SUPRAMOLECULAR HEALABLE MATERIALS THROUGH A COMBINATION OF p-p STACKING AND HYDROGEN BONDING: SYNTHESIS, RHEOLOGY AND HEALING

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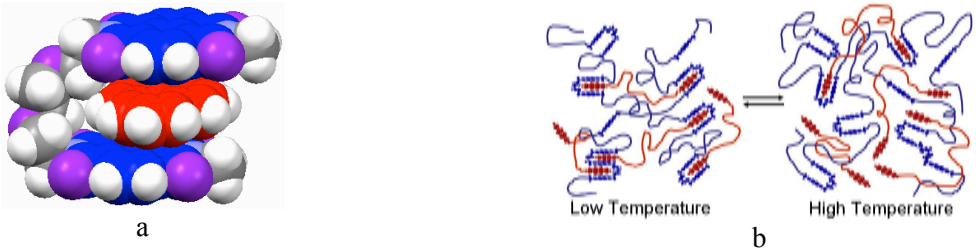
ABSTRACT

The discovery of polymers with tuneable physical properties is a rapidly expanding area of research. At the forefront of the field are healing polymers,[i] which, when fractured can regain the physical properties of the material either autonomically,[i] or in response to a stimulus.[i] Recently, there has been increased interest in the use of supramolecular polymers as healable materials. In a typical supramolecular polymer, relatively low molecular weight species are held together in the solid state by non-covalent interactions. This results in a dramatic increase in the apparent molecular weight of the polymer – enhancing the mechanical properties of the material. It has been suggested that fractures propagate through scission of the weak non-covalent interactions, rather than through breaking the stronger, covalent bonds. Thus, during the healing process the macromolecules surrounding the fracture site need only sufficient energy to re-engage their supramolecular interactions in order to regenerate the strength of the pristine material.

We have recently reported the synthesis of self-assembled polymer blends [ii,iii] formed from two distinct components that interact through the formation of multiple weak ($k_a \approx 130\ M^{-1}$) p–p stacking interactions. [iv] The first component of the blend featured p-electron poor diimide units separated by a short ethylene glycol spacer, the second component consisted of a polysiloxane with pyrenyl end-groups. The separation between diimide residues in one component was carefully designed to provide sufficient flexibility to enable the diimides to chainfold around, and bind the p-electron rich pyrenyl groups on the polysiloxane, resulting in the formation of a p–p stacked complex (Figure 1a). Complex formation between the two components serves to crosslink the blend, affording it self-supporting properties at ambient temperatures. The responsive nature of the supramolecular interactions permits disengagement of these crosslinks upon thermal stimulation (Figure 1b) allowing rapid crack healing (5 minutes) at elevated temperatures (≈50 °C) to be observed. [3]



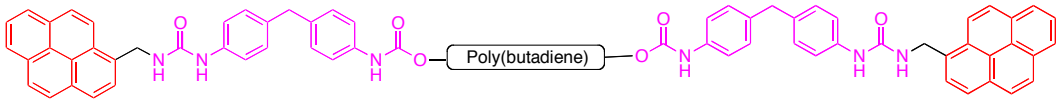
a b

Figure 1: (a) Space filling model of the proposed chain folded supramolecular complex. (b) Schematic of the thermal healing mechanism (chain-folding polyimide in blue, pyrenyl endcapped polyer in red).

Herein we report that by modifying the blend to contain simple hydrogen bonding motifs which complement the p–p stacking interactions, it is possible to produce tough elastomeric materials that retain their ability to heal.

The synthesis of pyrenyl endcapped hydrogen bonding component of the blend (**1**) was achieved accorded to our previously established one-pot, two-step synthesis.[v] Accordingly, methylene

diphenylisocyanate was added to hydroxy terminated polybutadiene (M_w = 2,300 Da) (NCO:OH ratio 2:1). The resulting isocyanate prepolymer was endcapped with aminomethyl pyrene to furnish the desired hydrogen bonding polymer (**1**) with p-electron rich endgroups as a slightly yellow elastomer. A solution blend of an essentially colourless solution **1** with the yellow solution of chain-folding polyimide **2** produced a deep red solution, which is indicative of p–p stacking interactions resulting in a charge transfer absorption. A film cast from this solution maintained the deep red colour of the solution and was elastomeric in nature (Figure 2).[vi]



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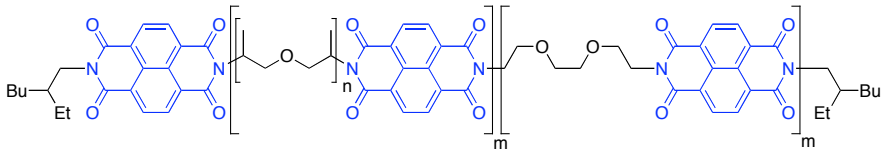

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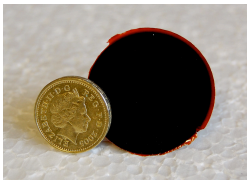

Figure 2: Structures of the blend components (1 & 2). Photographs of the red, elastomeric film cast from a blend of the components (1 & 2).

Healing studies were carried out by completely cutting the blend (**1**+**2**), placing the broken edges of the film in contact and annealing at 100 °C. Comparison of the tensile strength of the pristine blend (≈10^5 Pa) with that of the healed samples revealed that the novel supramolecular blend was able to undergo 5 break/healing cycles with essentially complete restoration of the physical properties of the material. We also will present in depth characterisation data for the healing blend in the solid state including variable temperature small angle X-ray scattering and infra-red spectroscopic analysis which provide insights into the novel healing mechanism which operates within this blend.

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