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Synthesis of high temperature polyaspartimide-urea based shape memory polymers

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ABSTRACT

Thermally activated shape memory polymers (SMPs) have attracted great interest in recent years for application in adaptive shape-changing (morphing) aero structures. However, these components require materials with transition temperatures well above the glass transition temperatures of most widely available SMPs while also maintaining processability and property tailorability. In the present study, a series of novel polyaspartimide-urea based polymers are synthesized and characterized. The glass transition temperature and shape memory properties are varied using a diisocyanate resin creating a urea crosslinking moiety between the polyaspartimide chains. Overall, a family of high temperature SMPs was synthesized and characterized showing high thermal stability (>300 °C), toughness, strong shape memory effects, and tailorable properties.

1. Introduction

Shape memory polymers (SMPs) are materials which show great promise in shape-changing (morphing) adaptive structures. This class of material must exhibit the ability to withstand large deformations, being “fixed” into a temporary shape, and then recover to the original un-deformed state when triggered and sufficiently unconstrained [1]. The recovery process is typically triggered by a change in temperature, although alternative stimuli including light, infrared laser, magnetic, electric or electromagnetic field have also been explored [2]. By understanding the relationship between the chemical composition, the triggering stimulus and key material properties, critical performance parameters can be optimized and applied to the next generation of adaptive structures that could include morphing aero-component, deployable space structures, unattended responsive ground sensors and soft robotics [3].

Covalently crosslinked amorphous thermoset networks are one type of SMP that are highly processable and more easily characterized than semi-crystalline polymers due to the absence of crystalline domains whose properties are highly path dependent. In contrast, amorphous thermosets have more consistent properties above and below the glass transitions temperature (T_g) and tunable properties in the “rubbery” regime that depend on the permanent covalent crosslink network established. This class of SMPs also has characteristics that include high degrees of shape recovery, tunable work capacity during recovery, and suppression of creep due to these strong chemical cross-links. The permanent shape is fixed through formation of the covalent crosslink network upon initial processing. These materials typically retain the “memory” of their original shape despite the large deformations and temporary shapes to which they may be reconfigured [4].

The key challenge in the design of thermal activated SMPs is to maintain a balance of large reversible strain capability, easy temporary shape fixing, and full shape recovery at the desired activation temperature while also maintaining the desired mechanical properties in the glassy state, the rubbery state, and during the transition between them. This paper discusses a novel approach to synthesizing a new polyaspartimide-urea based SMP with a tailorable chemical structure that is readily processable at low temperatures. This tailorable chemical structure provides the ability to control relative covalent crosslink densities and resulting properties. The aim of the current research is to characterize the relationship between chemical composition and the materials' thermomechanical properties in order to enable tailoring of the high temperature shape memory behavior. Polyurethanes and polyurea have previously been observed to exhibit shape memory properties [4], but have largely been investigated at lower transition temperature than those examined in this study.

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A polyaspartimide is synthetically produced by reacting a bismaleimide with a diamine in a Michael addition reaction. Bismaleimides, depending on chemical composition and chain lengths, possess a wide variety of glass transitions and are recognized for structural rigidity and durability [5,6]. Diamines are readily available with diverse chemical compositions, which can be used to tailor the flexibility and relative molecular weight between crosslinks. In this work, the selected bismaleimide and diamine are reacted to produce a linear polyaspartimide as shown in Fig. 1. The polymeric backbone offers two secondary amine protons that can be readily reacted at room temperature with a diisocyanate functionality to form a urea bond and produce a networked polymer with varying crosslink density. The proposed chemistry produces amorphous, high temperature SMPs with tailorable T_g, high thermal stability (>300 °C), and good toughness. Similar studies that correlate variations in crosslinking and glass transition temperatures of SMPs were conducted by Xie and Rousseau [7]. However, they focused on an epoxy-based chemical system which produced lower T_g values.

