

The Control of Molecular Interactions between Polyurethane Copolymers by Grafted Malic Acid and Its Impact on Polymer Characteristics

Yong-Chan Chung,¹ Jae Won Choi,² Joon Young Lee,³ Byoung Chul Chun²

¹Department of Chemistry, The University of Suwon, Hwasung 445-743, Korea

²Department of Nano Engineering, Center for Nano Manufacturing, Institute of Basic Science, Inje University, Gimhae 621-749, Korea

³Department of Polymer Engineering, The University of Suwon, Hwasung 445-743, Korea

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ABSTRACT: Malic acid, a molecule containing two carboxyl groups per molecule, was grafted to polyurethane (PU) through a carbamate group. The polymer was transformed to the anionic carboxylate form to observe the impact on the tensile strength and shape recovery of the PU. The electrostatic repulsion of the carboxylate reduced the molecular interactions between PUs, a result that was designed to improve the shape recovery at sub-zero temperatures while maintaining high and reproducible tensile strength and shape recovery at ambient temperatures. The grafted carboxyl group was quantitatively determined by acid–base titration, and the change in the molecular inter-

actions was confirmed via IR spectroscopy and differential scanning calorimetry. The viscosity experienced an unusual increase with increasing carboxylate content due to the covalent crosslinking caused by the grafting reagent. Shape recovery and retention were reproducible over repeated shape memory tests. Finally, the shape recovery behavior of each PU was compared at temperatures between -30 and 10°C . © 2012 Wiley Periodicals, Inc. *J Appl Polym Sci* 000: 000–000, 2012

Key words: malic acid; shape recovery; grafting; polyurethane

INTRODUCTION

Shape memory polyurethane (PU) has a phase-separated structure that is composed of hard and soft segments.^{1–8} Molecular interactions, such as hydrogen bonding and dipole–dipole interactions, bind the hard segments to form a hard domain, and the hard domain plays an important role in shape recovery at warm temperatures. The flexible, soft segment absorbs external stress and maintains polymer resilience at low temperatures. The molecular interactions may be a deterrent if shape recovery is tested at very low temperatures. The control of molecular interactions is necessary if the low-temperature shape recovery and the high-temperature shape recovery are to be attained. Low-temperature shape memory is necessary for elastomers and plastics due to their rigidity and brittleness at low temperature. Considering the industrial demands for the polymers performing under extreme conditions, the PUs

with low-temperature shape memory need to be developed.⁹

As a way to control molecular interactions, a grafted functional group is employed in the present investigation. The grafting of functional groups to polymers has been extensively researched for the development of new functional polymers without harming the basic structure.^{10,11} Ample examples of PUs with pendant functional groups developed for a variety of potential applications exist. For example, biodegradable PU containing a pendant amino group as an active site was conveniently synthesized from the diol-containing aspartic acid.¹² A pendant bromomethyl group was inserted into the soft segment for use in PU surface modification.¹³ PU was modified to a water-compatible form by incorporating a pendant carboxylate–ammonium salt group.¹⁴ As a method for grafting a functional group to PU, allophanate bonding has been successfully employed under very mild reaction conditions.^{15–20}

The changes in the molecular interactions and the impact on the tensile strength and shape memory properties are very intriguing. The repulsion between the anionic groups may reduce molecular interactions and contribute to shape recovery under freezing conditions. As a source of the anionic functional group, malic acid was selected due to the presence of two carboxyl groups and a hydroxyl for

Correspondence to: B. C. Chun (bcchun@inje.ac.kr).

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grafting to the PU. Malic acid is easily available due to its usage as a food additive to increase tartness. Previously, malic acid was used for the synthesis of a degradable polymer for biomedical applications, but it has not been applied to PU.^{21–23} The primary investigation presented examines whether the grafted malate ions improve or worsen the molecular interactions and how the grafted PU behaves at extremely low temperatures.

EXPERIMENTAL

Materials

Poly(tetramethylene glycol) (PTMG, $M_w = 2000$ g/mol, Aldrich, St. Louis, Mo), L-malic acid (Aldrich), and 4,4'-diphenylmethane diisocyanate (MDI, Junsei Chemical, Japan) were dried overnight under high vacuum (0.1 Torr) before use. 1,4-Butanediol (BD) was obtained from Duksan Chemical (Seoul, Korea) and dried under high vacuum overnight. *N,N*-Dimethylformamide (DMF, Duksan Chemical) and *N,N*-dimethylacetamide (DMAC, Duksan Chemical) were distilled over CaH_2 under nitrogen before use.

