



Effect of the polymer structure on the viscoelastic and interfacial healing behaviour of poly(urea-urethane) networks containing aromatic disulphides

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ABSTRACT

The macroscopic interfacial healing behaviour in a series of urea-urethane networks as function of the hydrogen bonds and disulphides content is presented. The polymers were prepared with different crosslinking densities but with the same amount of dynamic covalent bonds (disulphide linkages). Tensile and fracture measurements were adopted to evaluate the degree of recovery of the mechanical properties after damage. Healing kinetics and healing efficiencies were quantitatively determined as a function of network composition, healing temperature and contact time. Finally, the recovery of mechanical properties was correlated with the viscoelastic response of the networks through rheological measurements and time-temperature superposition principle (TTS). The application of the TTS approach on both fracture healing and DMTA and subsequent mathematical descriptive model led to a better understanding of the influence of polymer architecture and that of the amount of reversible groups on the healing process.

1. Introduction

Intrinsic healing polymers have gained an increasing amount of attention in the last years due to their appealing ability to, autonomously or on-demand, repair (multiple times) mechanical damage, such as surface scratches and through-the-thickness cracks. A great challenge in the development of these new materials is to achieve a combination of a reasonable healing capability (i.e. more or less complete recovery of the base mechanical properties after a modest healing time in the range of 1–24 h at or close to the intended use temperature) and mechanical properties comparable to those of conventional non-self-healing polymer grades of the same polymer family. Significant efforts have been made by the polymer community to conceive and synthesize new polymeric materials with a high healing capability based on reversible non-covalent interactions or reversible covalent bonds [1–4]. Polymers based on reversible supramolecular interactions (e.g. multiple hydrogen bonding [5,6], van der Waals interactions by side branches [7] or metal-ligand coordination [8]) can show excellent healing at (near) room temperature and can have mechanical properties similar to those of conventional polymers when measured under short-term quasi-static loading conditions. However, due to the dynamic nature of the reversible bonds, these self-healing polymers have a significant temperature-dependent behaviour and a poor long-term mechanical stability. On the other hand, polymeric networks based on dynamic covalent

bonds (e.g. polysulphide [9–11], acylhydrazone bonds [12], boronic ester bonds [13] or Diels-Alder reaction [14]) potentially offer higher and more stable mechanical properties over a wider temperature range as a result of the higher stability of the reversible bond moiety. The unavoidable down side of this it that these polymers have a lower healing capacity at room temperature. A combination of both strategies might be a good approach to obtain better healing polymers with improved mechanical properties.

Already in 1963, Tobolsky demonstrated the significant effect of reversible polysulphide crosslinks on the viscoelastic behaviour of different polymers such polyethylene tetrasulphide [15] and urethane elastomers [16]. The unusual stress-relaxation behaviour of such polymers was attributed to a dynamic polysulphide bond interchange mechanism. Recently, different polysulphide based polymers exhibiting decent mechanical properties as well as an efficient healing performance have been developed [17]. Various triggering agents such as temperature [10,11,18], redox reactions [19] or UV-irradiation [20] can be used to induce selective scission of polysulphide bonds. The reshuffling rate of polysulphide can be accelerated by catalysts [21,22] and its temperature reduced when the appropriate monomers are selected as recently shown with aromatic disulphide based poly(urea-urethane) system (PUU) healing at room temperature in the absence of a specific catalyst [23]. This crosslinked PUU system containing disulphide bridges connected to aromatic groups can be reprocessed after

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curing by applying high temperature and pressure in a mould, leading to products with a new shape without any loss in mechanical properties [24]. This system has been reported to be based on a unique combination of two self-healing mechanisms: H-bonds and aromatic disulphide metathesis. The latter mechanism is based on a [2 + 1] radical-mediated bonds exchange as reported somewhere else for disulphide containing polymers [25,26].

Despite the many attempts to develop new chemistries leading to strong and fast healing polymers, little attention has been yet placed on understanding the effect of the polymer architecture on healing even though polymer architecture is expected to have a major impact on kinetics and healing degree [27]. In the present work, we investigate the effect of the polymer structure on the healing behaviour of a series of PUU polymers with similar formulation and a fixed disulphide content but a variable crosslinking density. The testing framework includes a study of the main relaxation processes as detected by Dynamic Mechanical Thermal Analysis (DMTA) and a study of the recovery of the mechanical properties after cutting the samples at room temperature using dedicated tensile and fracture testing protocols. A Time Temperature Superposition protocol was applied to both the rheological and fracture results demonstrating a close relation between the main underlying processes responsible for macroscopic healing and polymer dynamics and the polymer architecture.

2. Experimental section

2.1. Materials

Poly(propylene glycol)s (PPG) of $M_n = 6000 \text{ g mol}^{-1}$ (PPG 6000, trifunctional) and $M_n = 4000 \text{ g mol}^{-1}$ (PPG 4000, linear difunctional) were purchased from Bayer Materials Science (Fig. 1). The M_n and M_w of PPGs were verified by size exclusion chromatography (SEC) and are provided in the Supporting Information. Isophorone diisocyanate (IPDI, 98%), dibutyltin dilaurate (DBTDL, 95%), bis(4-aminophenyl) disulphide (Linker) and tetrahydrofuran (THF) were purchased from Sigma-Aldrich and were used as received. The following synthesis steps were carried out in accordance with the procedure described by Recondo et al. [23].