The current paper focuses on the synthesis of amorphous SMPs with higher glass transition temperatures (110–164 °C) than previously examined commercially available SMPs (typically ≤ 110 °C) [7,8]. It is desired that the transition temperatures of the shape memory polymers be in excess of their operating temperature to ensure that shape memory polymers will not be prematurely triggered by the environment. For example, the operation temperatures of subsonic external aircraft skins can often reach 121 °C (250 °F), so SMPs and their composites that are targeted towards these applications require higher transition temperatures. Shape memory polymers that exhibit glass transition temperatures greater than 120 °C are uncommon among many of the current classes of previously examined thermosetting materials that include epoxies, polyurethanes, and styrene copolymers [7–10]. For example, a study involving a series of polyurethane thermosets conducted by Merline et al. recorded T_g temperatures ranging from 49 to 73 °C, respectively [9]. Styrene copolymers SMPs have also attracted much attention and typically have glass transitions temperatures ranging from 35 to 55 °C depending on crosslink densities [12]. A series of thermosetting epoxies SMPs were generated that exhibited transition temperatures ranging from roughly 31–94 °C, respectively [7]. This study included an SMP epoxy containing the Jeffamine D-400, the diamine examined in this study. However, the epoxy SMP exhibited a T_g of 44 °C which is substantially lower that the T_g of the BMI D-400 polymers discussed here [7].

Other studies did investigate higher temperature SMP epoxies with T_g's ranging from 69 to 113 °C [11]. An epoxy-based SMP was also previously available commercially with a T_g of 105 °C [8,10]. Despite a T_g that is slightly lower than desired for subsonic aero applications, this SMP showed strong promise for select aerospace applications. However, it is no longer available from the manufacturer. Even higher temperature polyimides, such as CP2, have been considered for their high temperature SMP properties and sharp T_g at 199 °C [Jacobs 2010]. However, significant processing challenges remain which may limit their application in fiber-reinforced shape-changing composites. In short, alternative aerospace-grade SMPs which are high temperature, processible, and easily tunable are needed.

The aim of the current investigation is to explore a family of SMPs that have the potential to meet this need with a high temperature SMP with desired mechanical, thermal, and processing properties. The reaction schematic illustrated in Fig. 1 represents the polymer backbone of the materials that have been produced. The linear system is generated by reacting 4,4-bismaleimidodiphenylmethane with an aliphatic diamine, Jeffamine D-400, in solution at a low temperature. Once the linear polyaspartimide is generated, the polymeric backbone is reacted further with the addition of 4,4′-diisocyanatodicyclohexylmethane, a diisocyanate, as represented in Fig. 2. The isocyanate functionalities react with the secondary amine protons, as mentioned previously, along the polymer backbone to form urea functionalities and crosslink the linear polymer chains. The resulting amorphous networked polymer was no longer soluble in common solvents indicating that crosslinking had taken place. Model compounds were also generated and studied to confirm the proposed reaction and structural compositions.

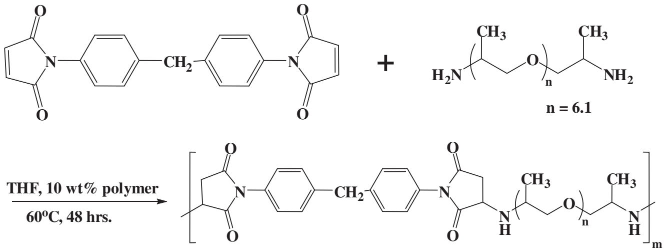

Fig. 1. Synthesis of BMI-JA-400.

2. Experimental

2.1. Materials

The 4,4-bismaleimidodiphenylmethane (Matrimid 5292A, BDM) was purchased from Ciba Specialty Chemicals Corporation and purified by recrystallization using toluene. The Jeffamine D-400 (Poly(oxy(methyl-1,2-ethanediyl)), alpha-(2-aminoethylenthyl) omega-(2-aminomethylethoxy), (JA-400)) was purchased from Huntsman. Once received, the material was stored/dried over activated 3A molecular sieves. The 4,4′-diisocyanatodicyclohexylmethane (Desmodur W, DW) was purchased from Bayer Material Science and used as received without further purification. The structures of DBM, JA-400, and DW are depicted in Fig. 3. All other chemicals were purchased from Sigma–Aldrich and used as received without further purification.