Synthesis of polyurethane

A mixture of MDI and PTMG was stirred at 50°C for 3 h under a nitrogen atmosphere in a 500-mL four-neck flat-bottomed flask equipped with a condenser and mechanical stirrer to prepare the prepolymer. BD dissolved in 20 mL of DMF was added to the flask as a chain extender and allowed to react for another hour under the same conditions. Subsequently, a second volume of MDI was added to the above reaction mixture, and the reaction was allowed to proceed for 1 h. Finally, a volume of malic acid (equivalent to the number of moles in the second volume of MDI) was added with an additional 100 mL DMF, and the mixture was stirred under the same conditions for 2 h. The final PU product was washed in distilled water until clearness, ethanol, and chloroform, and then dried in an oven (60°C) for 1 week to completely remove any remaining solvent. The specific mole ratios of the M1 and M2 series are summarized in Table I.

Mechanical and shape memory analysis

The specimens for the mechanical and shape memory tests were prepared by pouring a solution of PU and DMF (10 g of PU in 100 mL of DMF) into a Petri dish (12 cm × 1 cm) and then drying them at 60°C for 60 h to fabricate a thin film. The specimens were made from the thin film, and the tensile strength was measured according to the ASTM D638 standard using a universal test machine (UTM) equipped with a temperature-controlled chamber (Lloyd Instrument, Model LR50K) with a gauge length of 25 mm, crosshead speed of 10 mm/min,

TABLE I
Composition of the PUs

Sample code	Composition (mmol)				
	MDI-1	PTMG	BD	MDI-2	Malic acid
M1-1	50	20	30	–	–
M1-2	50	20	30	5	5
M1-3	50	20	30	10	10
M1-4	50	20	30	15	15
M1-5	50	20	30	20	20
M2-1	50	17.5	32.5	–	–
M2-2	50	17.5	32.5	5	5
M2-3	50	17.5	32.5	10	10
M2-4	50	17.5	32.5	15	15
M2-5	50	17.5	32.5	20	20

and a load cell of 2.5 kN. The UTM was also used to measure the stress and strain at various temperatures to investigate the effects on shape memory. This test was conducted according to method outlined in the literature.^{4–7}

General analysis

An Fourier transform infra red (FTIR) spectrometer (JASCO 300E) equipped with an attenuation total reflectance (ATR) accessory was used to measure the IR spectrum using the following scan parameters: 4 cm^{-1} resolution, 25 scans, and 2 mm/s scan speed. A differential scanning calorimeter (DSC-2010, TA instrument) was used to collect calorimetry data for both heating and cooling scans at a rate of 10 °C/min between –50 and 250°C. After melting at 250°C for 5 min and cooling quickly to –50°C, a 20 mg specimen was warmed to 250°C at 10 °C/min. The second heating scan was selected for comparison. Intrinsic viscosity was measured over an average of five experiments for PU dissolved in DMAC at four different concentrations (0.125, 0.25, 0.5, and 1 g/dL) by extrapolating viscosity data measured by an Ubbelohde viscometer at 25°C. A PU solution (1 g dissolved in 20 mL of DMF) was diluted with 10 mL of isopropanol and titrated with a 0.1M NaOH solution (50/50, water/isopropanol) using a drop of phenolphthalein indicator in ethanol. The carboxyl content of the PU (mmol/g) was calculated from the average of five titrations. The carboxyl group of the PU was ionized to the carboxylate form by dissolving the PU in a solution (50/50, DMF/isopropanol) containing an excess of NaOH (10 equiv to the carboxyl group), and the PU was washed thoroughly in deionized water and dried.

RESULTS AND DISCUSSION

Synthesis

The PU was synthesized using previously reported methods.^{4–7} Malic acid was grafted to the PU chain

