# Effect of the plasticizer on the self-healing properties of a polymer coating based on the thermoreversible Diels–Alder reaction

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## 1. Introduction

Smart polymers are materials able to respond to changes in external environments by developing readable signals and/or corrective actuation mechanisms; among them, self-healing polymers are gaining an increasing interest for their ability to heal cracks or mechanical damages thus extending their lifetime [1]. Different approaches have been followed to design and realize a self-healing mechanism: namely autonomous and heteronomous healing. The first approach is achieved introducing microcapsules [2–5], hollow fibres [6] or microvascular networks [7] inside the material, so that, in response to a mechanical damage, a healing agent can be released, and repairs the structure by spontaneous polymerization. With this approach the healing efficiency is granted only once, thus limiting their applications. Externally stimulated or heteronomous healing systems, on the contrary, exploit physical or chemical changes occurring in the material in response to stim-uli such as heat, light, electricity or magnetic field [8]. In Urban et al. works some examples of polymers self-repairing in response to UV-light radiation and magnetic field oscillation are reported [9–11]. The well-known Diels–Alder reaction, which is thermally reversible, can be used for designing thermosetting self-healing polymers [12–14]. In that case, multiple cycles of heating treatment for activating the healing reaction are possible. Frequently used Diels–Alder functional groups are furans and maleimides as dienes and dienophiles, respectively, allowing the material to heal in a narrow temperature range [15–22]. In Tian et al. work [23,24], a new molecule with both epoxide and furan groups was synthesized and crosslinked with maleimides, and the final material showed both mending ability and high mechanical strength. In these polymer networks at temperature above 120 °C the chemical linkages disconnect (through retro-DA reaction) and then reconnect upon cooling. It was also possible to graft furan and maleimide pendant groups to polymeric chains; crosslinking, via DA reaction, gave the polymer self-repairing properties. This approach has been followed for polyamides, polyketones and copolymers [25–28]. In another study, a reversible crosslinked healing gel totally based on DA bonds was synthesized in dimethylformamide (DMF) as sol-vent. Subsequently, it was included as a secondary phase within the structure of a conventional epoxyamine thermoset polymer [29]. Our study combines the idea of creating a network totally based on DA crosslinks with the use of thermosetting polymers for adhesives and coating application. Using an epoxy resins as precursors, a new thermosetting polymer network completely based on DA crosslinks has been realized. Benzyl alcohol was used as a plasticizer in order to improve the healing efficiency. During the curing process, DA adducts formation has been monitored by means of infrared spectroscopy. Thermal and mechanical characterization, together with optical microscopy observations and gloss measurements, demonstrated the ability to heal scratches and cracks several times

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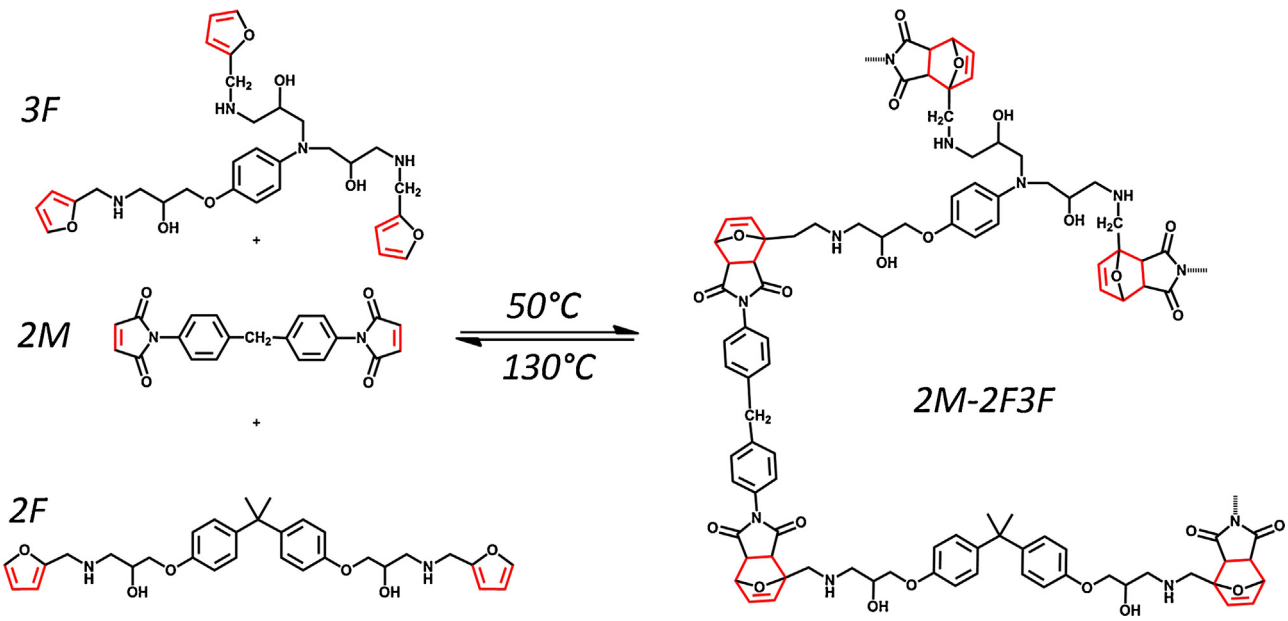