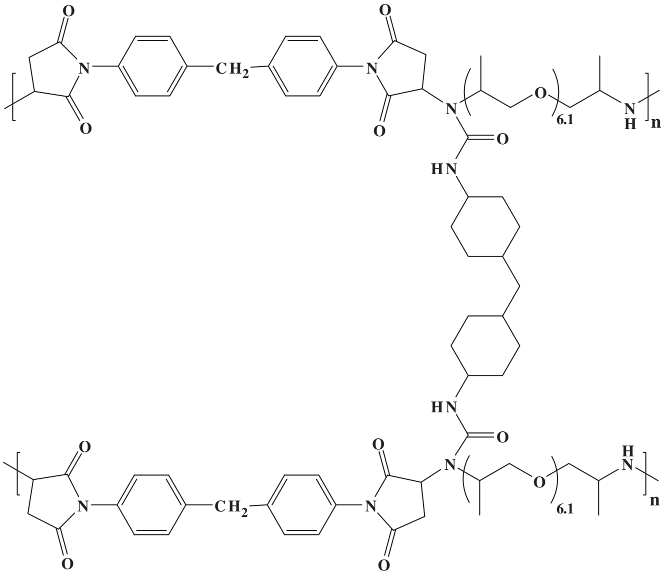

Fig. 2. BMI-JA-400 crosslinked with 4,4′-diisocyanatodicyclohexylmethane.

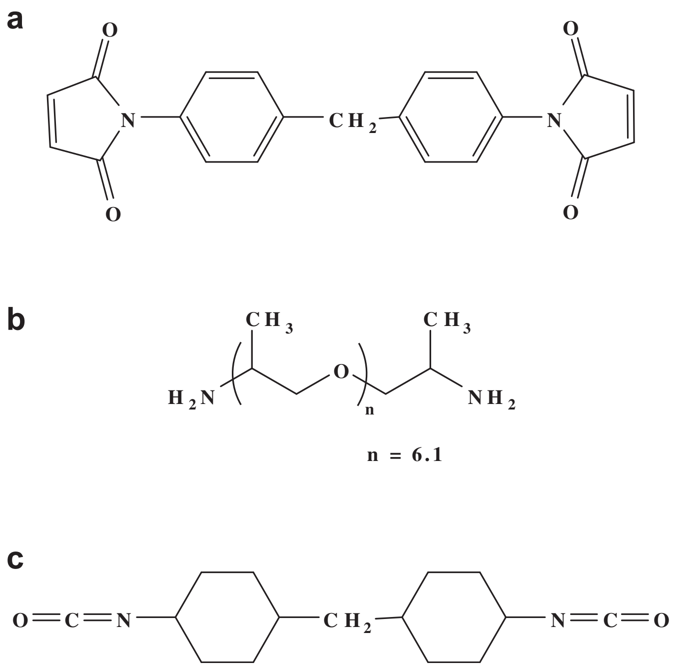

Fig. 3. Structures of (a) 4,4-Bismaleimidodiphenylmethane (BDM), (b) Jeffamine D-400 (JA-400), and (c) 4,4′-Diisocyanatodicyclohexylmethane (DW).

2.2. Instrumentation

Elemental Analyses were performed using a CHN analyzer through combustion processes. Intrinsic viscosities of the linear polymer in an N-methyl-2-pyrrolidine (NMP) solution were measured with a Cannon Ubbelohde viscometer at 30 °C at a concentration of 0.5 g/dL. ^1H NMR and ^{13}C NMR spectra were recorded using a Bruker Avance 400 spectrometer with deuterated $CDCl_3$ containing 0.1% (v/v) tetramethylsilane (TMS) as a reference. FT-IR spectra were recorded using a Thermo Nicolet Nexus 470 spectrometer. An electrothermal melting point apparatus was used to obtain melting point determinations. A TA Instruments 2950 series thermal analysis instrument was used to obtain thermogravimetric analysis (TGA) and collected data at a heating rate of 10 °C/min under flowing nitrogen. For dynamic mechanical analysis (DMA), tensile thin film specimens are machined (from the cast plates using an IsoMet 1000 precision saw) with dimensions 38 mm by 2 mm. The samples have a nominal thickness of 1.0 mm. A TA Instruments RSAIII dynamic mechanical analyzer is used to measure the storage and loss modulus of the post-cured resin specimens. The dynamic properties of the specimens were measured at a frequency of 1 Hz, a strain of 0.1%, and a heating rate of 2 °C/min from 25 °C to the high temperature (T_H) of the particular resin.