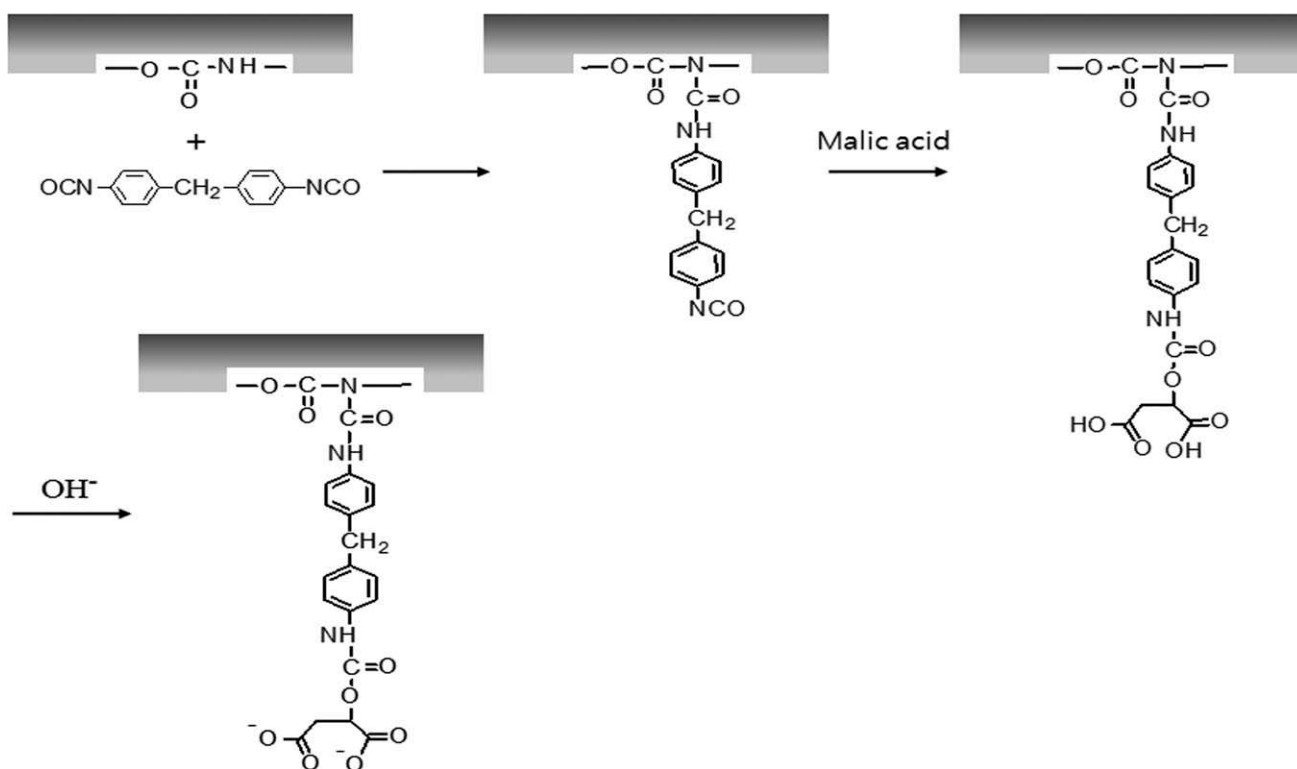


Figure 1 PU grafting with malic acid.

through a carbamate group and was ionized to the carboxylate form. The repulsion between the grafted malate ions is intended to disrupt the molecular interactions between the PU chains and to allow the PU to be flexible enough to move at subzero temperatures. The PU grafting with diisocyanate is well-researched and can be performed under very mild reaction conditions.^{15–20} In this experiment, the use of a catalyst such as dibutyltin laurate (DBTL) or triethylamine was not necessary because the grafting reaction was fast enough to finish without the catalysis. Malic acid was selected as the functional group because it contains two available carboxyl groups per molecule, and the hydroxyl group could be used for grafting to the PU chains. The scheme of the malic acid grafting is shown in Figure 1. Quantitative analysis of the attached carboxyl group was accomplished by base titration. The carboxyl content determined by titration was in agreement with the theoretical expectation, which suggested that the malic acid was almost reacted with the isocyanate group of PU chains (Fig. 2). Some of the second MDI could have been used for the covalent cross-linking with other PUs, reacted between themselves or with malic acids, and did not react at all. The low-molecular weight byproducts and the remaining reactants could be removed by the thorough washing process after polymerization. The covalent cross-linking could be recognized in the following characterizations. After the attachment of malic acid to the

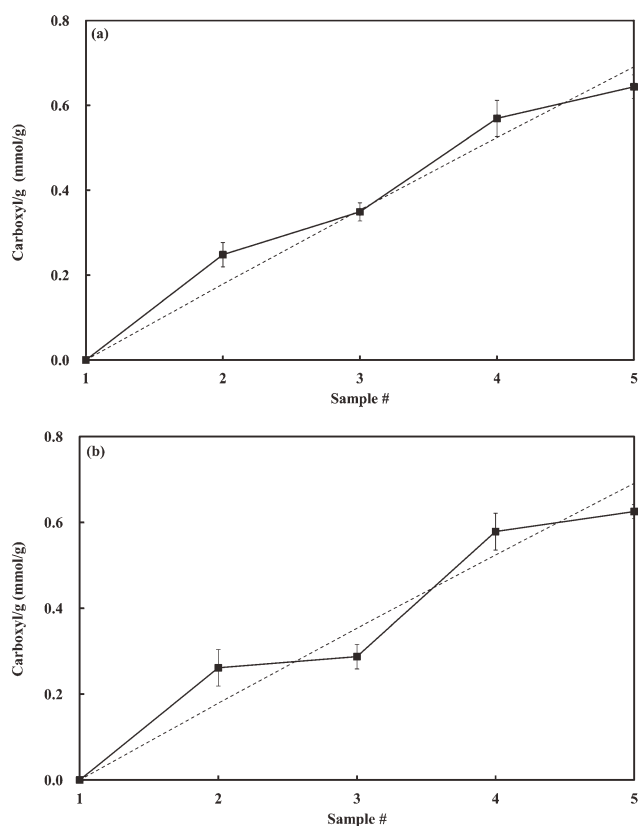


Figure 2 Carboxyl content profile of (a) M1 and (b) M2 series determined by base titration (dashed line indicates the theoretical amount).