**Scheme 1.** DA and retro-DA reactions.

with controlled thermal treatments and quantified the healing efficiency.

## 2. Experimental

### 2.1. Materials and methods

Furfurylamine (FA), 1,1′-(methylenedi-4,1-phenylene) bismaleimide (2M), N,N-diglycidyl-4-glycidyloxyaniline (DGGO), bisphenol A diglycidyl ether (DGEBA), dichloromethane and methanol were all purchased by Sigma Aldrich and used as received. Fourier transform infrared spectra (FTIR) were acquired using a Thermo Nicolet Nexus FTIR spectrometer. Spectra were collected from 400 to 4000 $cm^{-1}$. Thermo gravimetric analyses (TGA) were performed on a TA Instrument Q500 in nitrogen and air at a heating rate of 3 °C/min. Differential scanning calorimetry (DSC) was carried out with a Mettler–Toledo TA3000 instrument, indium and *n*-hexane calibrated, heating from 20 °C to 140 °C with a rate of 10 °C/min in a $N_2$ environment. Dynamic mechanical analysis (DMA) was conducted on a Mettler Toledo DMA/SDTA861 instrument from 20 °C to 180 °C at a 3 °C/min heating rate. Tensile properties were tested at room temperature by a Zwick/Roell Z010 under a constant crosshead rate of 25 mm/min (5 specimens, 18 mm gauge length, 5 mm width, 3 mm thickness). Gloss measurements were made on 100 μm thick coatings deposited on a white cementitious substrate at a reflective angle of 60°.

### 2.2. Synthesis of 3F and 2F compounds

First, 12 g of viscous resin DGGO were mixed with 12.6 g of liquid FA (in the stoichiometric ratio 1:3 molar) under stirring and left to react in methanol at 85 °C for 3 h. At the end of the reaction, the product (trifuran, 3F) was obtained by drying the sample under vacuum until constant weigh was reached. Similarly, 10 g of DGEBA were mixed and heated with 5.7 g of furfurylamine (in the stoichiometric ratio 1:2 molar) leading to the formation of bifuran, 2F following the same procedure. Yields were >95% in both cases. Chemical characterization of furan adducts was performed with FTIR spectroscopy, monitoring the progressive disappearance of peak of oxirane ring at 910 $cm^{-1}$.

### 2.3. Synthesis of 2M-3F2F polymer

The Diels–Alder based polymer was prepared by reacting a mixture of the two furan adducts (3F:2F = 1:1 molar ratio, 3F + 2F = 0.0106 mol), pre-heated at 70 °C for lowering their viscos-ity, with the bismaleimide powder (2M, 0.0132 mol) dissolved in dichloromethane. The reaction mixture was heated on a hot-plate at 50 °C with a magnetic stirrer until most of the solvent was evaporated. The resultant highly viscous liquid was poured in a mould and cured at 80 °C for 10 h in vacuum to remove the residual solvent. A highly crosslinked network (2M-2F3F) based on DA bonds was achieved as shown in Scheme 1.