2.3. Model compound synthesis

2.3.1. Synthesis of MC-1

The reaction schematic is illustrated in Fig. 4. A 50 mL single necked round-bottom flask equipped with a magnetic stirbar was charged with phenylmaleimide (4.00 g, 0.023 mol), isopropylamine (1.36 g, 0.023 mol), and THF (21.4 g, 20 wt%). The light yellow colored solution was capped and stirred at room temperature for 6 h. The resulting orange colored solution was filtered to remove any particles and then the THF was vacuum evaporated. The reaction yielded 5.30 g (98.9%) of pink solid. The solid was further purified by dissolving in ethyl acetate and passing through a silica gel column using ethyl acetate as the eluent yielding 5.20 g (97.0%) of white solid.

Elemental analysis was used to confirm the chemical composition; calcd (%) for $C_{13}H_{16}N_2O_2$ (232.27): C 67.23, H 6.94, N 12.06; found: C 67.19, H 6.93, N 11.99. FT-IR (KBr), cm^{-1}: 3467 (–C–N– of the succinimide ring), 3288 and 1598 (N–H), 3060 (aromatic C–H), 2966 and 2852 (aliphatic C–H), 1778 and 1709 (C=O). NMR spectroscopy was used to determine purity and structural composition of MC-1. ^1H NMR (400 MHz, $CDCl_3$, ppm); δ-7.39 (t, 1H, 1), 7.49 (t, 2H, 2, 6), 7.27 (t, 2H, 3, 5), 3.97 (t, 1H, 9), 3.10 (dd, 1H, 10a), 2.70 (dd, 1H, 10b), 3.02 (q-5, 1H, 11), 1.15 (t, 6H, 12, 13), 1.82 (s, 1H, 14). ^{13}C NMR (400 MHz, $CDCl_3$, ppm); δ-C^1–128.7, C^2–126.3, C^3–129.2, C^4–131.6, C^5–129.2, C^6–126.3, C^7–174.3, C^8–177.3, C^9–54.7, C^{10}–38.1, C^{11}–48.1, C^{12}–23.5, C^{13}–22.5. Melting point: 107–108 °C sharp.

2.3.2. Synthesis of MC-2

The reaction schematic is illustrated in Fig. 5. A 50 mL single necked round-bottom flask equipped with a magnetic stirbar was charged with MC-1 (0.5 g, 0.0022 mol), phenyl isocyanate (0.269 g, 0.0022 mol), and THF (14.62 g, 5 wt%). The transparent solution was capped and stirred at room temperature for 72 h. The solution was filtered to remove any particles and the THF vacuum evaporated. The reaction yielded 0.750 g (97.5%) of white solid. The solid was recrystallized in toluene yielding 0.69 g (90%) of white crystals.

Elemental analysis was used to confirm the chemical composition; calcd (%) for $C_{20}H_{27}N_3O_3$ (357.43): C 67.21, H 7.61, N 11.76; found: C 67.18, H 7.64, N 11.70. NMR spectroscopy was used to determine purity and structural composition. FT-IR (KBr), cm^{-1}: 3470 (–C–N– of the succinimide ring), 3415 (broad, urea formation), 3066 (aromatic C–H), 2932 and 2855 (aliphatic and cyclic aliphatic C–H), 1782 and 1726 (C=O), 1621 (N–H). ^1H NMR (400 MHz, $CDCl_3$, ppm); δ-7.35 (t, 3H, 1, 2, 6), 7.44 (t, 2H, 3, 5), 4.07 (q-4, 1H, 9), 3.04 (dd, 1H, 10a), 2.97 (dd, 1H, 10b), 3.77 (s-7, 1H, 11), 1.35 (d, 3H, 12), 1.26 (d, 3H, 13), 3.61 (m, 1H, 15), 1.96 (d, 2H, 16a, 20a), 1.70 (dt, 2H, 16b, 20b), 1.37 (m, 2H, 17a, 19b), 1.10 (m, 2H, 17b, 19b), 1.60 (s-6, 2H, 18a, 18b). ^{13}C NMR (400 MHz, $CDCl_3$, ppm); δ-C^1–128.3, C^2–126.8, C^3–129.2, C^4–132.4, C^5–129.2, C^6–126.8, C^7–174.0, C^8–175.5, C^9–50.9, C^{10}–36.4, C^{11}–47.7, C^{12}–22.0, C^{13}–21.3, C^{14}–155.6, C^{15}–49.4, C^{16}–34.1, C^{17}–25.0, C^{18}–25.6, C^{19}–25.0, C^{20}–33.9. Melting point: 157–158 °C sharp.

