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A combined fracture mechanical – rheological study to separate the contributions of hydrogen bonds and disulphide linkages to the healing of poly(urea-urethane) networks

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ABSTRACT

This work presents a detailed study into the rheological properties and fracture healing behaviour of two poly(urea-urethane) polymers containing (i) hydrogen bonds and (ii) hydrogen bonds and disulphide linkages. The experimental procedure here presented using the temperature and time superposition allowed for the identification of the contribution of each reversible bond type to the network behaviour (rheology) and healing (fracture). During the experimental data analysis it was found that the same shift factors required to construct the rheological master curves from separate isothermal small-amplitude oscillatory shear (SAOS) measurements at different temperatures could also be applied to obtain a master curve for the fracture healing data as a function of healing time and temperature. This work shows therefore the apparent direct relationship between rheological response and macroscopic fracture healing.

1. Introduction

In recent times several strategies have been investigated by polymer chemists to design and synthesize new polymeric materials with a so-called intrinsic healing functionality [1–6]. Intrinsic self-healing polymers have the natural ability to make surface scratches disappear and to restore mechanical integrity across a crack when exposed to an appropriate thermal stimulus. The mechanism behind the self-healing is the re-formation of broken (reversible) chemical and/or physical bonds. While spectroscopic and rheological techniques are useful tools to investigate the dynamic and reversible behaviour of healable polymers at the molecular level [7–10], robust techniques capable of quantifying the relevant interfacial healing processes at soft polymer interfaces are less well established [11]. To date, most researchers have used the recovery of tensile strength of broken samples as a measure of interfacial healing. However this testing method fails to capture the relevant chemical processes at the healing interfaces as well as the effective restoration of mechanical integrity. Recently, we presented a fracture mechanics testing procedure based on the application of the J-integral to determine the real state of interfacial healing for a supramolecular elastomer with a higher degree of accuracy than tensile testing [12]. The J-integral method, originally developed to determine the strain energy release rate for crack growth in elasto-plastic materials [13,14], is nowadays employed to experimentally evaluate the fracture energy of soft materials such as elastomers [15–17], making it also a most appropriate technique for quantification of mechanical properties restoration. In the fracture mechanical method, the structural discontinuity at the interface in its various stages of healing is properly taken into account when measuring the restoration of mechanical integrity as a function of healing time and temperature. The method also allows detecting the transition at the healing crack from a weak interface into a strong interface/interphase. It is then clear that healing in the so far studied intrinsic healing polymers involves both segmental and full molecular motion as well as local re-formation of reversible bonds with different bond energies.

The time and temperature dependence of molecular motions in supramolecular materials, elastomers and polymers is conventionally measured using small-amplitude oscillatory shear (SAOS) rheology and stress relaxation experiments. A full picture of the main relaxation processes exhibited by a polymer over a broad time or frequency domain can be obtained by the application of the time-temperature superposition (TTS) principle, in which the results at different temperatures and time scales are used to form a

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so-called master curve [18]. In the present work we use the TTS principle on both rheological and fracture mechanical data to demonstrate the correlation between these two tests thereby reinforcing the link between network behaviour and macroscopic healing. The measurements were performed on a poly(urea-urethane) network containing only hydrogen bonds or both hydrogen and dynamic disulphide linkages [19].

2. Experimental

2.1. Materials

Several experimental analyses, involving amongst others rheology and fracture mechanics testing, were carried out to evaluate the healing capability of elastomers incorporating reversible bonds. The healable material, synthesized based on a procedure as reported in literature [19], consisted of an isocyanate-terminated pre-polymer organized in a network connected by aromatic disulphides linkages and containing urea related H-bonds (here on PUU-SS). A permanently cross-linked polymer network not containing a reversible disulphide linker but keeping the urea H-bonds was also prepared (PUU-CC) to serve as the reference material. FT-IR and Raman spectroscopy were employed to follow the various steps in the polymer synthesis (Supporting Information, Figs. S1 and S2). A sketch of the structure of the two polymers is presented in Fig. 1.

2.2. Testing procedures

Swelling experiments were performed to determine cross-linking density in both polymers. Small samples were cut from the sheets synthesized and swollen for 48 h in tetrahydrofuran (THF). Mass swelling ratios were obtained by comparing the weight of the different samples before and after the swelling experiments.

Thermal properties of the PUU-SS and PUU-CC material were investigated by means of Differential Scanning Calorimetry (DSC) and thermogravimetric analysis (TGA) over the temperature range from −100 to 100 °C and from 25 to 400 °C, respectively; in both experiments a heating rate of 20 °C/min was employed.

