

Solvent-Free Preparation of Thermally Stable Poly(urethane-imide) Elastomers

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Solvent-Free Preparation of Thermally Stable Poly(urethane-imide) Elastomers

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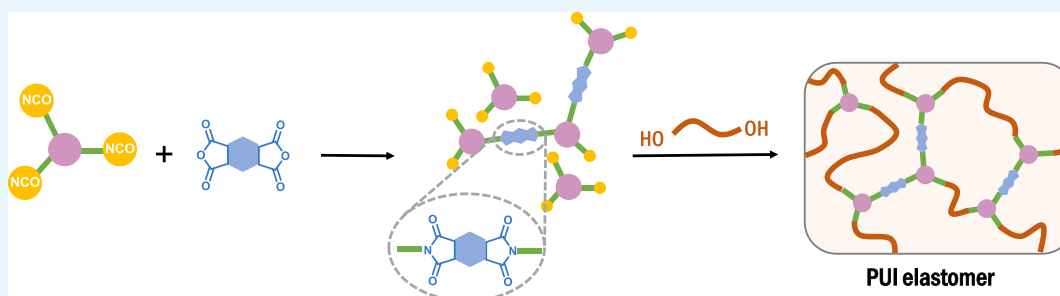
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ABSTRACT: Polyurethanes (PUs) are widely used in many applications due to their versatile chemical and physical properties. To meet the increasing demands on PU with respect to intrinsic mechanical and thermal properties, they can be modified with thermally stable aromatic imide structures to form poly(urethane imide) (PUI). However, the preparation of PUI materials has been limited by the need for strong polar solvents, which hinder their industrial scale development. In this work, we prepared imide-containing isocyanate-terminated prepolymers via the reaction of polymeric aromatic or aliphatic isocyanates and pyromellitic dianhydride in completely solvent-free conditions. The subsequent PUI elastomers made from these prepolymers exhibited enhanced char formation and stiffness in comparison to the reference elastomers without imide structures, among which the aromatic PUI elastomer shows improved flame retardancy according to the initial cone calorimetry measurement. This work demonstrates the potential use of imide prepolymers in other PU applications where high thermal stability and flame retardancy are required. The solvent-free synthesis also paves a way for the large-scale production of PUI materials.

KEYWORDS: polyurethane, imide, flame retardancy, thermal stability, solvent-free, elastomer

1. INTRODUCTION

Polyurethane (PU) is one of the most versatile polymers and exhibits a wide range of chemical, thermal, and mechanical properties.^{1–5} PU is used in a variety of applications such as soft cushioning foams, rigid thermal insulation foams, thermoplastic elastomers, coatings, and adhesives. With the fast development of the PU market, further improvement of the chemical and physical properties of PU materials will make them meet the increasing demands on high-performance materials and suit a rising number of applications. This can be achieved by the chemical modification of PU with thermally stable chemical motifs such as aromatic polyimides, which are one of the most remarkable structures with respect to their outstanding thermal, mechanical, and electrical properties.^{6–12} As aromatic polyimides have been used to enhance the thermal properties of various polymer matrices, such as poly(ether imide)s, poly(ester imide)s, and poly(amide imide)s,^{9,13–19} the incorporation of aromatic polyimides in PU promises the development of thermoplastics,^{20–26} rigid foams,^{27–32} and coatings^{33–36} with significantly enhanced thermal stability and

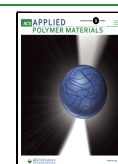
flame retardancy, which is especially important for construction and automotive industries.

Most imides are introduced in polymer matrices via the reaction between amine and anhydride.^{9,10} As isocyanates are used during PU synthesis, another more direct synthetic way to introduce imides is via the reaction between isocyanate and anhydride. Thus, the poly(urethane imide) (PUI) materials are typically prepared by the reaction of long-chain isocyanate-terminated prepolymers with dianhydrides.^{20,25,32,33,36–40} PUI materials are also reported to be prepared from the reaction of hydroxy-functionalized imide oligomers and diisocyanates^{41,42} or the reaction of amine-functionalized isocyanate prepolymers with dianhydrides.²³ However, a common feature of these

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preparations is the use of strong polar aprotic solvents, such as dimethylformamide, *N*-methyl-2-pyrrolidone, and dimethylacetamide that are hazardous and difficult to be removed, which limit the development of PUI materials in industrial scale production.^{43,44}

Recently, we have discovered that it is possible to perform the reaction of aromatic isocyanates and anhydrides in solvent-free conditions with high conversion. The use of secondary amine as a pre-catalyst and tertiary amine as a cocatalyst compensates the lack of catalytic effect from strong polar solvents and accelerates the reaction speed.⁴⁵ We also discovered that during the imide formation from aromatic isocyanate and anhydride with secondary amine as a pre-catalyst, the urea that forms from the reaction of aromatic isocyanate and secondary amine is the actual active catalyst. With the help of a tertiary amine as a cocatalyst, the deprotonated urea opens the ring of an anhydride to form an amic acid intermediate. The carboxyl group of the intermediate reacts with one more isocyanate group, followed by imidization with the release of CO₂ and the urea catalyst.