2.4. Polymer synthesis

2.4.1. Synthesis of BMI-JA-400

BMI-JA-400 was synthesized by following the literature method [13] with some modifications. A 100 mL single necked round-bottom flask fitted with a nitrogen inlet, a reflux condenser and magnetic stirbar was charged with BDM (2.00 g, 0.0056 mol), JA-400 (2.40 g, 0.0056 mol), and tetrahydrofuran (THF) (17.6 g, 20 wt% polymer). The mixture was stirred to a bright yellow colored solution and was heated at 65 °C for 24 h under a nitrogen atmosphere. The resulting viscous amber colored solution was filtered to remove any particles and the THF vacuum evaporated at room

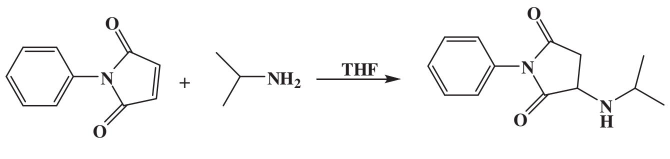

Fig. 4. Synthesis of MC-1.

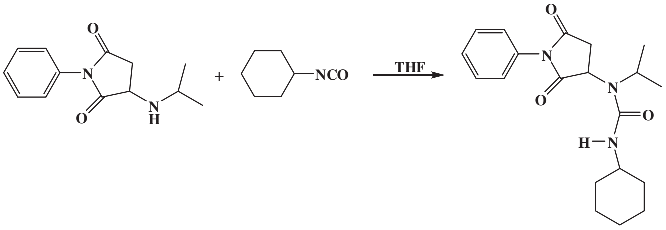

Fig. 5. Synthesis of MC-2.

temperature overnight, yielding an amber colored polymeric material in a quantitative yield (4.38 g, 99.6%). NMR spectroscopy was used to determine the complete removal of the solvent. This formula is referred to as material “REF” in the subsequent discussions of TGA and DMA following curing overnight at 120 °C.

Elemental analysis was used to confirm the chemical composition; calcd (%) for $C_{42.3}H_{60.6}N_4O_{10.1}$ (786.77): C 64.58, H 7.76, N 7.12; found: C 64.52, H 7.74, N 7.04.

2.4.2. Synthesis of BMI-JA-400-xdw shape memory polymers

The detailed formulations of the series of SMPs are summarized in Table 1. A 100 mL single necked round-bottom flask fitted with a nitrogen inlet, a reflux condenser and magnetic stirbar was charged with BDM (2.00 g, 0.0056 mol), JA-400 (2.40 g, 0.0056 mol), and THF (17.6 g, 20 wt% polymer). The mixture was stirred to a bright yellow colored solution and was heated at 65 °C for 24 h under a nitrogen atmosphere. The resulting viscous amber colored solution was filtered to remove any particles and the THF was reduced, increasing the polymer concentration to the values shown in Table 1. The weighed DW was then added to the reduced solution, resulting in a 35 polymer wt% solution. The highly viscous solution was stirred/mixed rapidly for 2 min. The homogeneous solution was transferred evenly into Teflon casting dishes (5.0 g solution per dish) and placed into an inert atmosphere for 16 h. The resulting polymeric films yielded an amber colored amorphous material in a quantitative yield (1.75 g per film). The generated films were heat treated at the respective high use temperature (T_H in Table 1) for 1 h to ensure reaction completion. Elemental analysis was used to confirm the chemical compositions. The theoretical and measured results are summarized in Table 2.

3. Results and discussion

3.1. Model compound characterization

Model compound, MC-1, was generated to confirm the proposed reaction mechanism and formation of the aspartimide bond linkage resulting from the combination of the maleimide and primary amine functionalities. Supporting ^{1}H and ^{13}C NMR spectroscopy and FT-IR spectra were taken and confirmed the chemical structure of the reaction product (not shown).

