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Development of Polymeric Phase Change Materials On the basis of Diels–Alder Chemistry

John P. Swanson,[†] Svetlana Rozvadovsky,[†] Jonathan E. Seppala,[‡] Michael E. Mackay,[‡] Robert E. Jensen,[§] and Philip J. Costanzo*[,†]

[†]*Department of Chemistry and Biochemistry, California Polytechnic State University, San Luis Obispo, California 93407-0402,* [‡]*Department of Materials Science and Engineering, University of Delaware, Newark, Delaware, and* [§]*Army Research Laboratory, Weapons and Materials Research Directorate, Aberdeen Proving Ground, Aberdeen, Maryland*

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ABSTRACT: Diels–Alder (DA) chemistry is increasing popular due to its simplicity and efficiency; however, one concept that has yet to be thoroughly explored is incorporation of DA linkages within materials for the development of polymeric phase change materials. It is well established that the retro-DA reaction results in a large endotherm, which could be a potential energy sink for phase change materials. Hydroxyl-terminated polybutadiene (HTPB) was selected as a prepolymer and modified with different DA linkages. Cured materials were prepared upon addition of diisocyanates and their physical properties of the cured elastomers were investigated using thermogravimetric analysis (TGA), differential scanning calorimetry (DSC) and rheological testing. The resulting thermally responsive HTPB (TR-HTPB) exhibited the ability to absorb energy and flow at elevated temperatures. Furthermore, they displayed unusual responses to repeated thermal cycling, including changes in thermal absorption and rheological characteristics.

Introduction

Briefly defined, phase change materials (PCM) are materials that exhibit a phase change upon application of a thermal stimulus. What makes a PCM different from other materials is that during this phase change the material may release or absorb a large amount heat. This is caused by the materials extremely high heat of fusion. For example, H_2O exhibits a heat of fusion of approximately 79.2 J/g, which makes it an ideal PCM. PCM may be organic (i.e., fatty acids, ice, and paraffin wax), inorganic (i.e., metals and salt hydrates), or composite materials (i.e., copper dispersed in paraffin wax). They are commonly utilized for a wide range of applications including thermal energy storage, waste heat recovery, thermal protection of electronic devices, and protection of food in transport or storage.[1−5] The wide range of possible PCM allows a user to select a system that operates over a large temperature range. Depending upon the application, systems can be designed to by compatible with current construction and packing technologies, nonreactive, chemically stable, and recyclable. Regardless of the composition of the PCM, the key characteristic is the ability to absorb a large amount of thermal energy while undergoing a phase change. The goal of this project is to prepare polymeric PCM from previously unremarkable polymeric materials. To complete this task, Diels–Alder (DA) linkages will be incorporated within the composite material.

DA chemistry has been studied extensively in the literature and the chemical reaction mechanisms are well understood.[6,7] The formation of the ring structure is temperature dependent and reversible. (Figure 1) Recently, many research groups have exploited the use of DA chemistry to prepare thermally responsive organic–inorganic polymer hybrids,[8−10] thermoplastic elastomers,[11,12] polyurethanes and foams.[13]

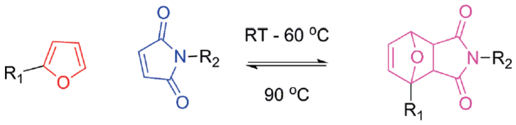

Figure 1. Reversible DA adduct whose formation is temperature dependent.

The thermal reversibility of the DA reaction has also been investigated as a candidate chemical reaction to store solar energy where it was found that the maximum heat capacity was 76% greater than water.[14] In other words, the retro-DA requires the absorption of thermal energy, which is a property coveted toward the development of polymeric PCM. Futhermore, if the DA linkages are incorporated along the main-chain of the polymeric composite, a thermal stimulus will induce the retro-DA and cross-linking points will be cleaved. If the glass transition temperature (T_g) of the base polymer is appropriate (i.e., below the retro-DA temperature), the material will undergo a phase change from an elastomer to a viscous liquid. This report details our efforts to explore the use of DA linkages as a mechanism to prepare PCM.

Results and Discussion

Synthetic efforts focused upon developing a simple and efficient method that is amenable to large scale production. A commercially available hydroxyl-terminated polybutadiene (HTPB) prepolymer was utilized as the base material. HTPB was chosen because of its low T_g (∼−77 °C). Scheme 1 details the synthetic route utilized to prepare the furan-terminated polybutadiene (PB-Furan *X*.0). HTPB was treated with either 2-furfuryl isocyanate in the presence of a catalytic amount of dibutyltin dilaurate (DBTDL) to form PB-Furan 1.0 or 2-furforyl chloride to generate PB-Furan 2.0. These reaction conditions were chosen because of their simplicity and efficiency which is required for postpolymerization functionalization methods.

