

ONE-COMPONENT INTRINSIC SELF-HEALING POLYMER FOR COATINGS BASED ON REVERSIBLE CROSSLINKING BY DIELS-ALDER-CYCLOADDITIONS

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ABSTRACT

Self-healing can be achieved in polymer coatings by the incorporation of extrinsic materials, i.e. a healing agent is embedded into the coating (e.g., within capsules). In contrast the polymeric coating itself can feature the ability for healing – for instance if reversible covalent bonds are introduced into the polymer network. The Diels-Alder reaction is one prominent example to obtain reversibility within self-healing/mendable materials.

In this context, a novel acrylic-based one-component polymer system has been synthesized, which contains both binding units for the Diels-Alder reaction (i.e. the maleimide and the furan moiety) as well as comonomers to tune the mechanical as well as thermal properties. The ATRP (atom transfer radical polymerization) of maleimide methacrylate (MIMA), furfuryl methacrylate (FMA) as well as of different alkylmethacrylates was utilized to synthesize well-defined functional terpolymers, which could be crosslinked subsequently via thermal treatment. The mechanical and thermal properties of these polymers have been investigated in detail. Moreover, the healing ability of these polymer coatings was studied. The influence of the crosslinking density, the kind of the comonomer and the healing temperature was investigated in detail. An efficient healing of these coatings could be observed. Additionally first attempts to tune the healing temperature of these coatings have been performed. The comonomers can also influence the required temperature for the retro-Diels-Alder reaction.

1. INTRODUCTION

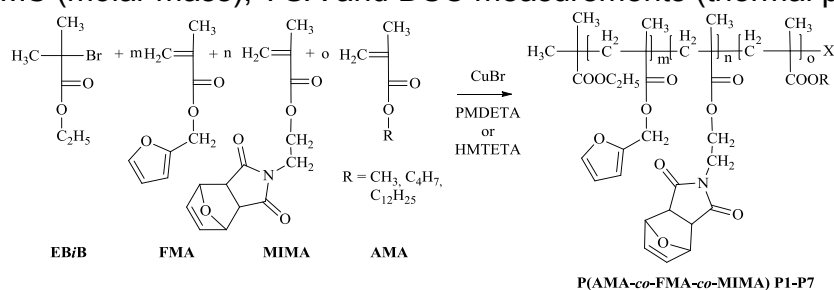
In recent years several approaches have been investigated in order to obtain self-healing polymer coatings.[1] These materials are of particular interest because coatings are particular prone to damage. Moreover polymer coatings fulfill different functionalities: the protection of the underlying material (e.g., polymeric coating on metals) as well as an aesthetic function. In contrast to embedded healing agents (i.e. capsule approach) intrinsic self-healing would allow a continuous healing.[1]

The utilization of reversible chemical bonds (non-covalent as well as covalent bonds) allows the design of intrinsic self-healing materials. One of the most prominent examples of self-healing polymers based on reversible covalent bonds is the Diels-Alder reaction. The cycloaddition has been successfully applied for bulk materials [2] as well as coatings [3].

Currently, all systems are based either on monofunctional polymers, which are crosslinked by low molar mass crosslinkers or on polymeric networks based on multifunctional monomers (*i.e.* polymerization by cycloaddition). Therefore, a multifunctional polymer bearing both functionalities – the furan as well as the maleimide – have been synthesized. The self-healing of these polymers was investigated.[4]

2. MATERIALS AND METHODS

A library of different terpolymers have been synthesized by the atom transfer radical polymerization (ATRP). [4] All polymers (see Scheme 1) contain the maleimide monomer (MIMA), furfuryl methacrylate (FMA) as well as different alkyl methacrylates (methylmethacrylate - **P1-P3**, butylmethacrylate - **P4-P6**, laurylmethacrylate - **P7**). The resulting copolymers were characterized by ¹H NMR spectroscopy (composition, ratio of both functional groups), SEC (molar mass as well as molar mass distribution), MALDI-TOF MS (molar mass), TGA and DSC measurements (thermal properties).



Scheme 1: Schematic representation of the copolymerization of alkyl methacrylates (AMA), FMA and MIMA by ATRP polymerization.

Films of these polymeric materials were obtained by thermal treatment of the soluble linear polymers. After cleavage of the furan protecting group of the MIMA a crosslinked polymer film was obtained. These films were insoluble in common organic solvents.

The self-healing of these coatings was investigated by scratch healing experiments. Self-healing on the nanoscopic level was investigated by AFM measurements (tapping mode with non-contact cantilevers; scratches were applied by dragging the AFM tip in the surface). Moreover, microscopic scratches were applied by a knife in a controlled manner. The healing of these scratches was investigated by SEM.

3. RESULTS

The controlled radical polymerization ATRP could be successfully applied for the synthesis of well-defined terpolymers with relatively narrow molar mass distributions. Polymers with molar masses between 5,000 and 15,000 g/mol could be obtained. The content of both functional groups was determined by NMR spectroscopy. **P1-P3** featured a content between 12 and 79%, **P4-P6** between 6 and 73%; **P7** 19%.