Table 1
Details of SMP synthesis.

Sample	DW to JA-400 Mole ratio (%)	Polymer conc. in THF (wt%)	T_H (°C)
50DW	25	31.5	145
75DW	37.5	30.1	155
100DW	50	28.8	165
150DW	75	26.4	175
200DW	100	24.4	185

Table 2
Compositions of SMP samples.

Sample			C (at%)	H (at%)	N (at%)
50DW	$C_{42.3}H_{60.6}N_4O_{10.1}$	Theoretical	65.12	7.91	7.63
	(918.45)	Measured	64.13	8.01	7.75
75DW	$C_{53.55}H_{77.85}N_{5.5}O_{11.6}$	Theoretical	65.35	7.97	7.83
	(984.29)	Measured	64.93	7.91	7.84
100DW	$C_{57.3}H_{83.6}N_6O_{12.1}$	Theoretical	65.54	8.02	8.00
	(1050.13)	Measured	65.51	7.89	7.94
150DW	$C_{64.8}H_{95.1}N_7O_{13.1}$	Theoretical	65.86	8.11	8.30
	(1181.81)	Measured	65.76	8.12	8.08
200DW	$C_{72.3}H_{106.6}N_8O_{14.1}$	Theoretical	66.11	8.18	8.53
	(1313.50)	Measured	65.94	8.17	8.38

Model compound, MC-2, was generated to confirm the proposed reaction mechanism and formation of the urea bond linkage resulting from the combination of the secondary amine proton from MC-1 and the isocyanate functionalities. Supporting ^{1}H and ^{13}C NMR spectroscopy and FT-IR spectra were also taken and confirmed the chemical structure of the reaction product (not shown).

3.2. Polymer properties

The intrinsic viscosity of BMI-JA-400 was recorded to be 3.18 dL/g and was soluble in a variety of organic solvents (DMAc, DMSO, THF, and NMP). Upon final reaction with the diisocyanate, the generated polymeric films became insoluble, but swelled in the organic solvents.

3.3. Polymer swell testing

Swell tests were conducted on each of the five generated thermosetting SMP materials to gage crosslink densities. A solvent base was selected covering a broad polarity index, water being the most polar (9.0), methanol (5.1), THF (4.0), and toluene being the least polar (2.4). Each sample was exposed for 24 h. From the graph illustrated in Fig. 6, comparative crosslink densities can be inferred for the SMPs. As a trend, the greater the amount of diisocyanate used during synthesis, a greater chemical crosslinking density was achieved resulting in a decrease in swelling by volume percentage. The least amount of activity is seen in the tests involving water and toluene. In water, a very small increase in volume is observed (∼1.0%) across all five materials. This is attributed to the adsorbed water on the exterior surface due to the high volume of hydrogen bonding associated throughout the chemical structure. In toluene,

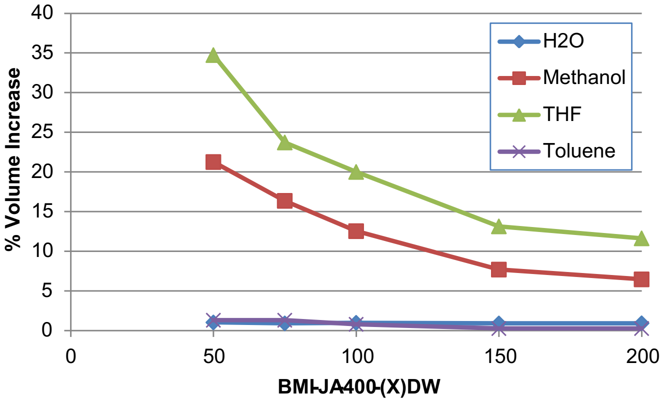

Fig. 6. BMI-JA-400-(X)DW swell test results.