Using the knowledge from this mechanism study, we prepared PUI elastomers with good thermal properties in completely solvent-free conditions in this work. As pyromellitic dianhydride (PMDA) is one of the most reactive dianhydrides due to the high electron deficiency of its anhydride groups, it was chosen to prepare imide-containing isocyanate-terminated prepolymers.^{8,46} The imide prepolymer was first synthesized via the reaction of PMDA with aromatic or aliphatic polyisocyanates in a 1:19 weight ratio using *N*-methylaniline (for aromatic isocyanates) or dibutylamine (for aliphatic isocyanates) as a pre-catalyst and *N,N*-dimethylcyclohexylamine (DMCHA) as a cocatalyst. Then, the PUI elastomers were prepared by reacting the imide-containing isocyanate prepolymer and polyester polyol with 1,4-butanediol as a chain extender in bulk conditions. Both PUI elastomers obtained from aromatic and aliphatic isocyanates exhibited enhanced thermal properties and stiffness in comparison to elastomers without imide structures. Moreover, initial cone calorimetry tests were performed, and PUI elastomer synthesized from aromatic isocyanate showed improved flame retardancy. Due to the concern of industrial production, this work paves a way for a completely solvent-free production of high-performance PUI materials with inherent thermal stability and flame retardancy. In addition, the current work also helps to reduce the use of conventional flame retardant additives.

2. EXPERIMENTAL SECTION

2.1. Materials. Pyromellitic dianhydride (97%), triethyl phosphate ($\geq 99.8\%$), *N*-methylaniline (98%), dibutylamine ($\geq 99.5\%$), *N,N*-dimethylcyclohexylamine (99%), and 1,4-butanediol (BDO) (99%) were purchased from Sigma-Aldrich. 1,4-Benzenedimethanol ($>99\%$) was purchased from TCI. 1,4-Butanediol was dried on molecular sieves; all other reagents were used directly without treatment. Polymeric methylene diphenyl diisocyanate Lupranate M20 (pMDI, NCO content = 31.5 wt %), hexamethylene diisocyanate trimer Basonat HI 100 NG (HDI trimer, NCO content = 22 wt %), diethylene glycol bis-chloroformate (DGBCF), 1,4-diazabicyclo[2.2.2]octane based urethane gel catalyst Lupragen®N202 and Lupraphen 6601/2 (Lupraphen, polyester polyol synthesized from adipic acid, 1,4-butanediol, and monoethylene glycol with a molecular weight of 2000 g/mol and OH_v = 56 mg KOH/g) were kindly provided by BASF Polyurethanes GmbH. The polyol was dried at 80 °C under vacuum for 2 h before use.

2.2. Preparation of PI-1 Prepolymer. Pyromellitic dianhydride (10.5 g, 48.26 mmol) and pMDI (200.0 g) were added in a dry 3-neck flask, and the mixture was heated to 100 °C under an Ar atmosphere. A catalyst solution was prepared by dissolving *N*-methylaniline (1.2 g, 11.11 mmol) and *N,N*-dimethylcyclohexylamine (0.7 g, 5.56 mmol) in 2.5 mL of triethyl phosphate. Then the catalyst solution was added into the flask, and the internal reaction temperature was kept at 140 °C. The reaction was monitored by ¹³C NMR spectroscopy, and the time when all dianhydride converted to di-imide structures was defined as the reaction time. A dark brown liquid was obtained at 140 °C, which solidified over time at room temperature. After the reaction, the NCO content of prepolymer was titrated as 28.1 wt %.

2.3. Preparation of PI-2 Prepolymer. Pyromellitic dianhydride (10.5 g, 48.26 mmol) and HDI trimer (200.0 g) were added in a dry 3-neck flask, and the mixture was heated to 100 °C under an Ar atmosphere. A catalyst solution was prepared by dissolving dibutylamine (1.4 g, 11.11 mmol) and *N,N*-dimethylcyclohexylamine (0.7 g, 5.56 mmol) in 2.5 mL of triethyl phosphate. Then the catalyst solution was added into the flask, and the internal reaction temperature was kept at 140 °C. The reaction was monitored by ¹³C NMR spectroscopy, and the time when all dianhydride converted to di-imide structures was defined as the reaction time. A dark brown liquid was obtained. After the reaction, NCO content of the prepolymer was titrated as 18.0 wt %.

