SELF HEALING IN ACTION

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Sophisticated polymeric materials with “responsive” properties like self healing are beginning to reach the market. The use of reversible, non-covalent interactions is a recurring design principle for these materials. Now, recently developed hydrogen bonding units allow for taking this design principle to its extreme. Supramolecular polymers, where hydrogen bonds are responsible for the interactions between the polymer chains, form materials whose (mechanical) properties strongly respond to a change in temperature or solvent. In this presentation, hydrogen bonded supramolecular polymers based on SupraB® are presented, and the use of these materials in self healing applications is discussed.

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1 Introduction

In the past 60 years, polymers have revolutionized our lives. Their low price, high processability and exceptional mechanical properties have led to the use of polymers in ever more sophisticated applications. Presently, a strong interest in “smart” polymers to be used in self healing applications is beginning to expand the potential field of application of polymeric materials even further. Key to the responsiveness of these smart materials is the reversibility of the noncovalent interactions that lead to the change in properties. This field of supramolecular chemistry has been developed over the past 25 years by synthetic chemists, and was strongly inspired by the ubiquity of reversible yet highly specific intermolecular processes in nature. Despite their short history, supramolecular polymers are already beginning to find commercial use, in applications that take advantage of the reversibility and responsiveness of non-covalent interactions. In this presentation the reversible SupraB-polymers and their (possible) uses as self-healing materials in different applications will be highlighted.

Autonomous healing, or repairing, of damaged polymeric materials have always been an attractive means to prolong the service life of polymeric devices, whereby these damages can range from cracks in polymeric structural engineering materials to scratches in polymeric coatings. Initially, healing systems used the increasing mobility of polymeric chains with heat. In this way, chain entanglements in the damaged region could reform upon heating, thereby repairing the damage.
This approach only works for thermoplastic systems and is hampered by high melt viscosities of the polymeric chains as this prevent good formation of interfacial entanglements. In another approach, chemical reactions have been used to repair damages to polymeric resins. Basically, reactive chemical formulations were brought on the damaged interfaces and repair took place by subsequent hardening of the formulation. As a consequence, the quality of the repaired crack is strongly depending on the interaction between the fractioned polymer and the reactive formulation, thus chemical compatibility and surface roughness are very important. Moreover, the device is not able to autonomously repair itself, as chemicals have to be added to the device.

Recently, a next step has been made in repairing polymeric resins by embedding the repairing chemical formulation inside the polymer matrix and using crack formation as initiator for the healing chemistry. In this way, a truly self-repairing polymer system is designed. However, such polymers have to contain reactive chemicals and possible toxic catalysts. Moreover, the chemical reaction only can take place once, and the presence of the capsules with the healing ingredients in the polymeric material may deteriorate the material’s mechanical properties. Therefore, this approach has been improved by designing a polymer that contains thermo-reversible linkages, that is a polymeric resin held together by linkages obtained via a Diels-Alder reaction. As this reaction is thermo-reversible, heating the resin to temperatures above 130°C results in a retro Diels-Alder reaction and consequently reversible opening of the cross-links followed by flow of the polymer and subsequently repair of the material. Although no catalyst is needed, this approach still uses chemical reactions in which covalent bonds are formed that are demanding on relative orientations and prone to side reactions that do not contribute to repairing.

Here, it is shown that the use of non-covalent, reversible cross-links opens the way to polymeric materials that behave as they were cross-linked at room temperature but still can be self-healed at elevated temperatures without the need of forming new covalent bonds, and hence without the need for reactive chemicals or (toxic) catalysts. This can be done by using supramolecular polymers, which are formed by the reversible association of low molecular weight prepolymer.

2 Supramolecular polymers

To obtain polymers with sufficient cross-linking density, a high association constant between the repeating units is a prerequisite. The reversible interaction that is used here is based on hydrogen bonding. Although hydrogen bonds between neutral organic molecules are not among the strongest non-covalent interactions, they hold a prominent place in supramolecular chemistry due to their directionality and versatility. Meijer and Sijbesma have shown that combining four hydrogen bonds in a functional unit, employing a particular arrangement, results in a strong increase of association strength between those units. These self-complementary quadruple H-bonding units based on 2-ureido-4[1H]-pyrimidinones (SupraB®, see Figure 1), are reported to dimerize in chloroform with an association constant of \( K_{\text{dim}}=6 \times 10^7 \text{ M}^{-1} \).
The reversibility of the linkages between the building blocks is instrumental in the development of materials that change their properties in response to environmental changes, so called ‘smart materials’. Although the supramolecular polymers based on bifunctional ureidopyrimidinone derivatives in many ways behave like conventional polymers, the strong temperature dependence of their mechanical properties really sets them apart from macromolecular polymers. At room temperature, the supramolecular polymers show polymer-like viscoelastic behavior in bulk and solution, whereas at elevated temperatures liquid-like properties are observed (Figure 2).