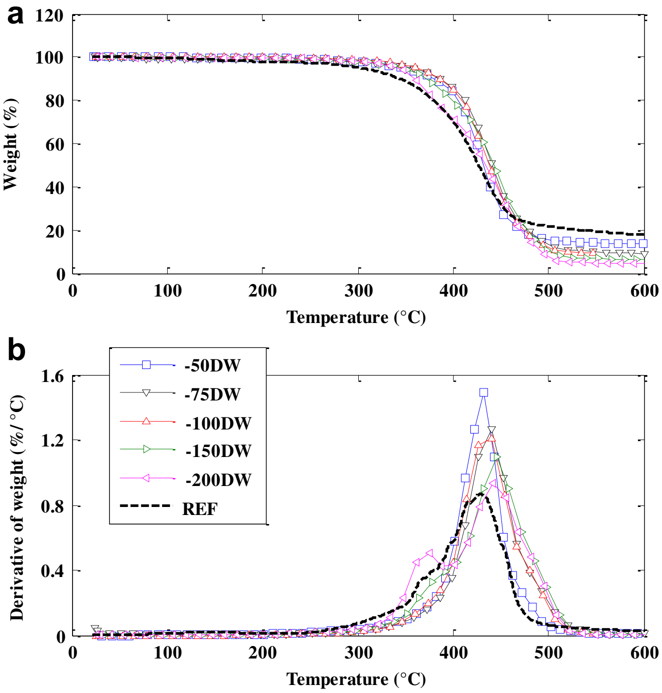

Fig. 7. TGA analysis results of the crosslinked BMI-JA-400-(X)DW systems (a) weight (%) and (b) derivative of weight (%/°C).

with the exception of the BMI-JA-400-50DW, each material remains chemically inert with minimal to no (<0.5%) chemical interactions. The BMI-JA-400-50DW, the least crosslinked material, showed ~1.3% volume increase in toluene. The materials showed the greatest interactions with methanol and THF. In both solvents, the lesser crosslink dense material (BMI-JA-400-50DW) swelled nearly three times the amount of the materials with the greatest crosslink densities (BMI-JA-400-200DW). It should be noted that the percent volume increase appears to plateau between the BMI-JA-400-150DW and the BMI-JA-400-200DW. This can be attributed to maximum potential crosslink density being approached at –150DW.

3.4. Thermogravimetric analysis

Fig. 7 show the overall comparison of the TGA curves and the derivative of the weights in nitrogen. The baseline BMI-JA-400 is also included in the figure as “REF” for comparison purposes. BMI-JA-400-150DW and BMI-JA-400-200DW show early thermal instabilities in both curves. This can possibly be attributed to a transport-limited reaction between secondary amines leading to species with premature thermal breakdown. Major chemical decomposition can be seen by examining the derivative of the weight curves. Each of the materials examined show thermal stabilities upward of 300 °C with minimal decompositions (<5%) before major decompositions beginning at ~400 °C. The initial temperatures of decomposition (T_D) for the SMP materials are listed in Table 3.

Table 3
Thermal properties of the crosslinked BMI-JA-400 systems.

Polymer	50DW	75DW	100DW	150DW	200DW
T_D (°C, in N_2)	348	354	361	346	340

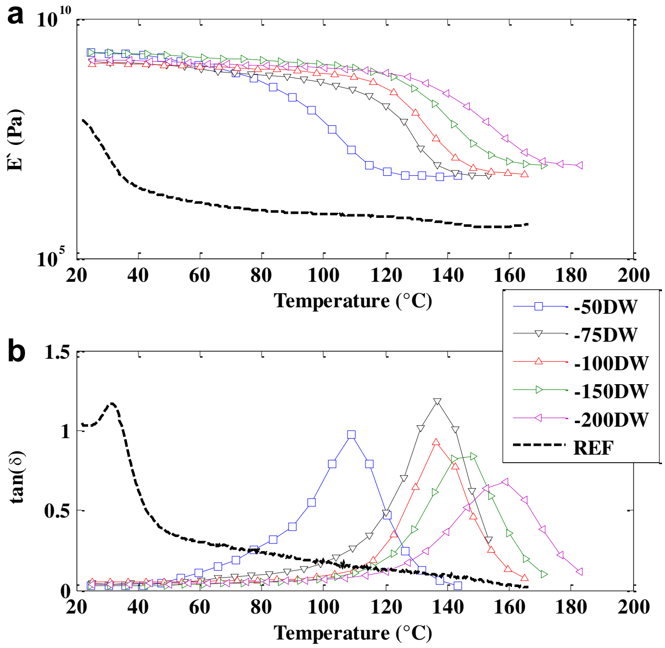

Fig. 8. DMA (a) storage modulus (E') and (b) tan(δ) results in tension.