2.4. Preparation of Elastomers. The preparation of PUI-1 elastomer is used as an example to illustrate the general synthetic route: PI-1 prepolymer was added in a sealed polypropylene cup and stirred at 800 rpm under vacuum in a speedmixer for 30 min at 140 °C before use. The polyol component that consisted of Lupraphen (106.8 g, 0.05 mol), BDO (18.9 g, 0.21 mol), and DGBCF (0.06 g, 0.26 mmol) was added in a sealed polypropylene cup and stirred at 800 rpm under vacuum in a speedmixer for 20 min at 80 °C. PI-1 prepolymer (80.0 g, NCO = 28.1 wt %) was added into polyol components, and the mixture was mixed in a speedmixer for 30 s under vacuum. After that, the mixture was poured in a metal mold which was pre-heated at 80 °C. After polymerization of the mixture, the material was further cured in a 90 °C oven overnight. The same procedure and conditions were used for the preparation of PUI-2 and reference elastomers in bulk.

2.5. Methods. ¹³C nuclear magnetic resonance (NMR) spectroscopy measurements for monitoring the imide formation were performed using either a Bruker UltraShield 400 MHz or Varian Mercury 400 MHz spectrometer at room temperature with a delay time of 2 s and 256 scans per spectrum, using acetone-*d*₆ as a solvent with tetramethylsilane as the internal standard. NCO titration was performed on a 916 Ti-Touch titration machine (Metrohm) equipped with an electrode using tetraethylammonium bromide (0.4 mol/L in ethylene glycol) as the electrolyte. The isocyanate was quenched with excess of dibutylamine, and the unreacted dibutylamine was titrated with 1 M HCl as the titrant. After getting the volume (*V*₁) at the end of the titration of the sample as well as the volume (*V*₀) of the blank titration at the same condition, the NCO content was calculated by the titration machine using the following equation

$$\text{NCO content} = \frac{(V_1 - V_0) \times c_{\text{HCl}} \times M_{\text{NCO}}}{m_{\text{sample}}} \quad (1)$$

Thermogravimetric analysis (TGA) measurement was performed on a TA Q550 analyzer (TA Instruments) under a N₂ atmosphere. Samples (around 10 mg) were heated from 28 to 800 °C (or 600 °C for aliphatic isocyanate-based elastomers) at a rate of 10 °C/min. Tensile testing was performed on a Z010 machine (Zwick/Roell) with a 500 N load cell using dumbbell-shaped specimens. The specimens had an effective length of 33 mm, a width of 6 mm, and a thickness of 2 mm. The elongation rate used was 20 mm/min. Dynamic mechanical analysis (DMA) measurement was performed on a DMA Q850 analyzer (TA Instruments) with a film tension setup. The test bars had a width of 5.3 mm and a thickness of 1.2 mm. For each measurement, temperature ramp from -80 to 180 °C was programmed with a heating rate of 3 °C/min at a frequency of 1.0 Hz.

Scheme 1. Synthesis of Imide Prepolymer PI-1 from Aromatic Isocyanate

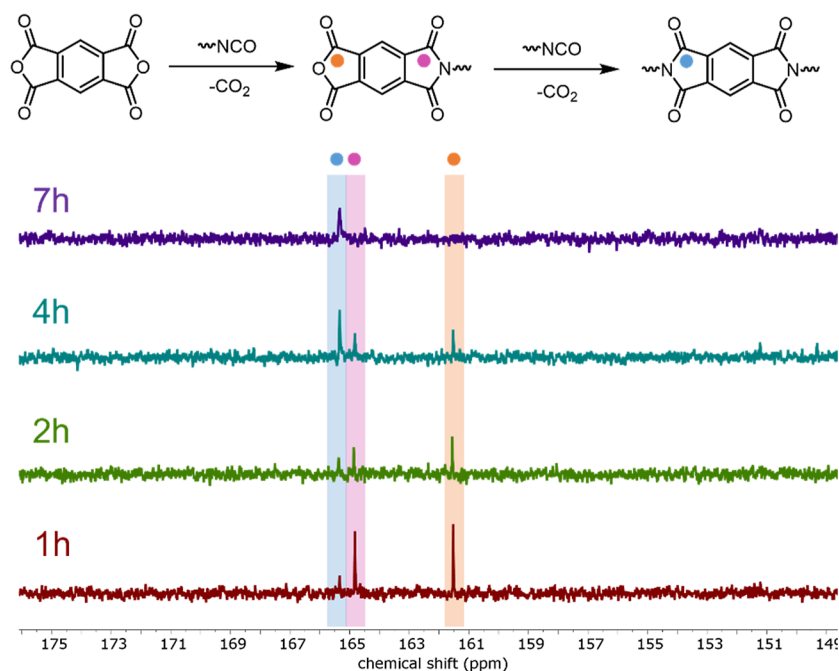
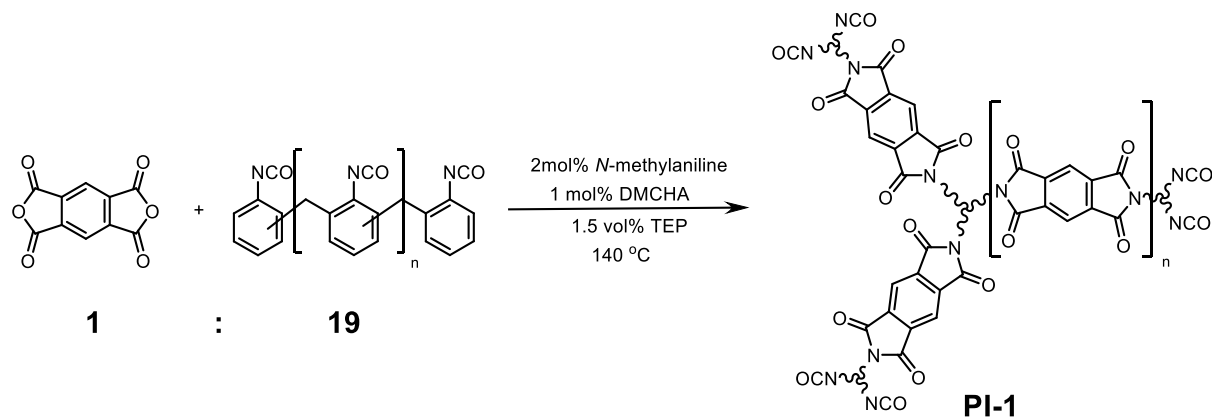