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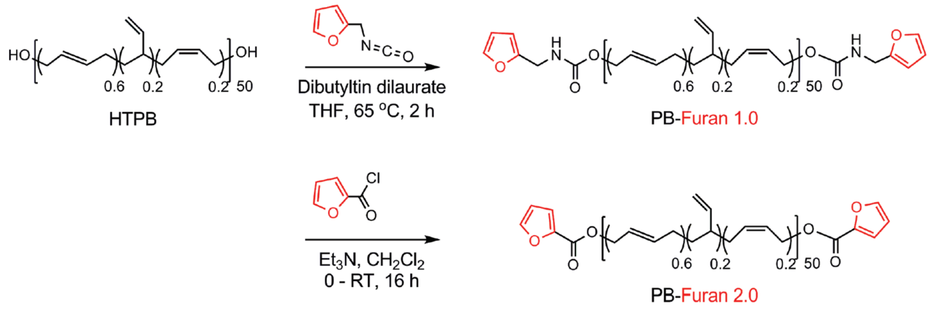
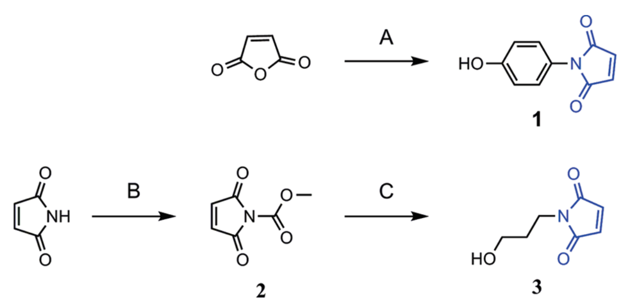
*To whom correspondence should be addressed. E-mail: pcostanz@calpoly.edu.

Scheme 1. Synthetic Route for Preparation of PB-Furan



Scheme 2. Synthetic Method for Preparation of Maleimide Compounds[a]



[a] Conditions: (A) (1) 4-aminophenol, acetone, room temperature, 2 h; (2) H_2SO_4, P_2O_5, DMF, 70 °C, 6 h; (B) methyl chloroformate, *N*-methyl morpholine, EtOAc, 0 °C, 30 min; (C) 3-aminopropanol, saturated $NaHCO_3$, 0 °C, 30 min.

Two different maleimide compounds were prepared to serve as dieneophilies to impart DA linkages along the HTPB backbone. Scheme 2 illustrates the synthesis of the maleimide compounds. Compound **1** and **3** were prepared according to previously reported methods.[15,16] Next, the maleimide was added to the PB-Furan to complete the DA linkages, which proceeded in quantitative yield. (Scheme 3) Chain-end functionalization was monitored via ^{1}H NMR spectroscopy. Interesting, there are a total of four different materials that could be prepared; however, the combination of compound **1** and PB-Furan 2.0 did not form the DA adduct. In general, formation and cleavage of the Diels–Alder adduct is facilitated by an electron deficient dieneophile and an electron rich diene. It is common for different dienes and dieneophiles to undergo the Diels–Alder reaction regardless of the electron-density as inverse electron DA reactions are possible; however, such linkages will not execute a retro-DA. The concept of the electron-rich diene and electron-poor dieneophile has a more significant role in the ability for the adduct to undergo the retro Diels–Alder reaction. While maleimides are typically viewed as electron deficient, the phenolic functionality upon compound **1** results in an electron rich dieneophile, where as PB-Furan 2.0 is electron poor due to the location of the ester bond upon the furan ring. This is nonideal and prevents the formation of the DA adduct. Such effects have been previously observed.[17]

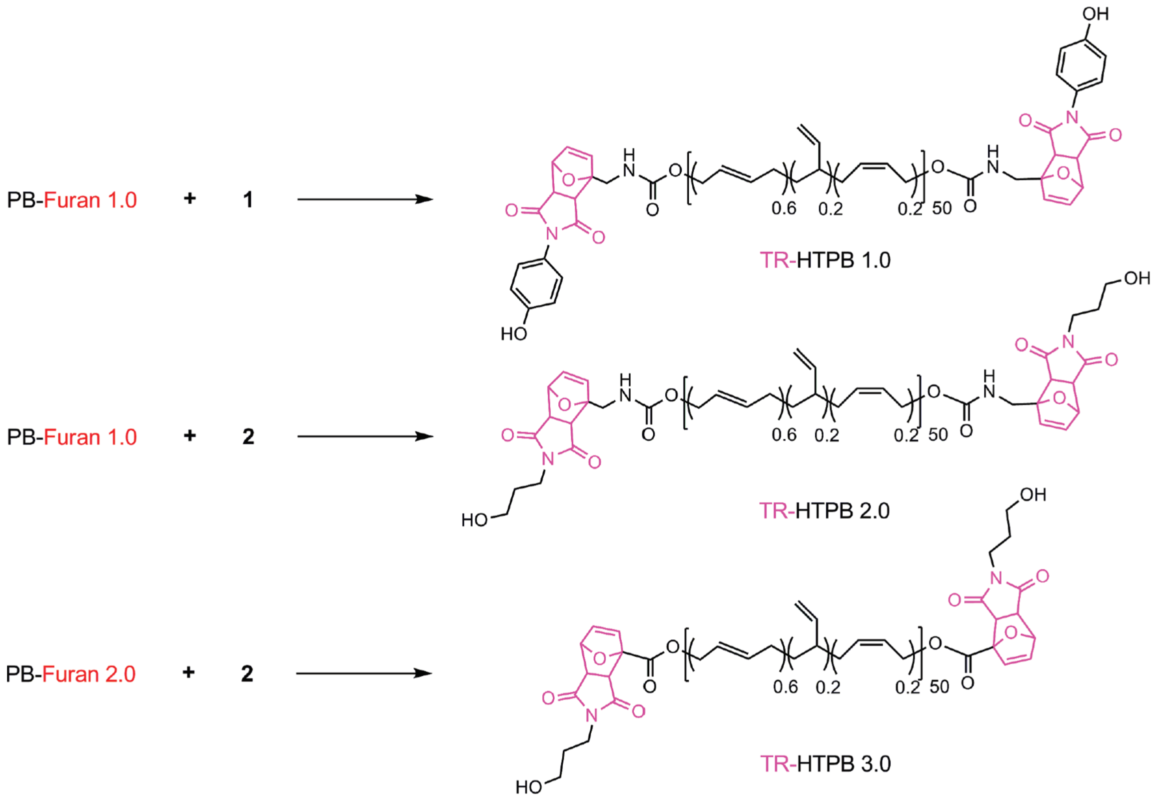
Next, a variety of elastomers were prepared with various amounts of DA linkages. Scheme 4 displays a representation of the materials made and their thermo-reversibility. TR-HTPB *X*.0 was formulated with various amounts of HTPB and cured with isophorone diisocyanate (IPDI), which was chosen due to previously established methods.[18] Table 1 lists the composition of the materials prepared in reference to the percentage of DA linkages present within the sample along with various physical property characteristics.