An identical procedure was followed for plasticized formulations. Benzyl alcohol (10%, w/w) was added into the solution at the beginning of the crosslinking reaction leading to formation of 2M-3F2F/BA polymer.

## 3. Results and discussion

### 3.1. Synthesis and characterization of 2M-3F2F polymer

The monitoring of the 2M-2F3F polymer synthesis and its curing process was carried out by means of FTIR analysis. There are three significant peaks that have been considered: one at 700 cm $^{-1}$, rep-resenting the C H bonds attached to the C C in the maleimide ring, which is involved in the DA reaction, the peak at 1774 $cm^{-1}$ typ-ical of the DA adducts of maleimides and the maleimide carbonyl peak at 1712 $cm^{-1}$ (invariant during the reaction). The first two peaks give a measure of the DA adducts formation from maleimide pendant groups; the third has been taken as a reference. In Fig. 1, FTIR spectra of 2M, 2M-2F3F uncured and 2M-2F3F after curing at 80 °C are presented. The presence of the peak at 1774 $cm^{-1}$ in the 2M-2F3F polymer reveals the DA adducts generation within their structure after the reaction. As expected the intensity of the peak at 700 $cm^{-1}$ is high in the 2M compound but its signal is reduced in the 2M-2F3F polymers; moreover after the curing process, the peak is even less intense but does not disappear.

Although the network is totally composed by DA bonds, not all pendant groups can react generating DA crosslinks. DA adducts conversion in the 2M-2F3F has been estimated by a spectroscopic quantitative analysis of absorbance spectra, comparing the

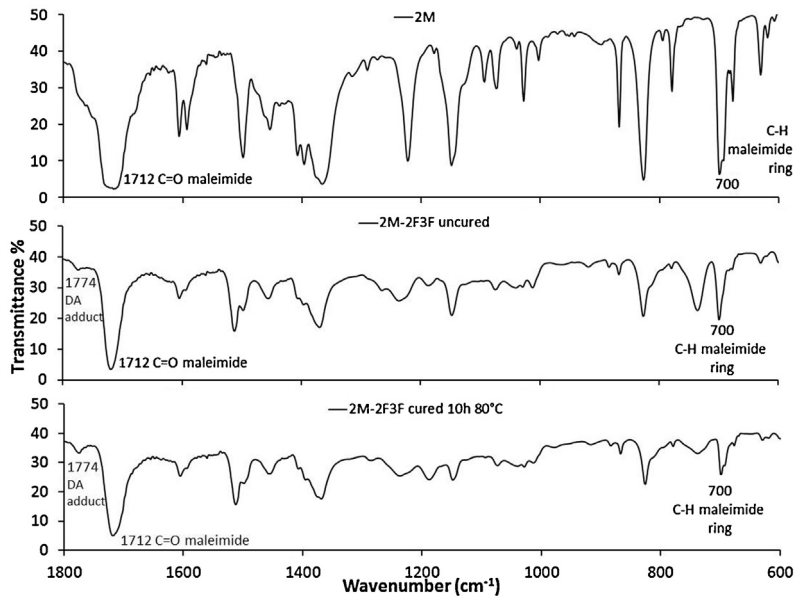


**Fig. 1.** FTIR spectra of 2M, 2M-2F3F not cured and 2M-2F3F cured for 10 h at 80 °C.

maleimide peak intensity at 700 $cm^{-1}$ ($I_m$) to the carbonyl peak intensity at 1712 $cm^{-1}$ ($I_c$) at different curing times.

In particular, the fraction of unreacted maleimide groups can be calculated using the following equation:

$$\%DA = \left(1 - \frac{I_m^x / I_c^x}{I_m^{ref} / I_c^{ref}}\right) \times 100$$

in which $I_m^x$ and $I_c^x$ are the maleimide peak intensity and the carbonyl peak intensity of the 2M-2F3F polymer after $x$ hours of curing time, whilst $I_m^{ref}$ and $I_c^{ref}$ refer to the intensity of the 2M. The percentage of DA conversion has been calculated at different curing time. Results are shown in Fig. 2. It seems that after 10 h of curing at 80 °C about 60% of the maleimide groups has reacted.