Figure 1. ^{13}C NMR (100 MHz, acetone- d_6) spectra of reaction between PMDA and pMDI in a 1:19 weight ratio with *N*-methylaniline as a pre-catalyst, DMCHA as a cocatalyst, and TEP as an additive. Full conversion was achieved after 7 h.

A preload force of 0.01 N, an amplitude of 100 μm , and a force track of 115% were used. The storage and loss moduli were recorded as a function of temperature. The glass transition temperature (T_g) was determined from the peak maximum of the $\tan(\delta)$. Cone calorimetry measurement was carried out on an iCone calorimeter (Fire Testing Technology Limited) under a heat flux of 25 kW/m^2 orientated to the ISO 5660-1:2015-03/Amd 1:2019-08 standard. The samples were cut into $100 \times 100 \times 4 \text{ mm}^3$ size and wrapped with aluminum foil for measurement. The obtained results are based on single measurements. Scanning electron microscopy (SEM) images were obtained in an FEI Quanta 200 3D instrument using an acceleration of 5 kV. Both surface and inside parts of char residue were investigated with a 100 μm scale. Before SEM observation, the samples were sputter-coated with gold. Raman spectroscopy was performed on a confocal Raman microscope WITec WMT 50 (WITEC) with laser of 532.3 nm.

3. RESULTS AND DISCUSSION

3.1. PUI Elastomers Prepared from Aromatic Isocyanates. The imide prepolymer based on an aromatic isocyanate (PI-1) was synthesized via reaction of PMDA and polymeric methylene diphenyl diisocyanate (pMDI) in a 1:19

weight ratio at 140 °C with 2 mol % *N*-methylaniline as a pre-catalyst, 1 mol % DMCHA as a cocatalyst, and 1.5 vol % triethyl phosphate (TEP) as an additive to prevent the sublimation of PMDA at high temperature (Scheme 1). During the reaction, it was found that the PMDA reacted in a two-step process. One-side imides were formed in the first hour, and diimides were formed within the next 6 h (Figure 1). The PI-1 prepolymer obtained had an NCO content of 28.1 wt %, which was determined by back-titration method (see Experimental Section).

PUI-1 elastomer was prepared by the reaction of PI-1 prepolymer and commercially available polyester polyol Lupraphen 6601/2 (Lupraphen) with a molecular weight of 2000 g/mol, using 1,4-butanediol (BDO) as a chain extender (15 wt % of the polyol component) in bulk condition (Figure S1). The molar ratio of NCO/OH was 1.02 (index 102). As DMCHA remained in the prepolymer, it also served as a urethane catalyst. 0.03 wt % diethylene glycol bis-chloroformate (DGBCF) was added to the imide-modified prepolymer to partially neutralize DMCHA, which slowed down the

urethane formation reaction during the elastomer synthesis for easier handling. The introduction of imide structural motifs in the isocyanate prepolymer leads to increased viscosity of the prepolymer; however, it is still possible to cast elastomers at 80 °C (see [Experimental Section](#)). The synthesis recipe can be found in [Table S1](#).

As a reference, the elastomer (ref 1) was prepared in bulk by reacting pMDI with the same amounts of Lupraphen and BDO, and benzenedimethanol (BDM) as a replacement of PMDA (index 102). As BDM has a similar molecular weight (138.2 g/mol) as the effective molecular weight of PMDA in the PI-1 prepolymer (130.1 g/mol), the aromatic content as well as the amount of polyol and BDO in the reference elastomer were almost the same as those in PUI-1 elastomer, with the key difference that BDM does not form imide bonds ([Figure S2](#)). A second reference elastomer (ref 2) was prepared by reacting pMDI with Lupraphen and 15 wt % BDO in a polyol component using the same index in bulk.

