



Crosslinked polyurea-co-polyurethane aerogels with hierarchical structures and low stiffness

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ABSTRACT

Resilient poly(urethane urea) aerogels are synthesized from aromatic diisocyanates, aromatic diamines, aliphatic polyols, and a trifunctional amine crosslinker. Polyurethane prepolymers are synthesized with isocyanate end groups by reacting the polyol with 4,4'-diphenylmethane diisocyanate in anhydrous *N*-methyl-2-pyrrolidone (NMP). The isocyanate-capped polyurethane segments are reacted with 4,4'-oxydianiline to obtain isocyanate end-capped poly(urethane urea) copolymers which are then crosslinked using 1,3,5-triaminophenoxybenzene (TAB) to obtain the gel networks. The gel networks are tailored by the choice of the polyol and by varying the crosslink density. The gels are dried under supercritical condition after exchanging NMP with acetone and acetone with liquid carbon dioxide. The resulting aerogels show density between 0.20 and 0.35 g/cm³, porosity between 71 and 85%, and surface area between 47 and 163 m²/g. The data suggest that the polyol weight fraction can be used as a parameter to control the shrinkage of aerogel specimens. The shrinkage data also correlate well with the extent of hydrogen bonding involving urea and urethane groups. A reduction of the amount of TAB leads to reduction of the extent of urea hydrogen bonding and an increase of urethane hydrogen bonding. These materials exhibit an onset of thermal decomposition at about 300 °C and offer compressive moduli between 12 and 52 MPa. The compressive modulus shows strong dependence on aerogel density.

1. Introduction

Aerogels are synthesized from co-continuous gel networks of a solid and a liquid. A gel is formed from a precursor sol via either crystallization-induced [1] or reaction-induced phase separation of the solid [2]. Traditionally, liquids are removed from the gel networks via supercritical drying to exploit the absence of liquid-vapor interface under supercritical condition and to avoid the solid network collapse due to capillary pressure.

Aerogels receive considerable attention due to their outstanding properties, including high porosity (often > 90%), low and controllable density, low thermal conductivity, and high specific surface area [3–6]. The attractive porous networks of syndiotactic polystyrene aerogels were recently used in high efficiency filtration of airborne nanoparticles with diameter in the range of 25–150 nm with air permeability of the order of 10⁻¹⁰ m² [7–9]. Aerogels of silica, metal alkoxides, cellulose, and other materials were first reported by Kistler [10] who developed the gels in an alcohol and removed the alcohol under supercritical condition. Kistler and co-workers [11,12] proposed aerogels as catalyst supports [11] and reported low values of thermal conductivity of silica

aerogels [12]. Silica aerogels dominated the aerogel landscape until the 1980's when Tewari et al. [13] proposed a safer supercritical drying process using liquid CO₂ with critical temperature and pressure, respectively 32 °C, 7.4 atm. The low temperature used in supercritical drying of CO₂ facilitated conversion of a number of polymeric gels into aerogels. Many polymeric gels cannot sustain the high critical temperature of ethanol, e.g., 241 °C and critical pressure, 6.3 MPa. Pekala [14,15] reported synthesis of resorcinol-formaldehyde (RF) aerogels via supercritical drying in CO₂. The RF aerogels provided surface areas as high as 900 m²/g [15].

Polyurethane aerogels were first documented in a patent filed in early 1996 [16] in an attempt to obtain polyisocyanate-derived foams free from the use of chlorofluorocarbons. Polymeric isocyanates were reacted with polyols, resorcinol, or other initiators in a low boiling point liquid to facilitate supercritical drying at relatively low temperatures. Optionally, the solvent was exchanged with liquid CO₂ followed by supercritical drying. These aerogels showed pore diameter between 1 and 100 nm and offered thermal conductivity of 20 mW/m-K at atmospheric pressure. Beismans and co-workers [17] synthesized polyurethane-based aerogels using solutions of polymeric aromatic

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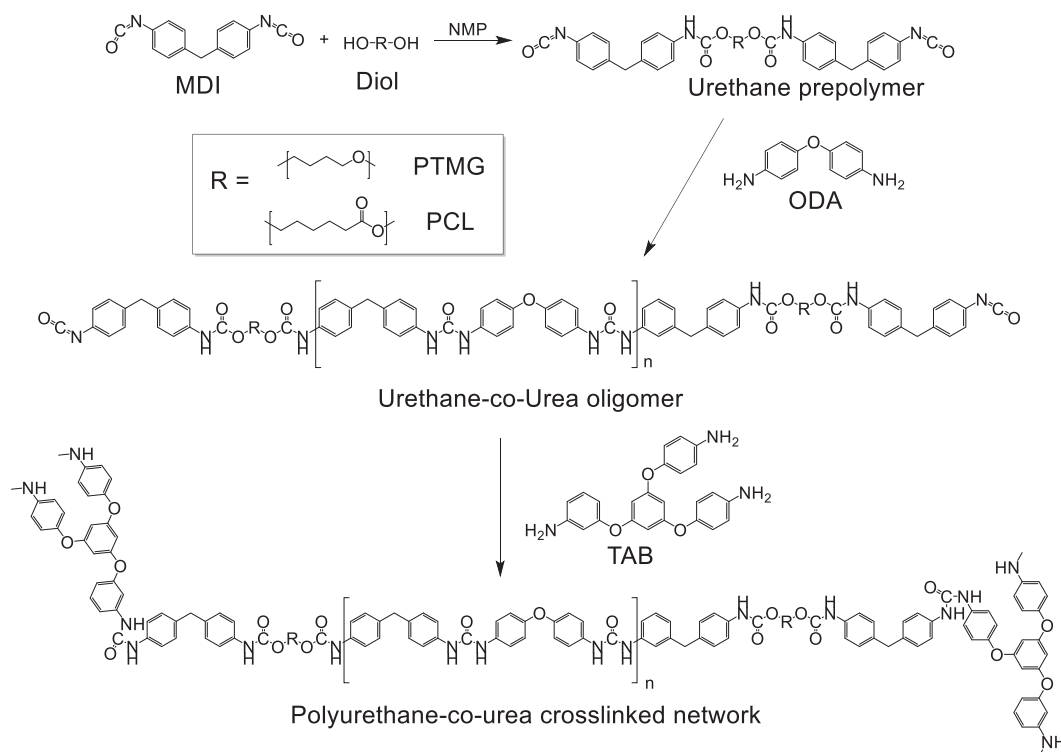