A multitude of physical properties were explored to determine the viability of a polymeric PCM. Thermal stability was evaluated with thermogravimetric analysis (TGA). Potential applications for this PCM composition require a 2 wt % loss temperature to be greater than 170 °C and a 5 wt % loss to be greater than 225 °C.[18] Table 1 lists the temperatures at which 2 and 5 wt % loss occurred for all sample prepared. All samples were thermally stable up to 180 °C, at which point degradation began to occur, the magnitude of which was dependent upon the percentage of DA linkages present. Samples comprised of TR-HTPB 1.0 degraded at lower temperatures due to the incorporation of a phenolic urethane along the polybutadiene backbone, as such moieties are known to degrade at elevated temperatures via decarboxilation. TR-HTPB 2.0 and TR-HTPB 3.0 utilized an alkyl maleimide which eliminated the phenolic urethane resulting in a more stable material. All of the cured TR-HTPB elastomers exhibited an appropriate amount of thermal stability within the operating window.

Differential scanning calorimetry (DSC) was utilized to probe the thermal properties of the material to determine if the presence of DA linkages would result in a thermodynamic sink. Figure 2 displays DSC analysis of the samples A (HTPB, 0% DA linkages), D (TR-HTPB 1.0, 100% DA linkages), E (TR-HTPB 2.0, 100%, DA linkages), and F (TR-HTPB 3.0, 100% DA linkages). A large endotherm is present in samples D and E while absent in samples A and F, which clearly indicates that the DA linkages absorb energy while undergoing the retro-DA. Although not displayed, samples B and C displayed a similar endotherm shape as that for sample D. Table 1 lists the magnitude of the endotherm for all samples prepared. A clear trend is observed when comparing the first cycle endotherm of the samples and the percentage of DA linkages within the sample. As the percentage of DA linkages decreases within the sample, the endotherm decreases according. In comparing samples D and E, a notable difference is observed in the shape and magnitude of the endotherm. It is well established that the furan/maleimide DA system exhibits a broad transition when inducing the retro-DA. As previously mentioned, by altering the structure of the diene and dieneophile, the electronics have been altered which affects the temperature and ease of the retro-DA. The incorporation of an alkyl maleimide results in a higher retro-DA transition point, which requires more thermal energy. Altering both the maleimide and furan (sample F) results in the elimination of the retro-DA.

After demonstrating that the DA linkages act as a thermodynamic sink, experiments were conducted to display the materials ability to undergo a phase change. Upon inducing the retro-DA, cross-links within the sample should be cleaved and the material should behave according to the physical characteristics of the HTPB prepolymer, which is similar to a viscous liquid due to the low T_g. To exemplify the flow properties of sample D, a free-standing elastomer was prepared within a glass sample vial. The leftmost picture in Figure 3 displays the free-standing foam. Subsequently, the vial was inverted and heated to 130 °C for 45 min. The middle frame in Figure 3 displays the sample