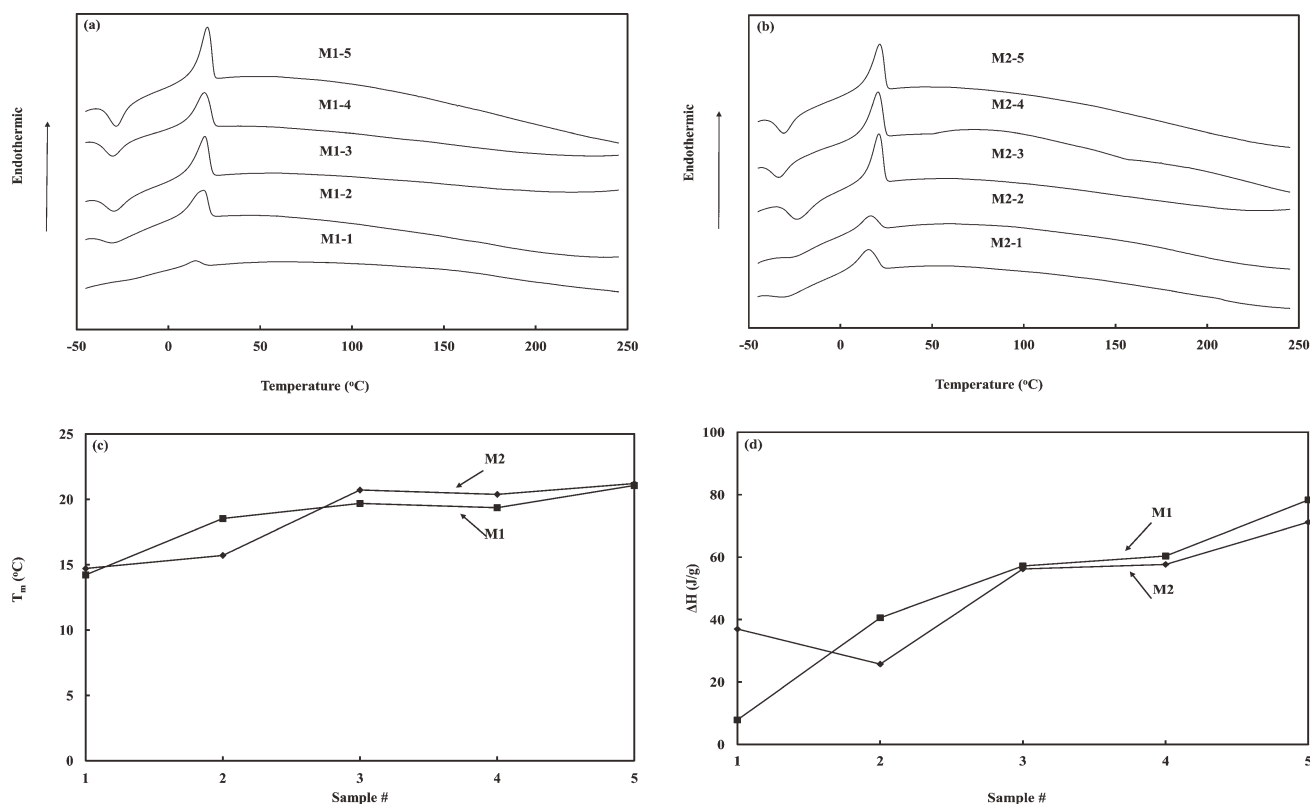


Figure 3 DSC thermograms of the (a) M1 and (b) M2 series. Comparison of (c) T_m and (d) ΔH of the M1 and M2 series.

PU was confirmed, the carboxyl groups of the PU were ionized to the carboxylate form by dissolving the PU in a solution (DMF/isopropanol) with an excess of NaOH (10 equiv to the carboxyl group), which was then used for analysis.

Thermal analysis

The thermal behavior of the M1 and M2 series was investigated by DSC from -50 to 250°C [Fig. 3(a,b)]. The glass transition temperature (T_g) of the soft segment in the PU was low (under -60°C) and difficult to detect by DSC; instead, the melting temperature (T_m) of the soft segment in the PU was determined. The T_m of the M1 series gradually increased with the increase of malic acid content; specifically, the results yielded values of 14.2°C for M1-1, 19.7°C for M1-3, and 21.0°C for M1-5. The M2 series showed a similar increase in T_m to the M1 series. The results showed temperatures of 14.7°C for M2-1, 20.7°C for M2-3, and 21.2°C for M2-5. The gradual increase of M1 and M2 series is compared in Figure 3(c). The enthalpy change (ΔH) for the phase transition, corresponding to the area of each peak, also increased with the malic acid content for both the M1 and M2 series. For example, 7.8 J/g for M1-1 increased to 57 J/g for M1-3 and 78 J/g for M1-5. Additionally, 36 J/g for M2-1 increased to 56 J/g for M2-3 and 71 J/g for M2-5, as shown in Figure 3(d). The gradual

increase in T_m and the significant enthalpy change for both the M1 and M2 series with an increase in malic acid content are due to the restricted molecular movement of PU chains covalently crosslinked by a grafting agent, the second MDI. Therefore, the covalently crosslinked structure raised the T_m and ΔH . Such phenomena were also observed in our previous crosslinked PUs.^{5,6} It is found from the DSC results that some grafting agents are involved in the covalent crosslinking of PU.