The trend shown in Fig. 2, suggests that extending the curing time does not lead to a further progression of the reaction. This is due to the fact that the crosslinking process proceeds until the $T_g$ of the material meets the cure temperature and vitrification occurs (see also Fig. 3). Being the polymer network thermoreversible at temperature exceeding 100 °C, it is not possible to further increase the process temperature because such a treatment would result into a partial debonding of DA adducts just formed. This could be therefore an intrinsic limitation of the particular formulation developed in this present work. DSC and DMA analyses help to better interpret the thermal behaviour of the 2M-2F3F polymer. Fig. 3 shows the heating DSC curve of the cured 2M-2F3F polymer. The curve has a first transition, corresponding to the $T_g$, at about 80 °C

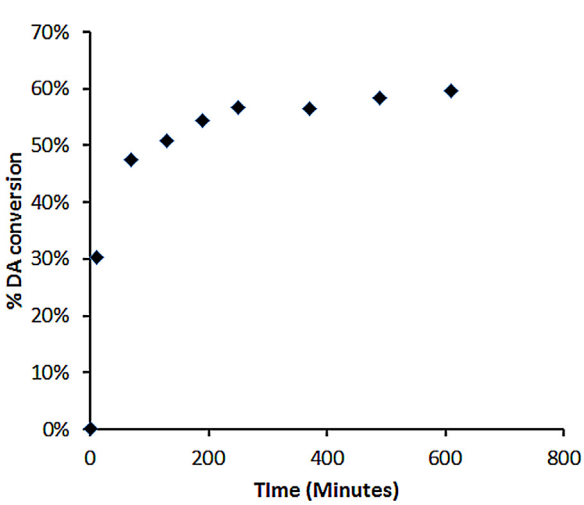


**Fig. 2.** isothermal (80 °C) conversion curve of the DA polymer.

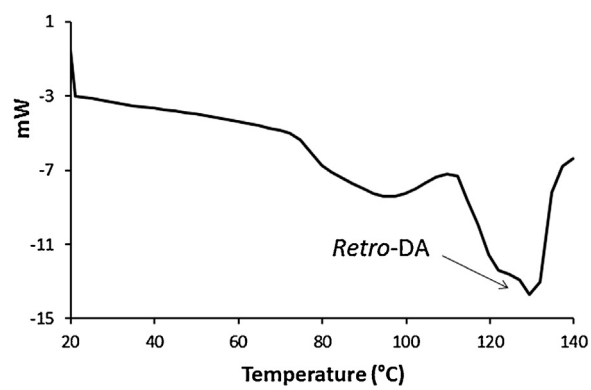


**Fig. 3.** DSC scan of 2M-2F3F polymer. Heating rate at 10 °C/min.

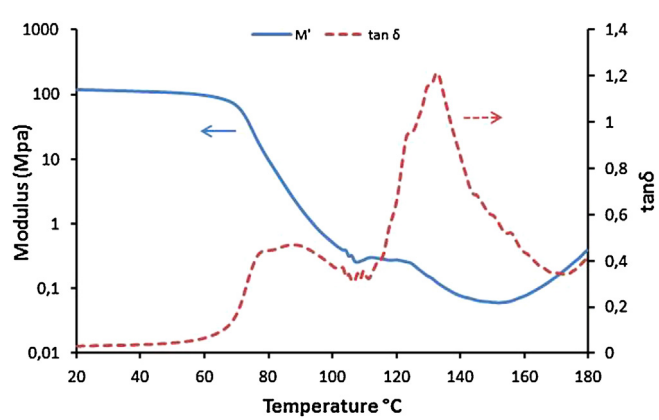


**Fig. 4.** DMA curves of 2M-2F3F polymer. Heating rate at 3 °C/min.

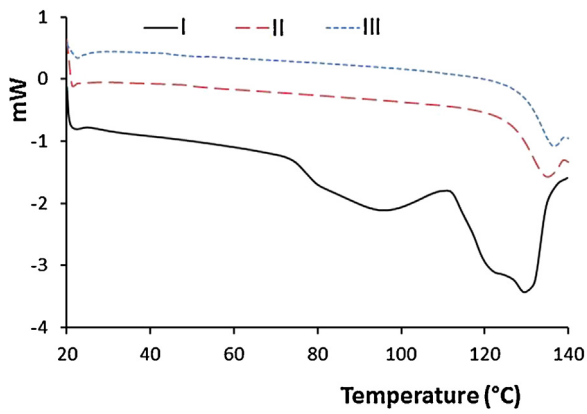


**Fig. 5.** DSC curves of 2M-2F3F polymer. Three heating cycle on the same sample at 10 °C/min.

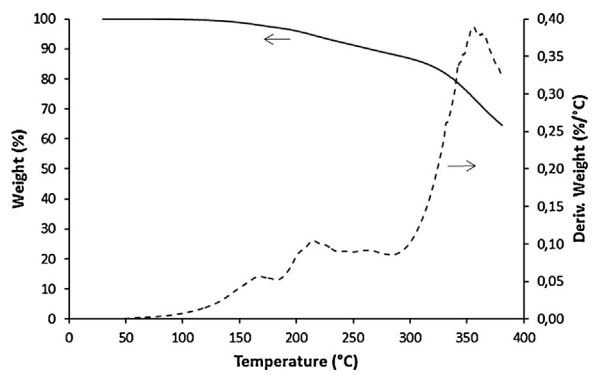


**Fig. 6.** TGA curve of 2M-2F3F/BA polymer.

and an evident endothermic peak at 130 °C, the latter indicating the retro-Diels–Alder reaction occurring in the polymer.

Such behaviour is confirmed by also the DMA analysis in which the tan $\delta$ curve also shows a peak around +130 °C and a glass transition at +80 °C (Fig. 4).