Scheme 3. Thermally-Responsive HTPB (TR-HTPB) Binders



Scheme 4. Synthesis Route for Preparation of TR-HTPB Elastomers

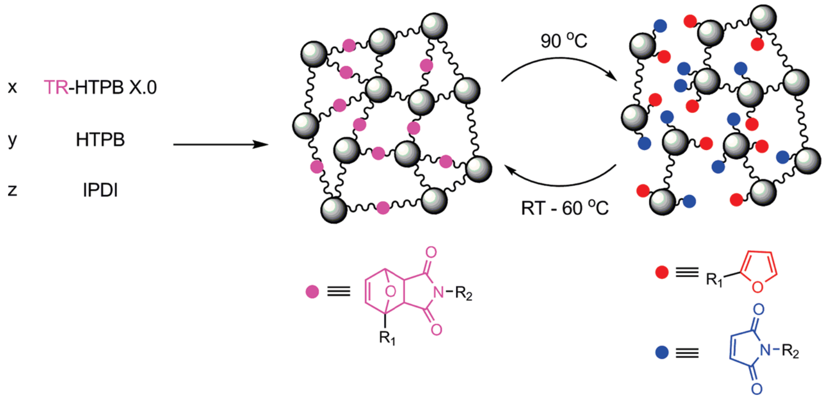


Table 1. Physical Properties of HTPB Elastomers Containing DA Linkages

			endotherm analysis (J/g)		thermal stability	
sample	prepolymers	% DA linkages	1st cycle	Annealed	*T* @ 2% wt loss (K)	*T* @ 5% wt loss (K)
A	HTPB	0	0.15	0.15	292	318
B	HTPB and TR-HTPB 1.0	33	11.83	0.77	265	313
C	HTPB and TR-HTPB 1.0	66	21.24	0.98	235	288
D	TR-HTPB 1.0	100	30.18	1.89	189	240
E	TR-HTPB 2.0	100	46.14	0.42	240	300
F	TR-HTPB 3.0	100	0.15	0.15	270	318

after cooling. The vial was rotated again and heat to 130 °C for 45 min. The rightmost picture in Figure 3 displays the sample after cooling. The material was easily manipulated depending upon the applied temperature and rotation of the holding container.

To further quantify this behavior, rheological measurement were taken. Samples were prepared by annealing sample D within Teflon plates at 90 °C for 5 min in geometric constrains to fit a parallel plate assembly. Figure 4 displays a temperature sweep profile. A significant change in modulus is observed as the temperature increases, with a maximum tan δ occurring at 126.6 °C, which correlates to the retro-DA temperature. Such decrease in the modulus indicates a change from solid-like to liquid-like behavior similar to a phase change.

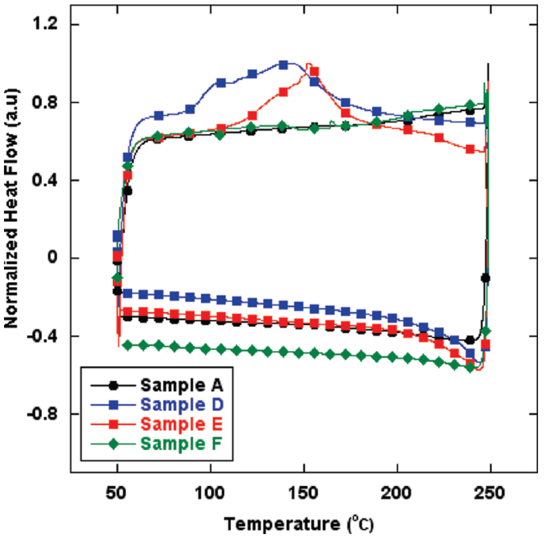


Figure 2. DSC analysis of samples A, D, E, and F corresponding to Table 1 [note: endotherm points up]. Conditions: 5 min isotherm @ 50 °C; heating rate −20 °C/min to +250 °C; cooling rate −10 °C/min to +50 °C.

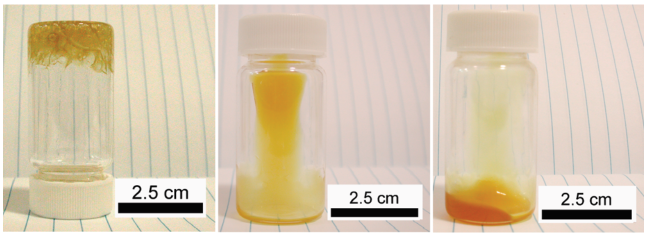


Figure 3. Pictographs of sample D after annealing at 130 °C for 45 min at different configurations.

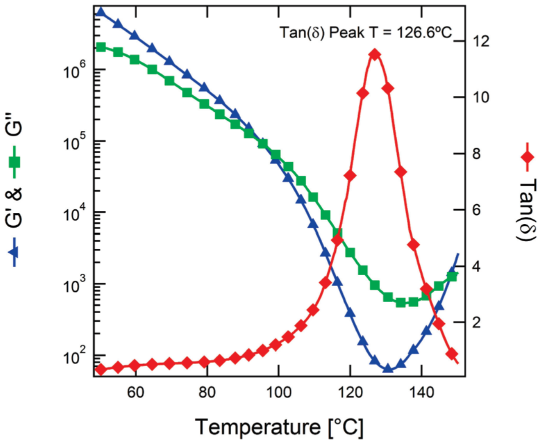


Figure 4. Temperature sweep of sample D. Conditions: frequency, 1 Hz; heating rate, 1 °C/min from 50 to 150 °C; 1% strain. The tan δ data was manipulated by a 10% Gaussian smoothing.