IR analysis

The IR spectra of the selected M1 (M1-1, M1-3, and M1-5) and M2 (M2-1, M2-3, and M2-5) series are compared in Figure 4. The new C–H bending peak at 1510 cm^{-1} , which was due to the grafted malic acid, grew as the malic acid content increased. This result indicates that the malic acid was grafted as intended. Intermolecular attractions, such as hydrogen bonding and dipole–dipole interactions, between the hard segments of the polymer can be observed from the IR spectra. The hydrogen bonded C=O stretching vibration appears from 1699 to 1706 cm^{-1} , slightly lower than for free carbonyl groups (1731 – 1733 cm^{-1}).^{24,25} As the malic acid content increased, the hydrogen bonded carbonyl peak of the M1 series significantly decreased relative to the free carbonyl [Fig. 4(a)]. A decrease in the hydrogen bonded

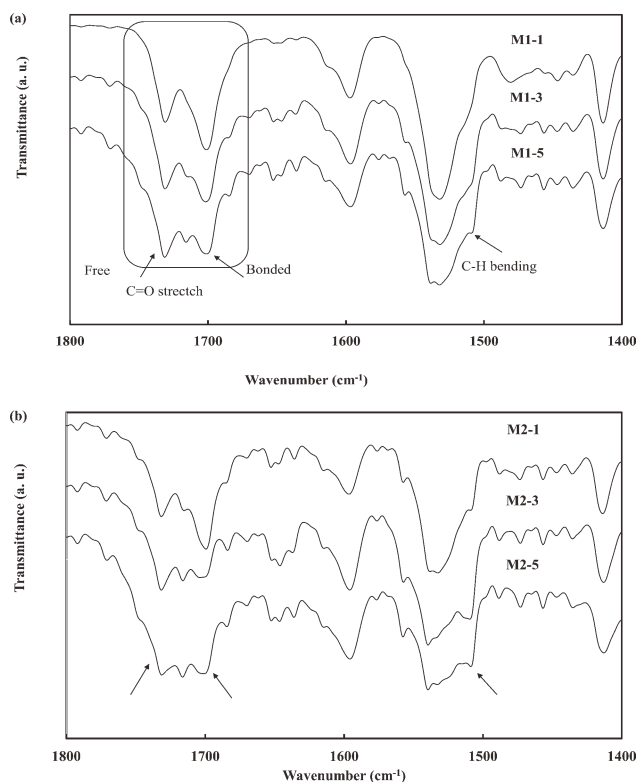


Figure 4 IR spectra of the (a) M1 and (b) M2 series.

carbonyl peak of the M2 series is also apparent [Fig. 4(b)], suggesting that the molecular interactions were significantly reduced by the carboxylate of malic acid. Both the M1 and M2 series were similarly affected by the carboxylate, which indicates that the hard segment content does not play an important role in molecular interactions. It was determined from the IR spectra that the carboxylate of malic acid was linked to the PU chains in both the M1 and M2 series and reduced the extent of molecular interaction between the PU chains.

Viscosity

The intrinsic viscosity of the M1 and M2 series was obtained from the extrapolated data of the reduced viscosity and is shown in Figure 5. In both the M1

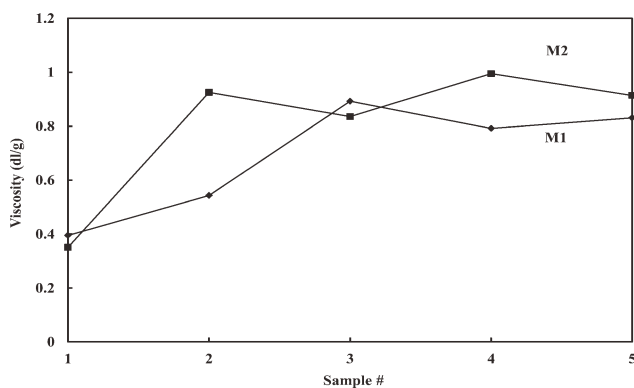


Figure 5 Intrinsic viscosity of the M1 and M2 series.

and M2 series, the viscosity increased as the sample number or malic acid content increased. The viscosity increase could have originated for two reasons: (1) the PU chains grafted with malic acid intermingled with each other and dragged on each other; (2) the grafting agent used for linking malic acid could have covalently crosslinked with another PU chain and increased the viscosity. Therefore, the intrinsic viscosity results suggest that the malic acid was coupled to the PU chains as designed.