DSC was also used to study the effects of multiple heating cycles on the sampled polymer. Fig. 5 shows three subsequent DSC scans performed at a rate of 10 °C/min on the same sample, letting it cooling down after every cycle at ambient temperature. A large endothermic peak is evident at about 130 °C in the first heating curve; in following heating cycles the peaks, despite being slightly pushed towards higher temperatures, still confirm the presence of retro-DA reaction.

The repeatability of the process of disconnection and reconnection of DA bonds has interesting implication as it is possible to perform multiple healing cycles on a same damaged spot.

In spite of the evidences of thermal analysis, the 2M-3F2F neat polymer was very brittle and showed visually a quite poor efficiency in the healing process of scratches and cracks induced on the surface. Brittleness and unsatisfactory healing performances are likely due to the low conversion and early vitrification. Introduction of a plasticizer may increase the free volume and molecular mobility of the polymer network, allowing to obtain a higher con-version of the crosslinking process. Benzyl alcohol has been chosen as a plasticizer for its good compatibility, low toxicity and relatively low volatility. FTIR analyses demonstrated that DA and retro-DA reactions are not affected by the presence of the plasticizer, while a TGA was needed to assess the suitability of BA with the thermal cycles used for the thermally induced self-healing experiments.

As shown in Fig. 6, the 2M-3F2F/BA plasticized polymer shows a good thermal stability in the whole temperature range needed to activate DA and retro-DA reactions. At 140 °C it only has <1% of weight loss. A significant weight loss which can be attributed to