Attempts to expose the polymeric PCM to multiple heat cycles provided unexpected results. First, upon exposing samples containing TR-HTPB 1.0 (samples B, C, and D) to multiple heating cycles, the magnitude of the endotherm decreased and curvature of the endotherm was flattened (Figure 5, sample D); however, a different effect was observed with sample E which contained TR-HTPB 2.0. After one heating cycle, sample E no longer displayed any absorption of thermal energy. It appeared some type of annealing process was occurring. Therefore, samples were treated at 130 °C for 2 h, which is above the retro-DA transition point to eliminate any thermal history. No hysteresis was observed for samples containing TR-HTPB 1.0, indicating a thermal equilibrium has been achieved, Figure 6. Annealing the samples resulted in a significant decrease of the endotherm. (Table 1) Additionally, after annealing, the magnitude of thermal absorption does not correlate to the percentage of DA linkages present within the samples. Attempts to cycle the material for rheological testing,

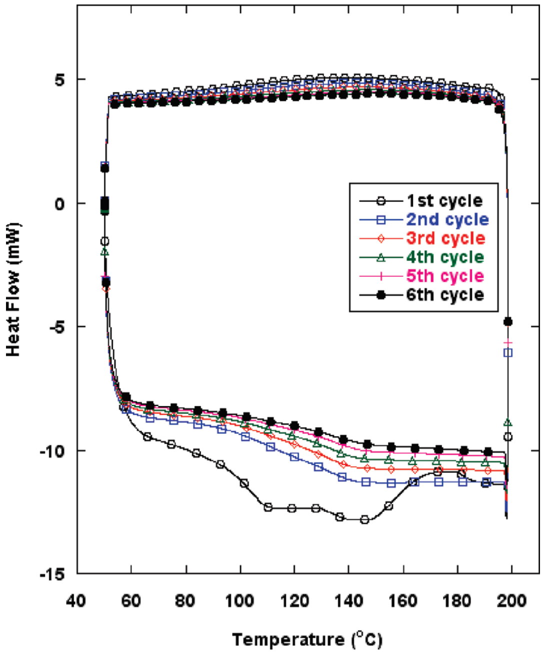


Figure 5. DSC analysis of sample D [note: endotherm points down]. Conditions: 5 min isotherm @ 50 °C; heating rate, −20 °C/min to +200 °C; cooling rate, −10 °C/min to +50 °C.

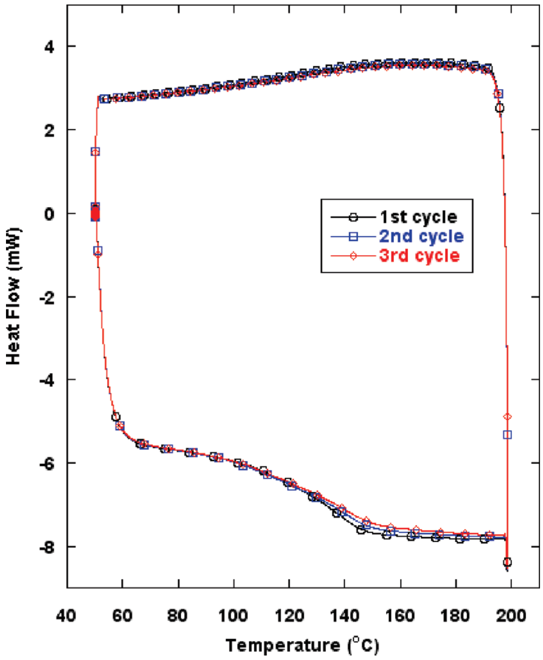


Figure 6. DSC analysis of sample D after annealing at 130 °C for 2 h [note: endotherm points down]. Conditions: 5 min isotherm @ 50 °C; heating rate, −20 °C/min to +200 °C; cooling rate, −10 °C/min to +50 °C.