Dynamic and steady-state rheological measurements were performed on a Thermo Scientific (model Haake™ Mars III) rheometer equipped with a temperature controlled test chamber. A 20 mm parallel plate geometry was employed for all the measurements. For the dynamic rheological tests, temperature sweep experiments at a frequency of 1 Hz were performed in the linear viscoelastic regime (0.5% strain). A heating rate of 5 °C/min from −30 to 180 °C was employed. Frequency sweep experiments (0.01–10 Hz) were also carried out in the small amplitude range (0.5% strain) at various temperatures. In order to construct rheological master curves, 20 °C temperature increments were adopted in the domain 20–180 °C. Steady-state relaxation experiments at a constant temperature of 120 °C were performed by applying a deformation step of 0.5% strain and recording the shear stress evolution for at least 10^4 s.

Single Edge Notch Tensile (SENT) fracture experiments were performed using a Zwick mechanical testing machine (model 1455) fitted with a 2 kN load cell. Rectangular samples (70 × 20 mm) were cut with a die from the moulded 2 mm flat polymeric sheets. A cut with a length of 10 mm was made into the centre of the longest side of each specimen using a sharp razor and the notch tip was immediately sprinkled with talcum powder in order to avoid contact between the freshly cut surfaces. Pre-notched samples were then clamped in the tensile machine with a gauge length of 40 mm and stretched until failure. Subsequently, fractured samples were accurately positioned in PTFE moulds and healed according to a previous published procedure [12]. The effects of both healing time and healing temperature on the recovery of fracture properties were investigated. Different samples were healed at various constant temperature for 1, 3, 6 or 24 h; the healing temperature ranged from room temperature (RT ≈ 20 °C) to 120 °C. In the case of healing above RT, heated samples were exposed to and equilibrated at RT for 30 min before being re-tested following the same SENT fracture protocol. Samples healed at RT were retested right after the healing treatment. A constant cross-head separation velocity of 1 mm s^{-1} (initial strain rate $\dot{\varepsilon} = 2.5 \times 10^{-2}$ s^{-1}) was employed in each experiment and force and displacement data were collected. All the fracture tests were performed at room temperature. The typical duration of a fracture mechanics test was less than 40 s. At least three samples were used for each testing conditions. Video images were recorded during each experiment in order to detect crack initiation and to follow crack evolution as shown in Fig. 2. In the video footage the different fracture behaviour at the healed crack can be observed highlighting the interface–interphase transition in the PUU-SS sample.

3. Results

3.1. Fracture and healing measurements

Fig. 3 shows representative Load–Displacement curves for virgin and (1 h) healed PUU-SS and PUU-CC samples. The PUU-SS material shows a clear temperature dependent recovery of the mechanical response with an increasing degree of healing with increasing healing temperature. The initial modulus value is quickly restored, but the load displacement curves consistently fall below the curve for the virgin material at higher strain levels. In contrast the PUU-CC system presents a limited recovery of the initial properties even after healing for 1 h at the highest temperature (120 °C).

From these Load–Displacement curves, fracture properties can be determined using the J-integral analysis method [12,16]. Critical fracture energy values, J_c, for each sample were calculated according to the following equation:

$$J_c\left[\mathrm{kJ}/\mathrm{m}^2\right] = \left.\frac{\eta U_c}{b(w-a)}\right|_{u_c} \quad (1)$$

where U_c is the energy calculated as the area under the Load–Displacement curves at the displacement u_c where crack propagation occurs as selected from the video recordings and J-integral approach, η is the proportionality factor related to sample geometry (a value of 0.9 was selected according to literature [16]); b, w and a are the sample thickness, sample width and pre-crack length, respectively.

It is worth noting that virgin PUU-SS showed a greater J_c value than virgin PUU-CC (see Supporting Information, Table S5) indicating that during fracture testing more energy is dissipated for the sulphur containing polymer. This may be related to the different kind of linkage (dynamic covalent versus permanent covalent for PUU-SS and PUU-CC, respectively) forming the two polymer networks [20]. The dynamic nature of the polysulphide bonds may thus introduce an additional dissipative process not available in the same polymer only containing one kind of reversible bonds (PUU-CC) [21].

At healing temperatures above 70 °C the fracture toughness values of the PUU-SS material clearly increased with healing time and temperature (Table S5). No such increase with contact time was observed for RT and 50 °C healing cycles. In case of the PUU-CC material the healed samples exhibited nearly equal low fracture energies regardless of the healing time and healing temperature.

The calculated J_c values were then used to obtain a more