2.2. Synthesis of tris-isocyanate-terminated pre-polymer (PU 6000)

Mixtures of PPG ($M_n = 6000 \text{ g mol}^{-1}$, 390 g, 65 mmol) and IPDI (45.45 g, 204.5 mmol) were fed into a 1 L glass reactor equipped with a mechanical stirrer and a vacuum inlet. The mixture was degassed by stirring under vacuum while heating to 70 °C for 10 min. Then, DBTDL (50 ppm) was added and the mixture was further stirred under vacuum at 70 °C for 45 min. The resulting tris-isocyanate terminated pre-polymer was obtained in the form of a colourless liquid and stored in a tightly closed glass bottle.

2.3. Synthesis of bis-isocyanate-terminated pre-polymer (PU 4000)

A mixture of PPG ($M_n = 4000 \text{ g mol}^{-1}$, 250 g, 62.5 mmol) and IPDI

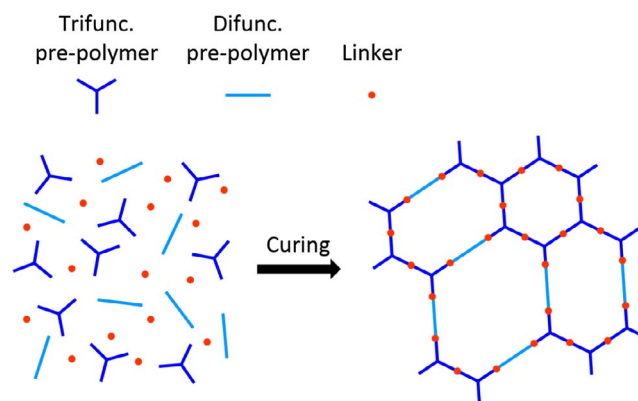


Fig. 2. Chemical route followed in the preparation of the polymers under study.

(27.75 g, 125 mmol) were fed into a 1 L glass reactor equipped with mechanical stirrer and a vacuum inlet. The mixture was degassed by stirring under vacuum while heating at 60 °C for 10 min. Then DBTDL (50 ppm) was added and the mixture was further stirred under vacuum at 60 °C for 70 min.

2.4. Synthesis of self-healing poly(urea-urethane) networks with different crosslinking density (PUU systems)

The preparation of polymers containing the same quantity of disulphide moieties but different crosslinking densities was accomplished by using different combinations of the trifunctional polyurethane and difunctional polyurethane pre-polymers described above (PU 6000 and PU 4000). With this particular choice of precursors it was possible to keep the crosslinker quantity constant (1.2 eq. with respect to the NCO groups) as the equivalent weight of a chain between an isocyanate moiety and a crosslinking point is always 2000 g mol^{-1} (see Fig. 2). We varied the trifunctional:difunctional pre-polymer ratio from 100:0 to 70:30 (4 different ratios) as reported in Table 1. The stirred mixtures were poured in an open mould and cured for 16 h at 60 °C to produce approximately 2 mm thick films.

By introducing difunctional units, the number of bonds between the trifunctional units increased producing networks with lower crosslinking densities and thus an apparent higher molecular weight between the centres of the transiently connected three-arm molecules. The four polymers developed (Table 1) therefore contain the same density of disulphide and hydrogen bonds but differ in the crosslinking degree yet maintaining comparable glass transition temperatures (T_g). Such an approach allows for a dedicated study on the effect of the polymer architecture on healing.

2.5. Dynamic Mechanical Thermal Analysis (DMTA)

DMTA measurements were performed on a Thermo Scientific (model Haake™ Mars III) rheometer equipped with a temperature controlled test chamber and adopting the 20 mm parallel plate

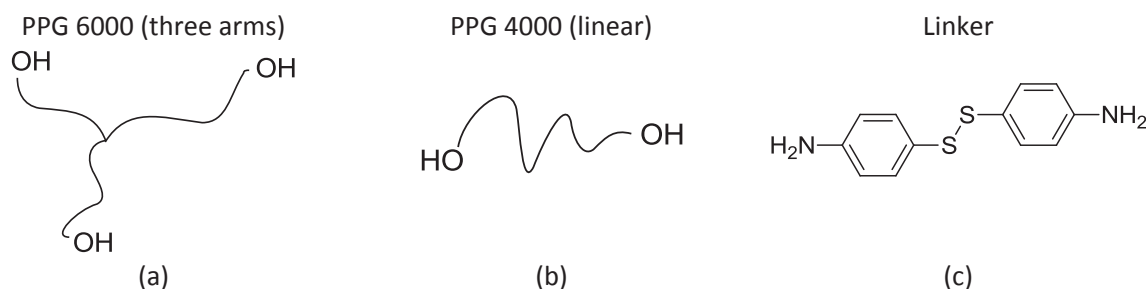


Fig. 1. Chemical sketch of PPGs (a-trifunctional, b-difunctional) and disulphide linker (c).

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