Fig. 1. Reaction scheme used in the synthesis of poly(urethane urea) gels, showing the urethane-co-urea oligomer and the poly(urethane urea) networks.

isocyanates in dichloromethane via isocyanurate ring formation or allophanate formation at higher temperatures. The aerogel with bulk density of 0.15 g/cm^3 offered thermal conductivity of $22 \text{ mW/m}\cdot\text{K}$. These researchers later synthesized polyurethane-based aerogels from commercially-available Suprasec[®] polymeric diisocyanate [18]. Pirard et al. [19] produced polyurethane gel networks by reacting polyisocyanates with polyols. The corresponding aerogels had density values between 0.11 g/cm^3 and 0.37 g/cm^3 . Some of the aerogel formulations showed narrow pore size distributions in mesopore range. Rigacci and co-workers [20] obtained polyurethane aerogels with density values in the range $0.12\text{--}0.22 \text{ g/cm}^3$ and thermal conductivity of $22 \text{ mW/m}\cdot\text{K}$ by reacting 4,4'-methylenebis(phenylisocyanate) (MDI) and multifunctional polyols in the presence of DABCO TMR[®] catalyst. Chidambareswarapattar et al. [21] reported an array of polyurethane aerogels with density as low as 0.094 g/cm^3 and surface area ranging from $0.5 \text{ m}^2/\text{g}$ to $241 \text{ m}^2/\text{g}$ using trifunctional isocyanates and multifunctional aromatic polyols. The use of dihydroxy benzophenone resulted in surface area of $0.5 \text{ m}^2/\text{g}$ while 1,1,1-tris(hydroxyphenyl) ethane and phloroglucinol triols produced higher surface area.

Lee et al. [22] investigated the properties of both polyurea and polyurethane aerogels. These researchers reacted MDI and polymeric MDI with either Jeffamine[®] or polyethylene oxide in the presence of triethylamine catalyst yielding respectively polyurea and polyurethane aerogels with surface area $190 \text{ m}^2/\text{g}$ and $47 \text{ m}^2/\text{g}$. Leventis et al. [23] produced polyurea aerogels from the reactions of multifunctional isocyanates and water and reported porosity as high as 98.6% and surface area approaching $320 \text{ m}^2/\text{g}$. Hydrophobic polyurea aerogels were also synthesized by reacting 1,3,5-tris(6-isocyanatohexyl)-1,3,5-triazinane-2,4,6-trione (N3300A) and water [24].

The present study sought to produce soft, low modulus poly(urethane urea) aerogels from MDI, aliphatic polyols, a short chain diamine for chain extension, and a trifunctional amine as the crosslinker of the linear urethane-urea segments. Two kinds of polyols were considered for this purpose – polycaprolactone polyol (PCL) with molecular weight 530 g/mol and poly(tetramethylene ether) glycol (PMTG) with molecular weight 650 g/mol . The prepolymer chains were extended

using 4,4'-oxydianiline (ODA), a flexible, short chain, aromatic diamine. Previous work [25] on polyurea aerogels indicated the possibility that inter-chain hydrogen bonding promoted by the urea linkages could offset gel shrinkage. Such hydrogen bonding possibilities were also expected in this work, especially for high aliphatic chain content. We also anticipated that the inclusion of polyurea segments in the same aerogel with polyurethanes would enhance the aerogel surface area based on the results of Lee et al. [22]. In addition, the inclusion of polyurethane segments in the same aerogel with polyurea was expected to render such aerogels softer compared to polyurea aerogels. One potential application includes soft cushions that also serve as thermal insulators for protecting delicate sensors from exposure to high temperatures.

2. Experimental

2.1. Materials

MDI was provided by Covestro (Pittsburgh, PA) as a white crystalline solid. MDI was stored in a vacuum-sealed jar at 0°C when not in use. 1,3,5-Tris(4-aminophenoxy)benzene (TAB) was provided by Triton Systems (Chelmsford, MA) and was available as a light tan powder. Anhydrous *N*-methyl pyrrolidone (NMP), DABCO[®] T120 catalyst, and ODA, and acetone were purchased from Sigma Aldrich (St. Louis, MI). Polycaprolactonediol (PCL) with a reported molecular weight of 530 g/mol was purchased from Sigma Aldrich (St. Louis, MI). Poly(tetramethylene glycol) (PTMG) with a reported molecular weight of 650 g/mol was purchased from Invista (Wichita, KS). Both polyols were heated at 60°C for 24 h under vacuum prior to use to ensure dryness.

2.2. Preparation of poly(urethane urea) aerogels

The solid content in the reaction system was fixed at 10% by weight in NMP. All reagents were individually dissolved in NMP at room temperature unless otherwise indicated. Fig. 1 shows the general reaction scheme for preparation of poly(urethane urea) gels. MDI was

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