3.5. Dynamic mechanical analysis

The DMA was used to investigate the dynamic properties of the materials over a range of temperatures. Three tests were conducted per material with each showing consistent results. The tensile storage modulus (E') versus temperature is shown in Fig. 8. Only one DMA test per SMP material is given in the figure for clarity. The baseline BMI-JA-400 is also included in the figure as “REF” for comparison purposes. The tan(δ) is defined as the relative ratio of the loss modulus (E''), to the storage modulus (E'). It represents the relative amount of energy being dissipated versus elastically stored in a material. For this study, the measured peak of the tan(δ) curve is used for identifying the T_g listed in Table 4. In addition, a high temperature modulus (signified as E_H) is defined as E' measured at T_H which marks the high temperature of the given material and a low temperature modulus (signified as E_L) is defined as E' measured at 25 °C. The T_D, E_H, and E_L from the DMA curves are summarized in Table 4. As expected, the T_g increases as the crosslink density increases. The results also indicate that the E_H increase as the crosslink density increases in the SMPs. There is not a discernible correlation in the measured E_L with the changes in crosslink density in the aspartimide-based SMPs because the permanent covalent crosslink network is dominated by the physical crosslink network at low temperatures. The ratio of E_L/E_H is observed to vary from 500 to 130 as the amount of crosslinking is increased.

Table 4
DMA properties of the crosslinked BMI-JA-400 systems (results are given as the average from three samples for each case).

Polymer	T_g (°C)	T_H (°C)	High temperature E_H (MPa)	Low temperature E_L (MPa)
50DW	110	145	3.69	1870
75DW	136	155	3.92	1240
100DW	137	165	5.41	1050
150DW	143	175	9.39	2250
200DW	164	185	12.6	1640

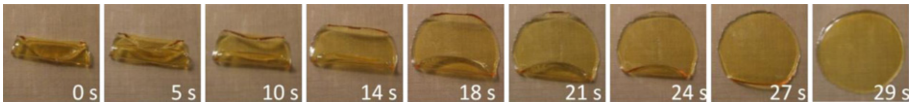

Fig. 9. Shape memory illustration of BMI-JA-400-100DW.

3.6. *Shape memory cycles*

Fig. 9 illustrates the potential shape memory capabilities of BMI-JA-400-100DW utilizing a 35 mm diameter disc with a thickness of 1 mm. The polymer was easily deformed into a rolled/cylindrical shape at 150 °C (above its T_g) and fixed into this temporary shape, when cooled back down to room temperature. The polymer qualitatively showed high toughness in both the glassy and rubbery states. Upon reheating to 150 °C (again above the T_g), the material returns to the original form within 30 s of thermal exposure. Time stamps are placed on each photograph in relation to shape memory recovery time when reheated above the materials T_g. The process was repeated ten times with no damage observed. In each case the material appears to recover fully to the initial shape other deformation modes including extension and twist were also observed with similar results. These phenomena will be quantified in future research with controlled strain and recovery [14,15].

4. Conclusion

The synthesis and characterization described in the current research has been conducted with the goal of providing a family of easily processable SMPs with good durability, and good shape recovery, and tailored high transition temperatures (above 120 °C). A series of polyaspartimide-urea based SMPs were successfully synthesized with increasing crosslink densities. Model compounds were synthesized to confirm the proposed reaction mechanisms. Elemental analysis and infrared spectroscopy indicated that the experimental determinations are chemically consistent with the proposed reactions. The thermal stability and thermal properties of the SMPs were also characterized. With an increase in the crosslink density, T_g was increased, a high level of thermal stability (>300 °C) was maintained, and the high temperature stiffness (E_H) of the material was increased. The resulting polymers were observed to have a high degree of toughness (fracture resistant under repeated deformation), where easily fixed into a variety of shapes, and appear to fully recover to their original shape. A more quantitative determination with larger samples is the subject of future research.

Acknowledgments

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