Tensile properties

The tensile properties of the PU depended on the malic acid content of the polymer and are shown in Figure 6. The maximum stress significantly increased with increasing malic acid content for both the M1 and M2 series, behaving like a crosslinked PU. For example, the average maximum stress of the M1 series increased from only 5.9 MPa for M1-1 to 36 MPa for M1-3 and 49 MPa for M1-5, while that of the M2 series increased from 5.0 MPa for M2-1 to 39 MPa for M2-3 and 59 MPa for M2-5. As indicated by the DSC results, the covalent crosslinking induced by the second addition of MDI was responsible for the remarkable increase in the maximum stress as the malic acid content increased. The average strain at break increased with an increase in

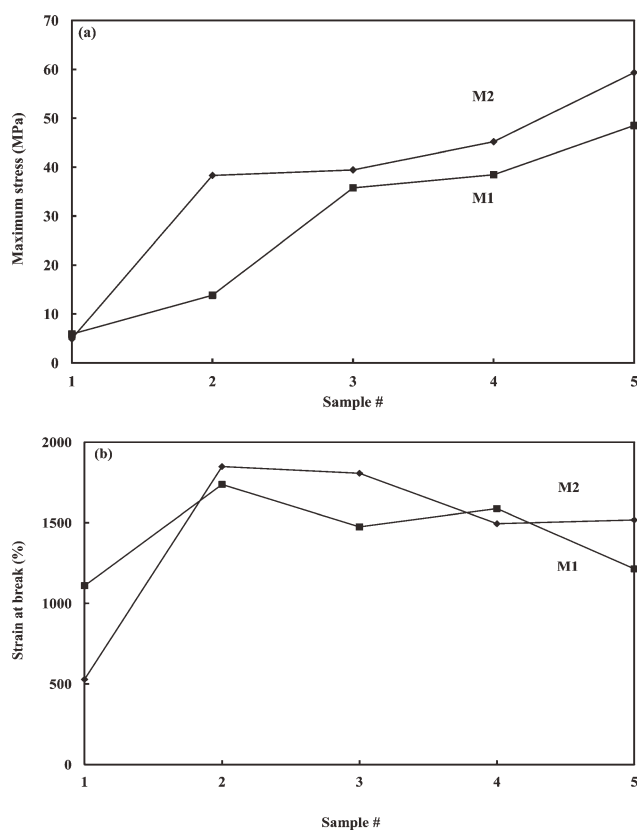


Figure 6 (a) Maximum stress and (b) strain at break for the M1 and M2 series.

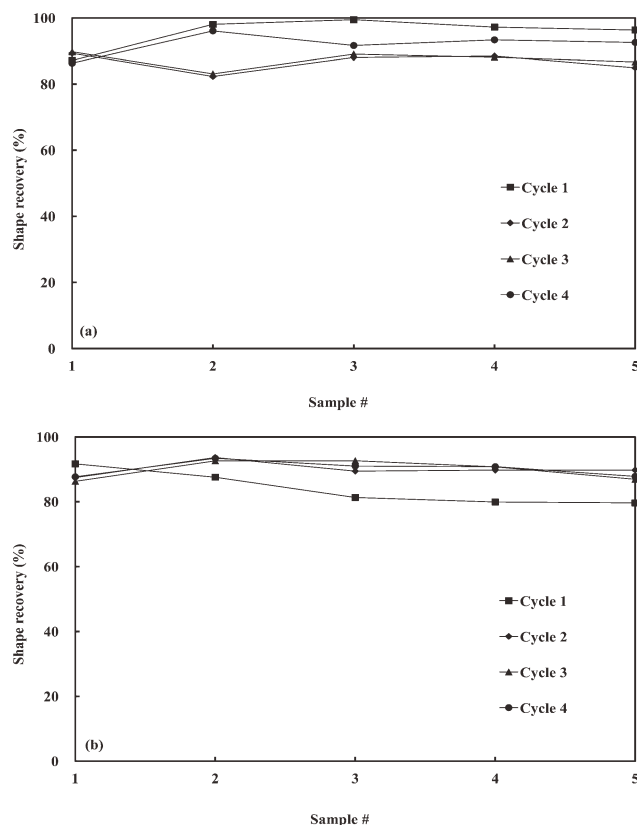


Figure 7 Shape recovery of the (a) M1 and (b) M2 series.

malic acid content for both the M1 and M2 series. For example, the average strain at break of the M1 series increased from 1100% for M1-1 to 1740% for M1-2 while the M2 series changed from only 530% for M2-1 to 1850% for M2-2. The increase appears to originate from the electrostatic repulsion between the carboxylate of malic acid that allowed free movement of the PU chains and resulted in greater strain as the malic acid content increased. The increase in strain at break was reduced if the malic acid content was further raised. The covalent crosslinking at high malic acid content was responsible for the limited increase in strain. Therefore, high tensile stresses and strains could be obtained relative to linear PUs even though the malic acid content was raised. The maximum stresses of the previously investigated glycerol and pentaerythritol crosslinked SMPUs were only 12 MPa and 17 MPa, with strains at break of 1100% and 1200%, respectively. Compared to the other crosslinked PUs, the PUs containing malic acid demonstrated better maximum stress and strain at break, even though a crosslinking agent was not used. The tensile properties of PU were fortified by the grafting of the malic acid to the PU chains.