The elastomers were characterized by TGA, tensile test, and DMA ([Figure 2](#) and [Table 1](#)). With the similar aromatic content, the decomposition temperatures of PUI-1 elastomer at 5% weight loss (T_{d5}) and 10% weight loss (T_{d10}) were slightly improved relative to that for reference elastomers due to the low imide content (2 wt %). However, the PUI-1

Table 1. TGA, Tensile Test, and DMA Results of PUI-1 Elastomer and Reference Elastomers without Imide Structures

	PUI-1	ref 1	ref 2
aromatic content (%) ^a	39	39	36
T_{d5} (°C)	300	293	294
T_{d10} (°C)	316	309	311
char at 800 °C (%)	16.9	10.9	12.4
Young's modulus (MPa)	55 ± 2	15 ± 2	10 ± 2
stress at break (MPa)	15 ± 1	25 ± 1	19 ± 1
elongation (%)	60	110	110
T_g (°C)	-10, 48	34	31

^aThe aromatic content is determined by the total weight percentage of aromatic compounds (isocyanates, imides, and BDM) in the elastomers.

elastomer showed significantly higher char formation at 800 °C, which is due to the presence of imide structures. In addition, the rigid imide structures led to a stiffer PUI-1 elastomer with a higher Young's modulus and lower elongation at break.^{47,48} Due to the low aromatic content and absence of imide structures, the Young's modulus of the ref 2 elastomer was the lowest. The increase of the stiffness of PUI-1 elastomer can also be partially explained by T_g as shown in the DMA result. The higher T_g of the PUI-1 elastomer at 48 °C leads to its higher Young's modulus that was measured at room temperature. Compared to the reference elastomers that had only one narrow $\tan(\delta)$ peak around 32 °C, the two $\tan(\delta)$ peaks of the PUI-1 elastomer indicate the occurrence of phase separation. The lower T_g is dominated by a soft segment, and the higher T_g is dominated by a hard segment, which is mainly based on strong π - π stacking interactions of imide structures and hydrogen bonding between imides and urethane bonds. On the other hand, the BDM chain extender used in ref 1 is more flexible compared to imide and has better compatibility with polyester polyol Lupraphen, acting as a compatibilizer between two phases. Therefore, the polymer network of the ref 1 elastomer is not phase separated, resulting in only one $\tan(\delta)$ peak in the DMA measurement.

3.2. PUI Elastomers Prepared from Aliphatic Isocyanates. In addition to an aromatic imide prepolymer, we found that imide prepolymer could also be prepared from the reaction between aliphatic isocyanate and dianhydride. Instead of *N*-methylaniline used in the synthesis of aromatic imide prepolymer, dibutylamine was used as a pre-catalyst for the synthesis of imide prepolymers from aliphatic isocyanates in terms of a shorter reaction time. The aliphatic isocyanate-based imide prepolymer (PI-2) was synthesized via the reaction of PMDA and a hexamethylene diisocyanate (HDI) trimer in a 1:19 weight ratio at 140 °C with 2 mol % dibutylamine as a pre-catalyst, 1 mol % DMCHA as a cocatalyst, and 1.5 vol % TEP as an additive ([Scheme 2](#)). The full conversion to the imide-containing prepolymer was achieved after 12 h ([Figure S3](#)). According to the back-titration method, the PI-2 prepolymer had an NCO content of 18.0 wt %.

The PUI elastomer based on aliphatic isocyanate (PUI-2) was prepared by reacting PI-2 prepolymer with Lupraphen and 15 wt % BDO as a chain extender in bulk condition (index 102). DGBCF (0.02 wt %) was also used to slow down the urethane reaction. As a reference, the elastomer (ref 3) was prepared by reacting the HDI trimer with Lupraphen and 15