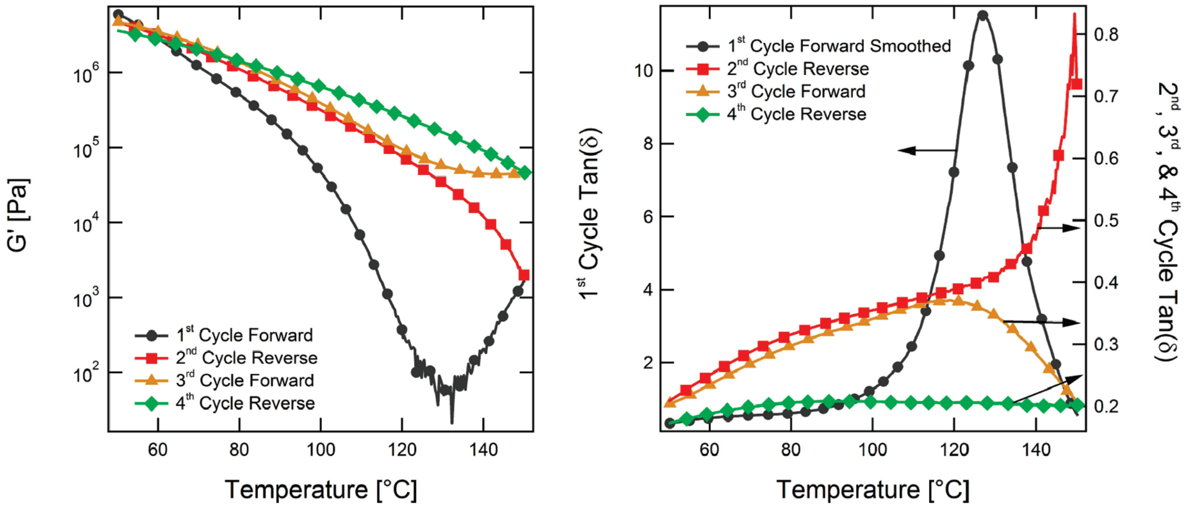


Figure 7. Temperature sweep of sample D. Conditions: frequency, 1 Hz; heating rate, 1 °C/min from 50 to 150 °C; 1% strain.

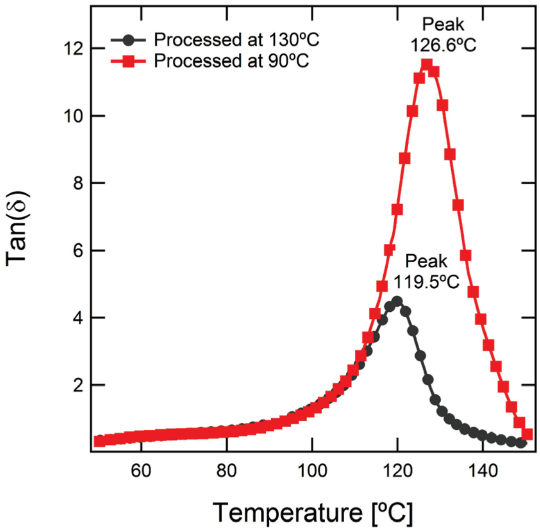


Figure 8. Temperature sweep of sample D prepared at 90 and 130 °C. Conditions: frequency, 1 Hz; heating rate, 1 °C/min from 50 to 150 °C; 1% strain.

displayed similar results as the DSC analysis, Figure 7. The magnitude of modulus change was significantly altered after one heating cycle. Furthermore, the tan δ was dramatically reduced after each heating cycle. To simplify rheological analysis, samples were prepared at 90 and 130 °C and underwent a temperature sweep. The sample annealed at 130 °C showed a significant change in the magnitude of tan δ, Figure 8. The smaller tan δ is indicative of a more solid like response.

To explain the annealing process within samples containing TR-HTPB 1.0 and the lack of annealing in samples that contain TR-HTPB 2.0, the potential diene and dieneophiles must be identified. Initial models assumed that DA adducts would be cleaved at elevated temperatures and as the sample was cooled, 100% recovery of the adducts would occur. Ideally, the system would only include the furan as the diene and the maleimide was the dieneophile, but the backbone of the HTPB contains multiple alkene functional groups which could serve as dieneophiles, in particular the 1,2 additions which constitute approximately 20% of the HTPB backbone. Furthermore, the fast curing typically associated with polyurethane systems results in the polymer chains being trapped in a nonequilibrium chain conformation. Annealing the sample at elevated temperature cleaves the DA adducts and allows the polymer chains to relax into a more equilibrated thermodynamic conformation. The diene and dienophile must be oriented in the proper alignment for the formation of the DA adducts to occur, and the polymer chain relaxation disrupts the alignment and inhibits the formation of the DA adducts. Figure 9 displays a schematic of the cleavage and reformation of the nonreversible DA adducts within the TR-HTPB elastomer. The formation of nonreversible DA adducts also explains the lack of annealing within the samples that contain TR-HTPB 2.0. Formation of the nonreversible adducts is accelerated at elevated temperatures which are required to cleave the DA adducts present within TR-HTPB 2.0. After the initial cleavage of the DA adducts, nonreversible adducts are immediately formed inhibits any further annealing phenomenon.

To test this hypothesis, a constant temperature time sweep experiment were conducted, Figure 10. As time increases, the modulus and viscosity increase whereas the tan δ decreases. Such an effect indicates structure formation, most likely crosslinking induced by annealing. Figure 11 displays two potential models for formation and cleavage of DA adducts within the TR-HTPB 1.0 elastomers. If the top model was accurate, one would expect the annealed sample to exhibit a larger Tan δ due to a lower cross-link density at elevated temperatures; however, the opposite trend was observed as the initial sample exhibited the highest tan δ. Therefore, the bottom model which contains the nonreversible DA adducts is more applicable in describing the TR-HTPB 1.0 elastomers after annealing.

