Stimuli-Adaptable Materials - DTU Orbit (31/12/2018)

**Stimuli-Adaptable Materials**

The work presented in this Thesis deals with the development of a stimuli-adaptable polymer material based on the UV-induced dimerisation of cinnamic acid and its derivatives. It is in the nature of an adhesive to adhere very well to its substrate and therefore problems can arise upon removal of the adhesive. This is also known from skin adhesives where it is very undesirable to cause damage to the skin. The overall idea of this project was to resolve this problem by developing a material which could switch between an adhesive and a non-adhesive state. Switchable adhesion is known in the literature but the presented work has a new approach to the field by basing itself on the idea of developing a network into which a photo-active polymer is mixed and which function as an adhesive. Upon irradiation with UV-light for a short time a non-adhering inter-penetrating network material would be formed. Two simple models for the extent of reaction for the system are presented and show that the timescale for the reaction is minutes to hours. This was further investigated with IR-spectroscopy and UV-absorbance spectroscopy. UV-spectroscopy confirmed that a change in the material occurs upon irradiation with UV and that the reaction time is in the range of minutes. A number of polymer derivatives with cinnamic acid or cinnamylidene acetic acid were prepared and the material properties of these were studied before and after irradiation with UV-light. For the cinnamylidene acetic acid derivatised polymers a macroscopic change was observed upon dissolution of the irradiated compound. The irradiated polymers formed threads or fibres when exposed to water while the unexposed polymers dissolved as a hygroscopic powder. Cinnamic acid derivatised poly(ethylene glycol) (PEG) was studied in detail and three different polymers were derivatised, namely a 4-armed star PEG (Mn = 2000 g/mol), a short linear PEG (Mn = 1000 g/mol) and a long linear PEG (Mn = 4000 g/mol). The derivatised polymers were mixed to create three different photo-active materials and these were investigated with rheology before and after irradiation with UV-light for one hour. It was observed that the largest change occurred for the system consisting solely of the cinnamic acid derivatised 4-armed star PEG. The development of the material properties of this material was studied in details by exposing the compound to UV-radiation for up to 120 h and determining the rheological properties after the exposure. It was found that approx. 24 hours was needed to form a manageable film and that approx. 70 hours were needed to obtain stable rheological properties. The exposure times were larger than expected but it was assumed that this would be resolved by preparation of the inter-penetrating network materials. A number of inter-penetrating network materials where both the permanent Network as well as the switching segment was made up of PEG-polymers were prepared. It was found that for a material with relatively long chains in both permanent Network (Mn = 10000 g/mol) and switching segment (Mn = 15000 g/mol) no changes occurred upon exposure to UV-light. It is expected that this is because Mn of polymers is above the molecular entanglement weight. Inter-penetrating network materials with Mn = 4000 g/mol in the permanent network were prepared. Initially a linear photo-active PEG was mixed into the material. This material exhibited a decrease in the values for G and G after irradiation with UV-light for 30 minutes. The reason for the decrease in the two rheological parameters is unclear but the change encouraged further work with this type of systems. Two inter-penetrating network materials with the star-shaped cinnamic acid derivatised PEG as switching segment were prepared and irradiated with UV-light for 72 hours. The network with r = 0.75 in the permanent matrix proved the expectations by clearly showing a solvent effect when the photo-active polymer was introduced into the permanent network. In addition a significant increase of G and G was observed after 72 h of irradiation with UV-light proving the formation of a second network consisting of the photo-active polymers. A network with r = 0.5 in the permanent matrix was also investigated but gave very different results due to the lower value for r. The applied r-value is significantly closer to the critical rc-value and thus resulted in problems with the film formation. The data showed that the secondary network dominates the rheological properties of this network. A material with shorter chains in the permanent network (Mn = 1000 g/mol) was also investigated but showed no change after irradiation with UV-light for 15 minutes. This is related to the stiffness of permanent matrix. First steps to creating an inter-penetrating network with two different polymers were taken by incorporating the cinnamic acid derivatised PEG-stars into a poly(propylene oxide) network. However exposure to UV-light did not result in any changes of the material properties. It was also tested if the photo-active PEG could be incorporated into a poly(dimethyl siloxane) network, but the addition of the photo-active PEG resulted in complete hindrance of the cross-linking of the poly(dimethyl siloxane). A number of problems were identified throughout the work, primarily concerning the mismatch between the expected exposure time needed to induce changes in the materials and the exposure time observed experimentally. This can partially be explained by mobility of the polymers and concentration of the photo-active cinnamic acid. Studies presented in the literature show that the position of the cinnamic acid groups is very important for the dimerisation to occur. The nature of polymers makes encounters between end groups less likely and this affects the dimerisation. Furthermore, an NMR-study showed formation of the cis-isomer of cinnamic acid. The isomerisation of cinnamic acid only occurs if dimerisation is hindered. This underlines that the circumstances are not ideal for dimerisation.

**General information**

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