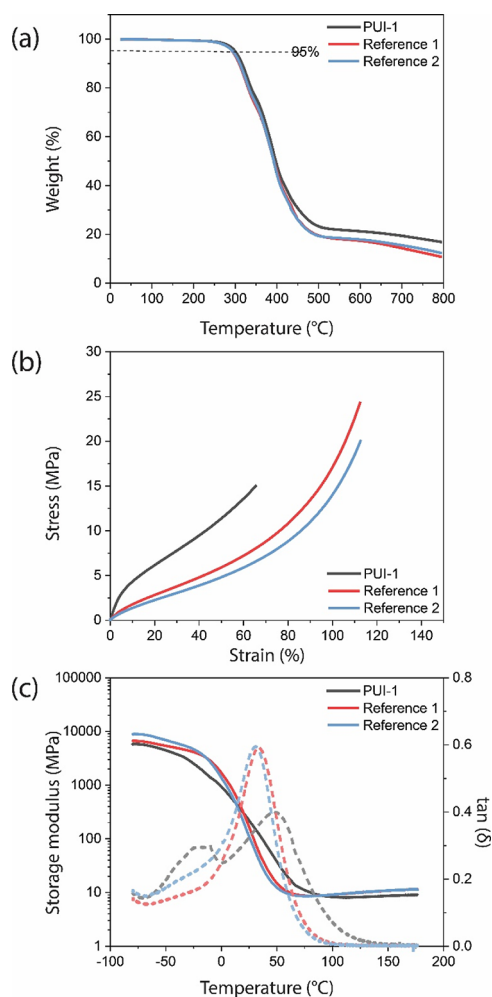
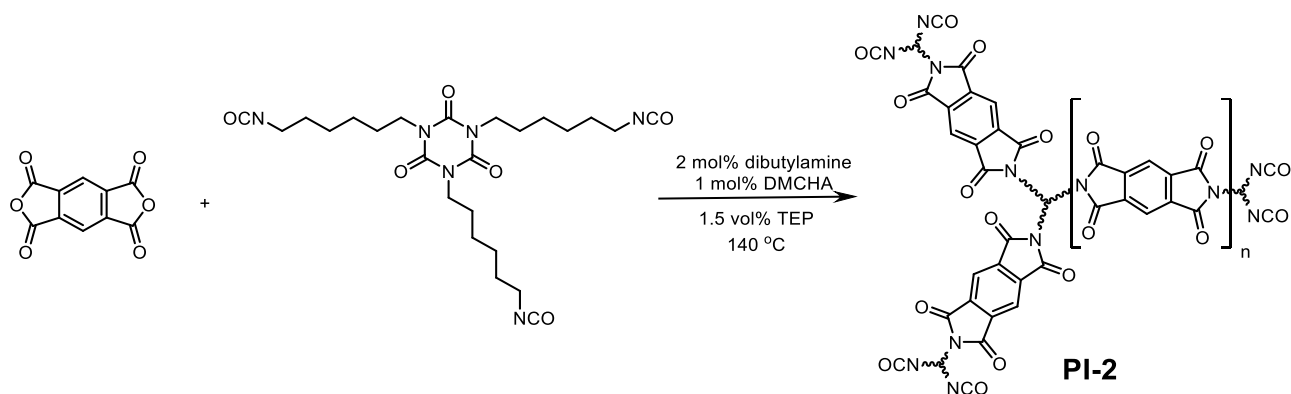


Figure 2. (a) TGA curves, (b) tensile test, and (c) DMA curves [solid line: storage modulus; dash line: $\tan(\delta)$] of PUI-1 elastomer and reference elastomers without imide structures.

Scheme 2. Synthesis of Imide Prepolymer PI-2 from Aliphatic Isocyanate



wt % BDO in a polyol component using the same index in bulk. The synthesis recipes can be found in Table S2.

The TGA, tensile test, and DMA results of the elastomers prepared from aliphatic isocyanates are shown in Figure 3 and Table 2. Compared to ref 3, the elastomer with no imide structure but the same amount of BDO in the polyol component, PUI-2 had a similar decomposition temperature

Table 2. TGA, Tensile Test, and DMA Results of the PUI-2 and Ref 3 Elastomers

	PUI-2	ref 3
T_{d5} (°C)	322	320
T_{d10} (°C)	337	337
char at 600 °C (%)	5.7	4.4
Young's modulus (MPa)	10 ± 0.6	8 ± 0.4
stress at break (MPa)	5 ± 0.6	4 ± 0.3
elongation (%)	61	70
T_g (°C)	25	12

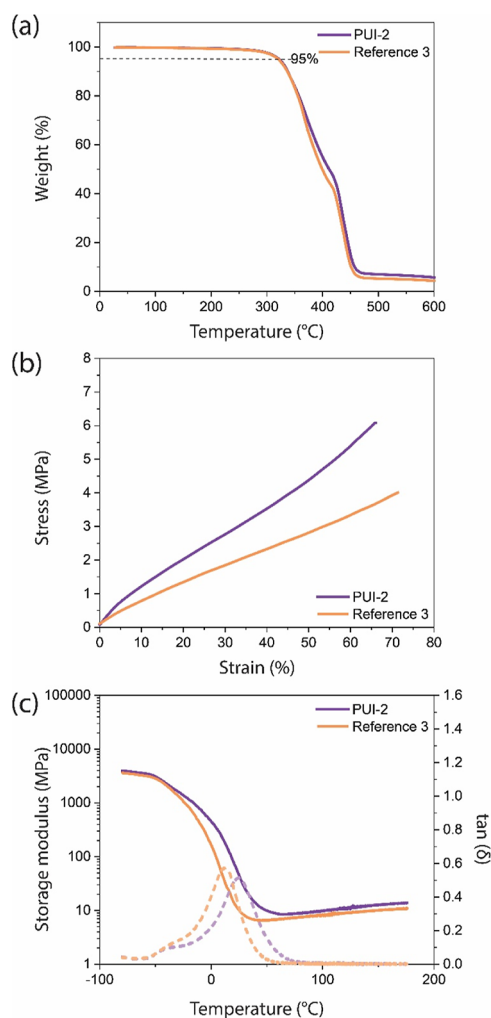


Figure 3. (a) TGA curves, (b) tensile test, and (c) DMA curves [solid line: storage modulus; dash line: $\tan(\delta)$] of PUI-2 and ref 3 elastomers.