Thermal shape memory property

Shape memory tests were repeated under cyclic stretch-release conditions at the soft segment ($T_m \pm$

30°C). The previously known T_m of PU, with PTMG as the soft segment, was used as a reference for comparison. In this case, the hard segments retain the distorted shape below the T_m and recover the original shape above the T_m . In contrast, the soft segments absorb the applied tensile stress by unfolding the entangled chains. In Figure 7, the cyclic shape memory tests of the M1 and M2 series show that shape recovery was reproducible over four test cycles. The shape recovery of both the M1 and M2 series was above 80% and did not significantly decrease after four test cycles. For example, the shape recovery of M1-5 changed from 96% in the first test to 93% in the fourth test, while the shape recovery of M2-5 increased from 80% in the first test to 88% in the fourth test. The shape recovery tests demonstrated that the PU with malic acid maintained good shape recovery and reliability under the test conditions. In contrast, the shape retention was relatively unaffected by the linking of the malic acid. For example, the shape retention of M1-1 (50%) slightly increased to 59% for M1-5, while that of M2-1 (51%) changed to 52% for M2-5. The shape retention was not affected by linking the malic acid because the stretched PU specimen was already contracted at -25°C due to the strong shape-recovering force and the grafted structure did not make a difference. The relatively low shape retention of M1 and M2 series, compared to the previous shape memory PUs, could arise from the fact that the covalent crosslinking by the second MDI, as seen in the DSC, viscosity, and tensile strength results, induced the shape recovery to the original length and decreased the shape retention. Similar to the results for the shape recovery, the shape retention remained unchanged after cyclic testing. A comparison of the shape recovery and retention of both the M1 and M2 series is provided in Table II; the difference between the M1 and M2 series is not obvious, suggesting that the hard segment content does not play an important role.

Representative samples from both the M1 (M1-1 and M1-5) and M2 (M2-1 and M2-5) series were

TABLE II
Shape Memory Properties

Sample code	Shape memory (%) ^a	
	Recovery	Retention
M1-1	87	50
M1-2	98	65
M1-3	99	67
M1-4	97	49
M1-5	96	59
M2-1	91	51
M2-2	88	50
M2-3	81	52
M2-4	80	51
M2-5	80	52

^a First-cycle shape memory results.