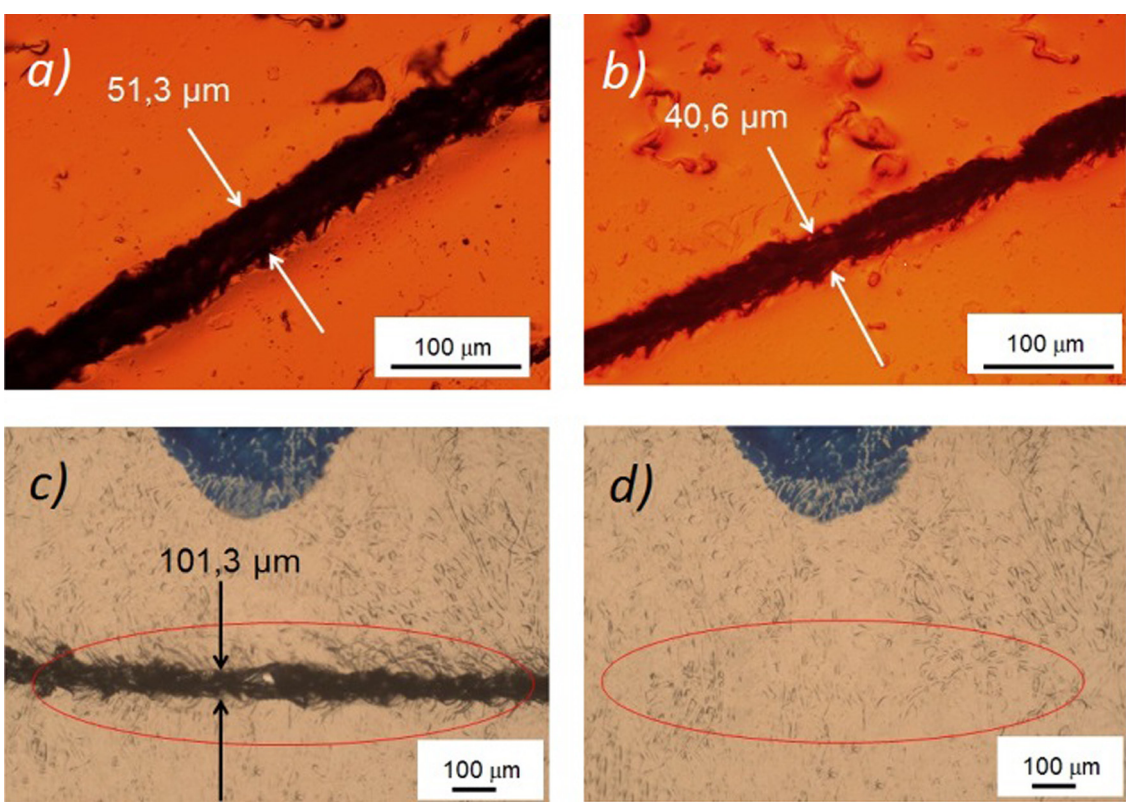


**Fig. 7.** Optical microscope images of (a) 2M-2F3F polymer scratched, (b) 2M-2F3F polymer after 10 min heating treatment at 120 °C, (c) 2M-2F3F/BA polymer scratched, (d) 2M-2F3F/BA polymer after 10 min heating treatment at 120 °C.

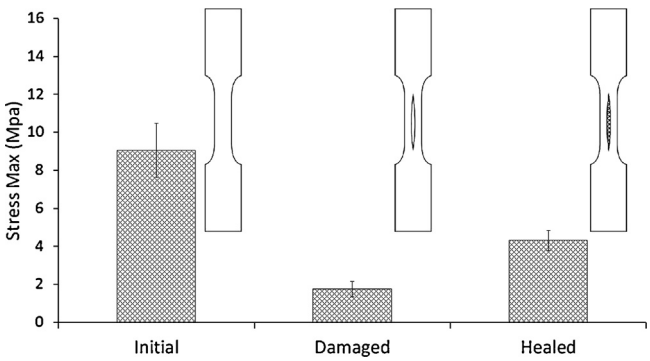


**Fig. 8.** Mechanical strength for virgin, mechanically damaged, and thermally healed DA polymers.

BA evaporation starts above 200 °C. The DA polymer network plasticized with 10% of benzyl alcohol showed macroscopically much better mechanical and self-healing properties, which are described in detail the Section 3.2.