As the SupraB unit is readily accessible from bulk chemicals on a large scale, the application of the SupraB- technology in polymers of industrial relevance is straightforward. This has resulted in the development of SupraB-materials based on, amongst others, polysiloxanes, poly(ethylene/butylenes), polyethers, polyesters, and poly(meth)acrylates. In all these compounds, the material properties have been shown to improve dramatically upon functionalization, and materials were obtained that combine many of the mechanical properties of conventional macromolecules with the low melt viscosity of organic compounds. Consequently, in this strategy the gap is closed between polymers and oligomers using the best of both worlds.
Moreover, the use of monomers with a functionality of three or more, will give rise to network formation. However, in contrast to condensation networks, the ‘self-healing’ supramolecular network can reassemble to form the thermodynamically most favorable state, thus forming denser networks.xvii

3 Self-healing properties

Because of the thermo-reversible nature of supramolecular polymers with SupraB, applying heat results in a decrease in the hydrogen bonding interactions between the polymer chains and consequently a strong decrease in dynamics of the individual polymers. The reduced melt viscosities allow easy flow of the polymeric materials and can be used to repair damages. Upon cooling, the hydrogen bonding interactions between the chains are rebuilt and consequently the non-covalent cross-linking in the material, giving the material its properties back.

The applicability of this approach has been demonstrated in coatings made of elastomers consisting of hydrogenated polybutadiene modified with SupraB (polymer 1). Polymer 1 shows visco-elastic behavior and flows at temperatures above 100°C. Consequently, a coating consisting of polymer 1 was damaged with a sharp object, followed by heating to 140°C. At this temperature the hydrogen bonding between the polymers is strongly reduced and because of the relative low molecular weight of the polymer, a good flow of the material is observed. This results in leveling out of the coating in the damaged area. After cooling down the original coating properties are restored again and the damaged area is not visible anymore (Figure 3a).

In another approach, a hard siloxane coating was made using polymer 2, a telechelic PDMS functionalized with SupraB. This material has a thermal transition above 100°C. Indeed, a spin-coated film of polymer 2 could be repaired after damage by heating the film to 140°C. Again, the thermal reversibility of the SupraB-units allowed good flow at this temperature and subsequent healing of the film (see figure 3b).

Figure 3: Self-healing at 140°C for polymer 1 (top) and polymer 2 (bottom)
The self-healing approach can also be used for functional coatings. Here, an adhesive is combined with the SupraB technology resulting in polymer 3: a soft PDMS prepolymer functionalized with SupraB. This supramolecular PDMS adhesive shows good adhesion to glass, probably because of the high flow of the material at high temperatures allowing good wetting of glass-surface. Not only the adhesion is good, but also the cohesive strength because of the presence of the hydrogen-bonding interactions in the polymeric material. As a result, gluing two glass slides together with this SupraB-adhesive, resulted in a very strong adhesion. However, heating the bonded glass-slides to 140°C weakened the hydrogen bonding interactions and, therefore, resulted in cohesive failure and consequently in debonding of the two glass slides.

In addition, these debonded slides could be bonded again by repositioning them followed by cooling down to room temperature. In conclusion, the thermo-reversible nature of this Supra-adhesive allows strong temporarily bonding of substrates and the possibility to repair the adhesive linkage by applying heat.

4 Conclusions

Polymeric materials modified with ureido-pyrimidones (SupraB®) show strong temperature dependent properties because of the presence of strong hydrogen-bonding interactions: material properties belonging to cross-linked materials at room temperature, and low viscous melts at elevated temperatures. This property allows these materials to be used in self-healing applications in which the temperature can be used as a trigger for the healing process. In this way, no reactive chemicals are needed and no covalent bond formation has to take place, increasing not only the fidelity of the healing process but also the number of times that healing can take place. These features can be applied to generate self-healing coatings and adhesives that fully benefit of the reversibility of hydrogen bonding interactions.

REFERENCES