while the char formation was slightly higher. The rigid imide structures also led to slightly higher Young's modulus, stress at break, as well as a higher T_g of PUI-2 elastomer than that for the ref 3 elastomer. Although only a small improvement in the physical properties was observed due to the low imide amount (2.5 wt %), this still indicates that the imide structures can be potentially used to improve the mechanical properties of the aliphatic isocyanate-based elastomers.

3.3. Flame Retardancy of PUI Elastomers Prepared from Aromatic Isocyanates. Based on the TGA results of PUI-1 and PUI-2 elastomers, the PUI elastomer prepared from aromatic isocyanates exhibits higher char formation at high temperature, which implies good combustion behavior. Therefore, the flame retardancy of the PUI-1 elastomer as well as refs 1 and 2 elastomers were preliminarily evaluated by cone calorimetry measurement. The time to ignition (TTI, s), peak of heat release rate (PHRR, kW/m²), time to PHRR (t_p , s), total heat release (THR, MJ/m²), total smoke production (TSP, m²), time to extinguishment (t_e), and mass residue (wt %)

are shown in Figure 4 and Table 3. In terms of the flame retardancy, the flame retardants generally contribute to either or both gas phase and condensed polymer phase during the combustion.⁴⁹ The heterocyclic imides incorporated into the polymer main chains realize the flame retardation in the condensed phase. The lower PHRR of the PUI-1 elastomer compared to those of the reference elastomers was attributed to the imides that accelerated the formation a thick char layer on the material surface after ignition. The char layer insulated the remaining material, retarding the pyrolysis and shielding the material surface from heat and oxidation.²⁰ As a result, the effective combustion time of the PUI-1 elastomer was 575 s, while it took 682 and 621 s for the refs 1 and 2 elastomers to extinguish. The subsequent THR of the PUI-1 elastomer was 78 MJ/m², which was lower than the values of both reference elastomers, indicating the

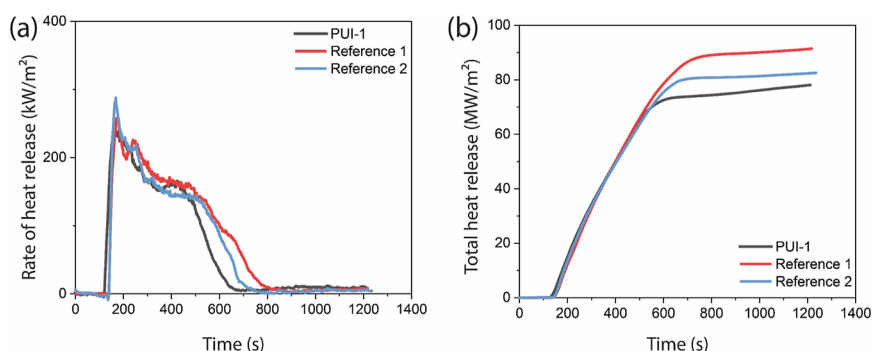


Figure 4. HRR and (b) THR curves of PUI-1 and refs 1 and 2 elastomers measured by a cone calorimeter under a heat flux of 25 kW/m².

Table 3. Cone Calorimetry Results of PUI-1 and Refs 1 and 2 Elastomers Measured Under a Heat Flux of 25 kW/m²

sample	TTI (s)	PHRR (kW/m ²)	t_p (s)	THR (MJ/m ²)	TSP (m ²)	t_e (s)	residue (wt %)
PUI-1	121	244.3	166	78.0	12.5	741	28.9
ref 1	140	257.6	170	91.2	15.7	852	28.9
ref 2	140	288.0	168	82.3	18.3	789	26.9

better flame retardancy of the PUI-1 elastomer even with only 2 wt % imide structures. In addition to lowering the THR, reducing the smoke production is another important target for the flame-retardant materials, as the gas released during combustion is one of the fire hazards. The TSP of the PUI-1 elastomer was much lower than the reference elastomers, which is due to the thick char layer that reduced the smoke production.

The char residues of PUI-1 and refs 1 and 2 elastomers obtained after cone calorimetry measurement (Figure S4) were further studied by SEM, as shown in Figure 5. Due to the positive effect of imides on char formation, a dense char layer was formed on the surface of the PUI-1 elastomer (Figure 5a), which provided an effective insulation of the internal material from the flame. Without the imides, a less pronounced char layer was formed on the surface of the reference elastomers. Thus, both surface and interior char residues of the reference elastomers were more fragmented.