### 3.2. Healing properties

The self-healing properties of the neat and plasticized DA polymers were first investigated through optical microscopy. The resulting images are shown in Fig. 7. A razor blade was used to make a scratch on the sample surface. The sample was then heated at 120 °C for 10 min. Fig. 7a and b shows the effect of the heating treatment on the 2M-3F2F neat polymer. The average width of the crack, being 51.3 μm before heating, became 40.6 μm, thus resulting in a minimal healing of the scratch. The low mobility of the high $T_g$ chains does not allow the material to totally recover the damage. Fig. 7c and d shows the same experiment repeated for the 2M-3F2F/BA formulation. The same heating cycles allows for the total recovery of a 100 μm scratch. The same location on the surface has been scratched and re-healed two more times with the same effectiveness demonstrating that multiple healing cycles are feasible.

A more quantitative assessment of the healing performances was done through tensile tests carried out on virgin, mechanically damaged, and thermally healed samples. The results concern-ing maximum stress values are shown in Fig. 8. The mechanical strength of the 2M-3F2F/BA polymer is about 9 MPa. After causing a 15 mm lengthwise damage on the sample (images of a virgin, an artificially damaged and a healed sample are shown in the inset), the stress values drop significantly to less than 2 MPa. After the 120 °C/10 min healing cycle, the mechanical properties are partially restored leading to a maximum stress of 4.3 MPa. The significant 48% recovery in maximum stress reached by the 2M-3F2F/BA poly-mer indicates an efficient thermoreversibility of the DA network. In previous reports, the healing efficiency of DA based formulation has been investigated through different mechanical tests. In compact tension experiments the healing efficiency as a percentage of the load recovered stays within a 37–80% range [29,30]. On dumbbell-shaped samples a 55% tensile strength recovery has been reported [31], thus confirming the results of our formulation.

The healing behaviour of the 2M-3F2F/BA polymer was also assessed in term of gloss recovery after a mar test. The optical mea-surements were firstly taken on a virgin sample, then the surface was marred with a steel scrub to obtain a matt finish, and finally the gloss measurements were repeated after the thermal healing cycle. Results are shown in Fig. 9.

The virgin DA coating surface is very bright resulting in an average gloss value of 93.5 GU; the same surface, once marred, becomes opaque thus inducing a significant drop of the gloss values down

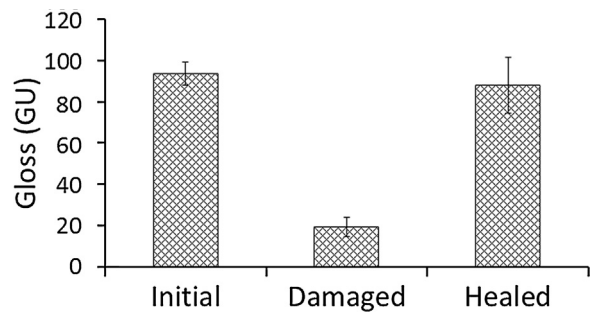


**Fig. 9.** Gloss values for virgin, marred and thermally healed DA polymers.

to 19.4 GU. The healing treatment allows the material to almost completely recover its original gloss (88.0 GU), corresponding to an aesthetic healing efficiency of about 95%. The procedure was repeated three times always observing an excellent gloss recovery.

## 4. Conclusive remarks

A new crosslinked polymer based on thermoreversible Diels–Alder reaction was presented. Thermoreversibility was proved by FTIR spectroscopy, DSC and DMA. It was however observed that thermoreversibility alone is not enough to provide an efficient thermally stimulated healing behaviour. The smart behaviour of the polymer was significantly improved by the addition of low amounts (10% w/w) of a proper plasticizer, benzyl alcohol in the specific instance, which is thermally stable in the temperature range needed to activate the retro Diels–Alder reaction. The plasticized formulation showed an excellent recovery of aesthetic appearance of the scratched surface. The use of benzyl alcohol as a plasticizer is intrinsically a limitation, however a good thermal stability and no exudation in practical use conditions were verified. The thermally stimulated healing behaviour was positively demonstrated more times in the same place. An evaluation of the healing efficiency was done through proper mechanical and gloss tests, showing an efficiency of around 48% and 95% respectively. Diels–Alder polymers are promising candidates for the development of heteronomous self-healing coatings with multiple healing efficiency, and excellent aesthetic recovery of the surface appearance.

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