Conclusions

HTPB was efficiently modified to contain DA linkages. The chain-end transformation was completed in high yield and throughput, utilizing a synthesis that is potentially amenable to large scale production. The TR-HTPB resin was implemented to prepare TR-HTPB elastomers with various amounts of DA linkages. The resulting elastomers were characterized with thermo gravimetric analysis (TGA), differential scanning calorimetry (DSC) and rheological testing. DSC analysis showed that the TR-HTPB elastomers exhibited a large endotherm upon initial heating. Rheological and DSC testing showed that repeated heating cycles resulted in an annealing of the TR-HTPB elastomer and the formation of irreversible cross-links. Manipulation of the dieneophile altered the thermal stability and the temperature to induce the retro-DA.

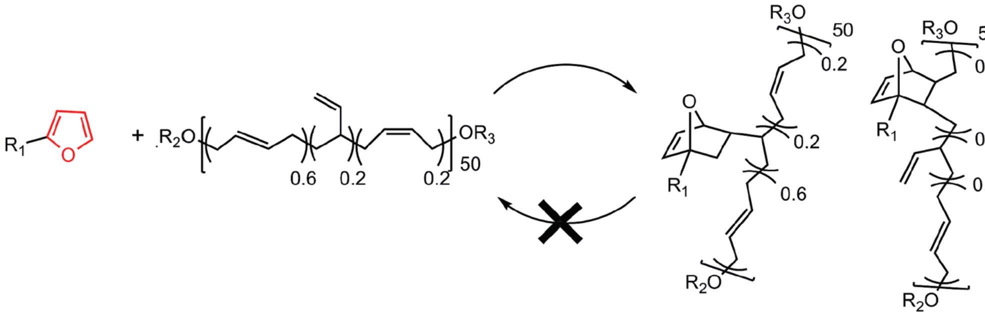


Figure 9. Possible formation of nonreversible DA adducts between the furfuryl chain end and polybutadiene backbone.

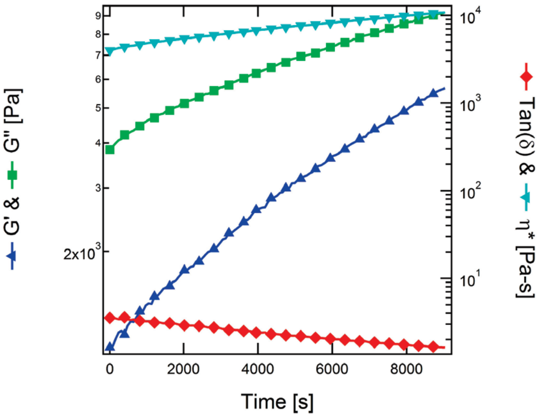


Figure 10. Constant temperature, time sweep of sample D. Conditions: frequency, 1 Hz; 110 °C; 1% strain.

Experimental Section

Materials. All materials were purchased from commercially available sources and used without further purification. HTPB was purchased from Sartomer as R45HTLO. Compound **1** and **3** were prepared according to previously published methods.[15,16]

Instrumentation. ^{1}H NMR was conducted on either a 300 (Cal Poly) or 600 (ARL) MHz Bruker instrument in acetone-*d* or $CDCl_3$ with a standard bore broadband probe (5 mm OD tubes, 32 scans, 5 s d1). All resonances were reported as ppm reference to the residual solvent peak. Chain end analysis was completed by ^{1}H NMR. All chain end transformations were indicated to be greater than 95%.

A TA Instruments DSC Q1000 was utilized to observe potential endotherms within the TR-HTPB elastomers caused by the incorporation of DA linkages. All samples underwent a 5 min isotherm at 50 °C and were then heated to 250 °C at a heating rate of 20 °C/min. After reaching peak temperature, the samples were cooled to 50 °C at a cooling rate of 10 °C/min. The typical sample masses were approximately 15 mg, which were sealed in aluminum hermetic pans. DSC analysis was completed at both the Army Research Laboratory and Cal Poly.

Disks were prepared by placing ~20 mg of sample in an 8 mm barrel die between clean Teflon spacers and steel anvils. The samples were heated to either 90 or 130 °C under 0.4 kN of pressure for 5 min, and subsequently quenched with H_2O to room temperature. Rheological analysis was conducted on a TA Instruments ARES-G2 strain controlled rheometer (New Castle, DE). Eight mm parallel plates were equilibrated at the starting temperature for 30 min and zeroed. To facilitate uniform contact, the disk was loaded onto the plates and 1 N of force was applied as the temperature was raised to 90 °C. The sample left to relax at 90 °C, and then cooled to starting temperature. Oscillatory shear tests were run at a frequency of 1 Hz with a 1% strain rate. When applicable a 1 °C/min heating rate was utilized. Tan δ is defined as the ratio between the lost and storage modulus. All test where conducted in a N_2 atmosphere. Rheological testing was completed at the University of Delaware.

Thermal gravimetric analysis was performed using a TA Instruments TGA 2950. Samples with an approximate mass of 20−30 mg were heated from 25 to 600 °C at a rate of 10 °C/min under an air atmosphere. TGA analysis was completed at both the Army Research Laboratory and Cal Poly.