The char residue was also studied by Raman spectroscopy as shown in Figure S5. The two strong, overlapping peaks at 1348

and 1586 cm⁻¹ are assigned to D band (amorphous structure) and G band (graphitic structure) of C=C bonds, respectively. After being deconvoluted of the overlapping peaks by fitting to a Gaussian peak shape, the integral ratio of the D band to the G band is used as a characteristic parameter to determine the graphitization degree of the char residues.⁵⁰ The lower the value of I_D/I_G , the higher the degree of graphitization is, which indicates the better capability of the char to prevent polymer volatiles from external release. The I_D/I_G ratio of PUI-1 and refs 1 and 2 elastomers are 1.88, 1.94, and 2.06, respectively. The imides in the elastomers helped to promote the char into a graphitic structure, leading to low I_D/I_G ratios.

4. CONCLUSIONS

The combination of imides and PUs leads to PUI materials with improved inherent thermal properties and stiffness. In the current work, we investigated a two-step, completely solvent-free synthetic way to introduce imides in PUs. Isocyanate-terminated imide prepolymers were first prepared. The subsequent aromatic and aliphatic isocyanate-based PUI elastomers (PUI-1 and PUI-2) exhibited higher char formation as well as higher Young's modulus compared to elastomers without imide structures. Moreover, the PUI-1 elastomer also showed enhanced flame retardancy with lower PHRR, THR, and TSP.

Our solvent-free synthetic route of an imide prepolymer removes current limitations caused by the use of organic solvents and allows greener and more processable large-scale

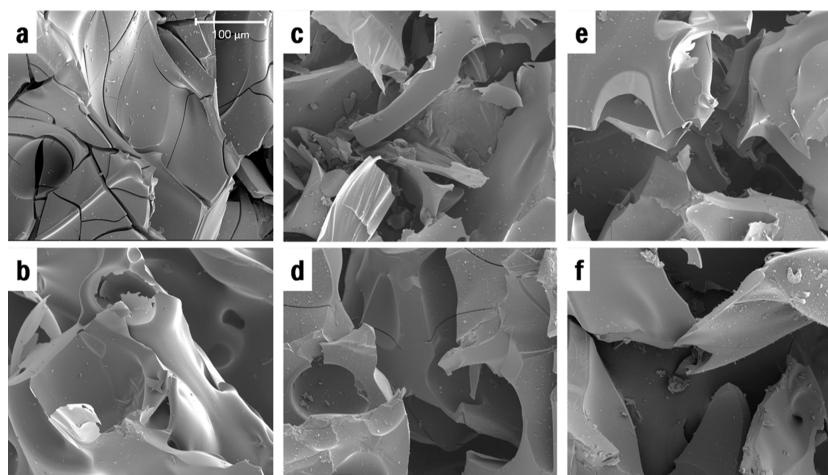


Figure 5. SEM images (100 μm, 5 kV) of elastomer char residues obtained from (a) PUI-1 elastomer surface, (b) PUI-1 elastomer interior, (c) ref 1 elastomer surface, (d) ref 1 elastomer interior, (e) ref 2 elastomer surface, and (f) ref 2 elastomer interior.

industrial production. The improved thermal stability, especially flame retardancy of the PU materials, demonstrates the potential use of aromatic imide prepolymers in other PU applications, such as rigid foams and compact thermosets, where thermal stability and flame retardancy are required. Due to the higher viscosity of imide-containing aromatic isocyanate prepolymers relative to standard isocyanates, they can be preferably applied in PU applications which tolerate higher viscosities, such as hot cast PU elastomers, sealants, adhesives, and rigid foams for sandwich panels. The thermal properties of PUI materials could be further improved by increasing the content of imide motifs in imide prepolymers. In addition, the use of imide motifs helps to improve the intrinsic thermal properties of PU materials and reduces the need of conventional flame-retardant additives. Synergy with other flame-retardant strategies like polyisocyanurate formation or flame-retardant additives may also be expected, and this is a relevant topic for future investigations.

Despite the focus of this work on thermal properties, the PUI materials may also have other improved physical properties. As imide structures exhibit high surface energy, a low dielectric constant, a low refractive index, and a low coefficient of thermal expansion, it is expected that the combination of imides and polyurethane will lead to PUI materials that can be used in, for instance, adhesive applications, electrical devices, and as photoconductors.^{9,51,52}

■ ASSOCIATED CONTENT

SI Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/acsapm.3c00626>.

Additional detailed experimental data including photos of PUI-1 and reference elastomers, synthesis recipes of all elastomers, different moieties in PUI-1 and ref 1 elastomers, real-time ¹³C NMR spectra of PUI-2 prepolymer synthesis, photos of char residues, and Raman spectra of char residues (PDF)

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Notes

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