reaction of isocyanates with water in the atmosphere since no bands appear in the carbonyl region (1800–1640 cm⁻¹).

3.4.3. Comparison of different chain extenders

A PU foam with 1,4-BDO as the chain extender was examined for comparison. 1,4-BDO is the most common chain extender used in PU

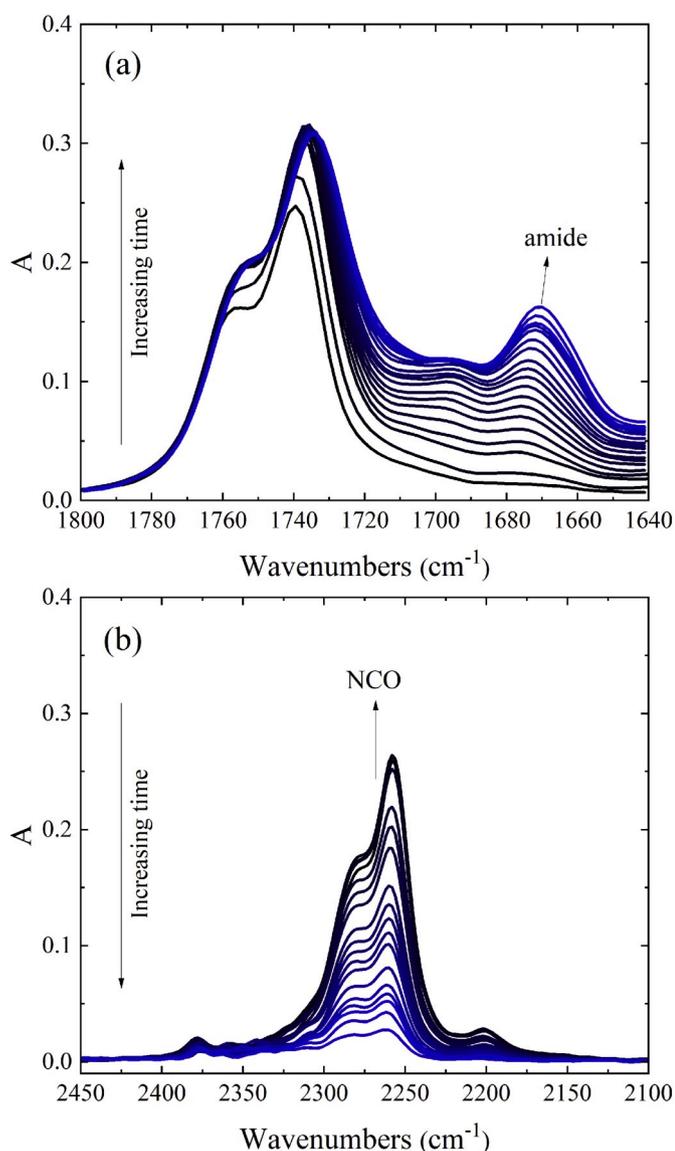


Fig. 7. Infrared spectra collected during reaction of dimethyl malonate, triethylamine and phenyl isocyanate in the carbonyl region (a) and isocyanate region (b).

foam formulations. Because of its highly active primary hydroxyl groups, the addition of 1,4-BDO enhances formation of urethane linkages. This results in a slightly faster rate of viscosity increase compared to the foam with no chain extender, though insufficient to prevent membrane rupture as seen in the SEM micrographs above. As mentioned above, on adding malonic acid salt, the foam shows a higher degree of closed-cells. The degree of cell opening has been reported to be related to mechanical properties: the presence of closed cells generally increases foam stiffness due to the combined effect of cell wall and cell edge [38].

Urea hard domains in foams serve as physical crosslinking points and allow for the rise in polymer modulus. Although the addition of malonic acid salt disrupts the hydrogen bonding interaction, the foams show comparable ordered morphological features to those with conventional chain extenders such as diethanolamine and 2-methylaminoethanol [24, 39]. Therefore, malonic acid salt provides an alternative in foam applications from the choice of chain extender.

4. Conclusions

In this study, a malonic acid salt prepared from malonic acid and

triethylamine was used as the chain extender in polyurethane foam formulations. A combination of infrared spectroscopy, viscosity measurements and cellular structure characterization has been employed to study how this chain extender affects the polyurethane foaming reaction and morphology development. On adding malonic acid salt, the viscosity build-up is accelerated during reactive processing. The resulting changes in the reaction kinetics lead to foams with a higher degree of closed cell structure. Concerning the phase separated morphology, we found that the foams show comparable ordered morphological features to those with conventional chain extenders as reported previously, although the introduction of malonic acid salt disrupts the hydrogen bonding interaction to some extent. Additionally, it has been demonstrated that this chain extender can act as a crosslinker and provide additional CO₂ for foaming during reaction due to its unique chemical structure. This study offers an opportunity to not only introduce malonic acid as the chain extender in polyurethane foam applications but also elucidate chain extender effects on foam morphology development.

Author contribution

Dr. Weiwei Zhao carried out all the experiments. Mr. Brad Nolan assisted Dr. Zhao with foaming experiments. Professor Harry Bermudez and Professor Shaw Ling Hsu are the co-investigator of this project. Dr. Umesh Choudhary and Mr. Johan van Walsem assisted with the acquisition of Malonic Acid.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CRediT authorship contribution statement

Harry Bermudez: Investigation. **Shaw Ling Hsu:** Investigation.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.polymer.2020.122344>.

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