Synthesis of FuranTerminated Polybutadiene (*PB-Furan X.0*)

PB-Furan 1.0. A magnetic stir bar, HTPB (10.5 g, 9.3 mmol OH), dibutyltin dilaurate (0.5 mL, 0.93 mmol), and $CHCl_3$ (25 mL) were loaded into a 50 mL round-bottom flask. Next, 2-furfuryl isocyanate (1.0 mL, 9.3 mmol NCO) was added and the reaction was stirred at 50 °C for 2 h. The reaction was cooled to room temperature and solvent was removed via rotary evaporation to yield PB-Furan in quantitative yield. ^{1}H NMR: δ (ppm) 7.37 (1H, s), 6.32 (1H, s), 6.25 (1H, s), 5.8−4.8 (50.48 H, br), 4.47 (2H, s), 2.4−0.9 (93.61H, br).

PB-Furan 2.0. A magnetic stir bar, HTPB (20 g, 17.9 mmol OH), Et_3N (3 mL, 21.48 mmol) and CH_2Cl_2 (100 mL) were loaded into a 300 mL round-bottom flask and cooled to 0 °C. Next, 2-furfuryl chloride (1.88 mL, 19.7 mmol) was added and the reaction was stirred at room temperature for 24 h. The resulting reaction mixture was subsequently washed with H_2O (75 mL, 3×) and brine (50 mL, 2×), and then dried over anhydrous $MgSO_4$, which was then removed via filtration. Solvent was removed via rotary evaporation to yield PB-Furan in 91% yield. ^{1}H NMR: δ (ppm) 7.46 (1H, s), 7.05 (1H, d), 6.41 (1H, br), 5.8−4.8 (50.48 H, br), 4.27 (2H, br), 2.4−0.9 (93.61H, br).

Typical Synthesis of HTPB Containing DA linkages (*TR-HTPB X.0*). A magnetic stir bar, PB-Furan *X*.0, and THF (80 mL) were loaded into a 250 mL round-bottom flask. Next, compound **1** or **3** (1: 1 mol ratio of diene to dienophile) was added to the 250 mL round-bottom flask. The reaction was stirred at 65 °C for 16 h. The reaction was cooled to room temperature and solvent was removed via rotary evaporation to yield TR-HTPB *X*.0 in quantitative yield. ^{1}H NMR: δ (ppm) 7.04 (2H, d), 6.89 (1H, d), 6.82 (2H, d), 6.79 (2H, d), 6.53 (3H, br), 5.8−4.8 (91.03H, br), 4.5 (2H, s), 2.4−0.9 (169.40H, br).

Typical synthesis of TR-HTPB Elastomers. TR-HTPB *X*.0, HTPB and dibutyltin dilaurate were mixed with a Thinky ARE-100 mixer for 1 min at 2000 rpm. Ratios of TR-HTPB *X*.0 to HTPB to dibutyltin dilaurate were dependent upon the desired characteristics of the final material. Next, an appropriate amount of cross-linker (isophorone diisocyanate) was added and mixed for 30 s at 2000 rpm. All elastomers were prepared using a 1: 1 ratio of OH to NCO. The HTPB prepolymer has a functionality of approximately 2.5, which results in network formation in the presence of a difunctional isocyanate. The resulting resin mixture was cast into molds and cured at either room temperature or 50 °C for 24 h.

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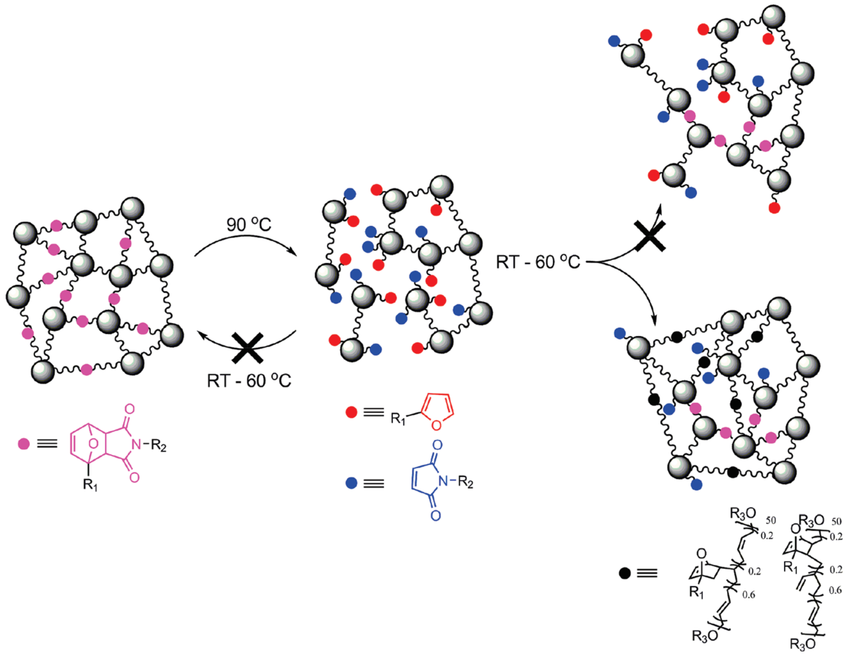

Figure 11. Revised schematic of the cleavage and reformation of the DA adducts within the TR-HTPB elastomer.

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