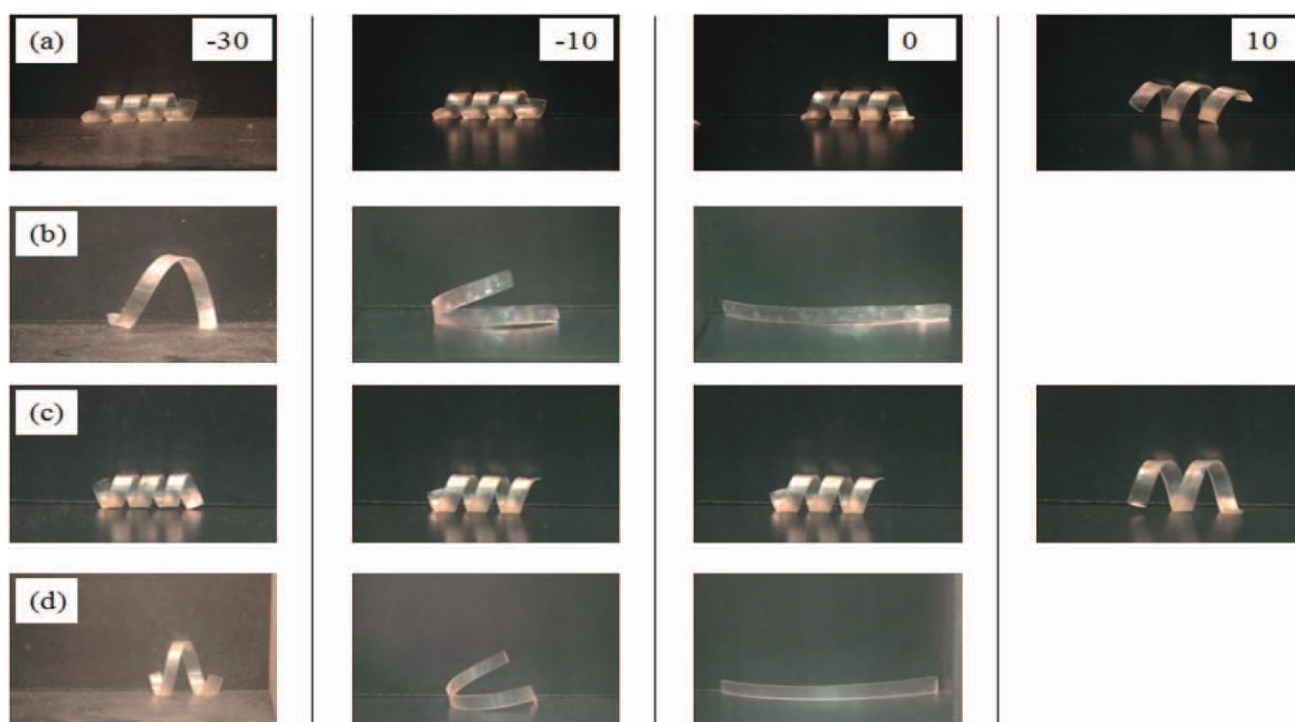


Figure 8 Shape recovery tests at various temperatures for (a) M1-1, (b) M1-5, (c) M2-1, and (d) M2-5 (number indicates the surrounding temperature). [Color figure can be viewed in the online issue, which is available at wileyonlinelibrary.com.]

selected to compare their shape recovery from -30 to 10°C . Spiral samples were bound and stored in a temperature-controlled chamber for at least 3 h before testing and were allowed to return to their original linear shape for 30 min. The resulting pictures are shown in Figure 8. All of the samples with the grafted malic acid (M1-5 and M2-5) instantly recoiled, even at -30°C , and returned to their original linear shape below 0°C ; however, the samples without malic acid (M1-1 and M2-1) did not recover their linear shape, even at 10°C . Other samples (not

shown) also showed quick shape recovery at low temperatures if grafted with malic acid. The molecular interactions formed in linear PU, hydrogen bonding, and dipole-dipole interactions are significantly interrupted due to the electrostatic repulsion by the grafted malic acid. This effect results in a torsional freedom for the PU when untwisting from the distorted shape at the freezing temperatures, allowing for the easy recovery relative to the linear samples (Fig. 9). This experiment clearly demonstrated, irrespective of the hard segment content, the importance

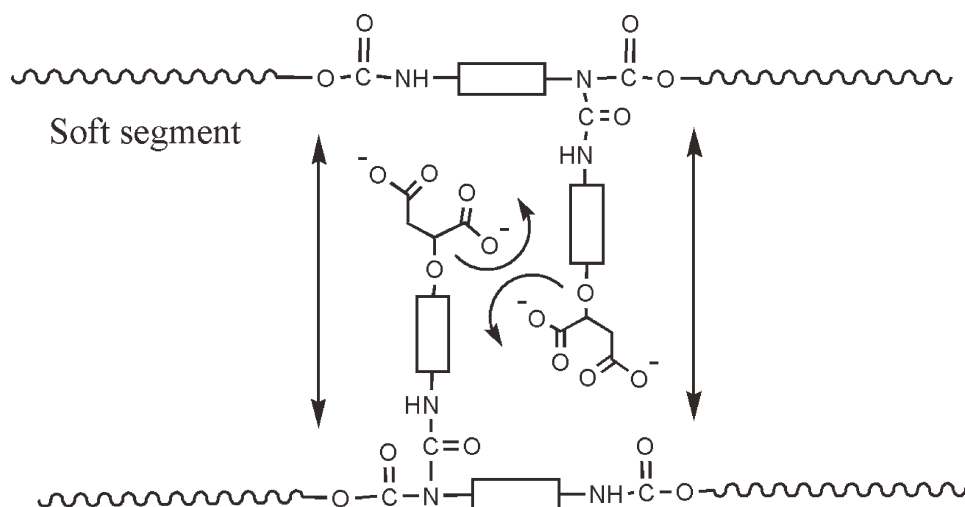


Figure 9 Stylized view of molecular repulsion between PUs grafted with malic acid (rectangle represents the rigid MDI).

of the grafted malic acid to shape recovery under freezing conditions due to the electrostatic repulsion between the PU chains. Because of its excellent shape recovery at subzero temperatures, PU with the grafted malic acid has potential applications in products that operate under cold conditions, such as sealing, vibration damping materials, arctic hoses, gaskets, automotive parts, and textiles.

CONCLUSIONS

PU was grafted with a malic acid and was quantitatively ionized into the carboxylate form. Molecular interactions between the PU chains were reduced due to the electrostatic repulsion of each carboxylate and were confirmed by DSC, IR, and intrinsic viscosity results. The tensile properties improved after the malic acid grafting, and the shape recovery and shape retention results were also excellent and reproducible. The shape recovery test, performed between -30 and 10°C , demonstrated that the grafted malic acid played an important role in recovering the original shape at the freezing temperature. Control of the molecular interactions was possible through the selection of the grafted functional group; thus, extraordinary behavior, such as the shape recovery under the freezing temperatures, could be realized.

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