Subsequently, the thermal properties of the polymers were investigated. The TGA measurements (Figure 1, right) revealed on the one side the thermal stability of the polymers, on the other hand the mass loss around 130 °C corresponds to the furan from the protecting group. In addition DSC measurements were performed to investigate the thermal properties (Figure 1, left). **P7** showed an endothermic peak in

the 1st heating curve (120 °C), which corresponds to the retro-Diels-Alder reaction as well as the evaporation energy of the released furan. The glass transition temperatures (T_g) of the non-crosslinked copolymers could also be observed. In the 2nd heating curve the endothermic peak caused by the retro-Diels-Alder reaction could also be observed. However, the peak was much smaller, because no additional furan is released. Additionally not all functional groups combine upon cooling after the first cycle.

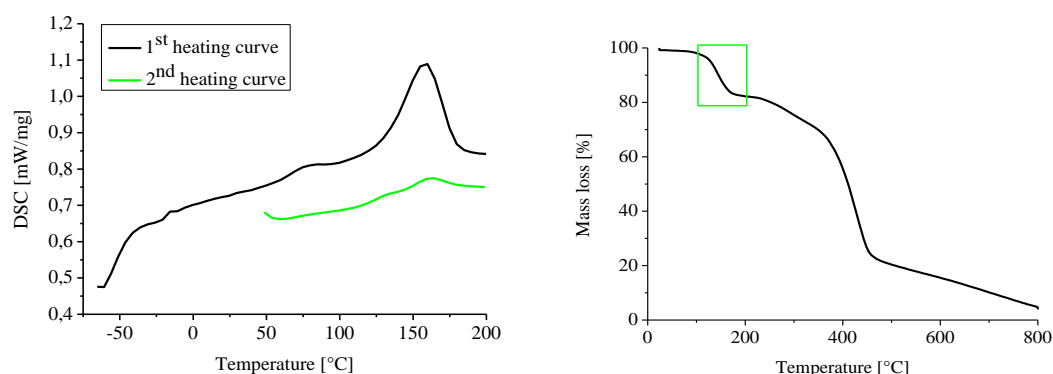


Figure 1: DSC analysis of copolymer **P7** (left); TGA of copolymer **P6** (right).

All polymers of the polymer library were investigated in scratch healing experiments. Coatings based on **P1-P3**, which contain methylmethacrylate as comonomer, could not be healed after being scratched. The mobility of the polymer chains is not sufficient due to the high glass transition temperature. In contrast, poly(butylmethacrylate) features a lower T_g . Therefore polymer coatings, based on butylmethacrylate as comonomer (**P4-P6**), could be healed, if the scratches were on the nanoscopic level.

A further lowering of the T_g could be obtained by the incorporation of laurylmethacrylate as comonomer (**P7**). The scratch healing of this material was investigated by SEM (Figure 2). The applied scratch was annealed at elevated temperature (160 °C). A beginning of the healing process could already be noticed after 1 min; the healing was complete after 3 min.

The usage of the unpolar lauryl methacrylate causes a slight increase in the retro-Diels-Alder temperature. However, the usage of more polar comonomers (e.g., OEGMA) did not lead to a significant decrease of the retro-Diels-Alder reaction.

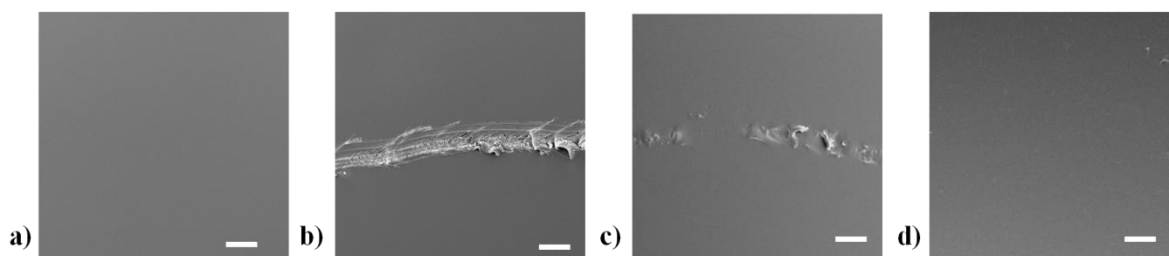


Figure 2: Investigation of the scratch healing of copolymer **P7**. a) Crosslinked film, b) scratch c) scratch after annealing at 160 °C for 1 min and d) scratch after annealing at 160 °C for 3 min (scale bars = 100 μ m).

4. CONCLUSIONS

A library of one-component intrinsic self-healing polymers was synthesized. These polymers are solution-processable and hard coatings can be formed by thermal treatment of preformed polymer films. The addition of low-molar mass crosslinkers is not required in contrast to many other examples described in the literature. Moreover, the thermal properties, and as a consequence, the mobility of the polymer chains within the network, can be tuned by the corresponding comonomer (alkylmethacrylates). The terpolymer based on lauryl methacrylate revealed the best self-healing properties. Scratches could be healed at elevated temperatures (160 °C) within a few minutes.

ACKNOWLEDGEMENTS

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