UV-CURABLE EPOXY PRIMER FOR ADHESION BETWEEN METALLIC OXIDES AND THERMOPLASTIC POLYURETHANE

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Abstract
We report results on the development of an innovative fast-curing coupling method using a UV-curable epoxy primer based on a cycloaliphatic di-epoxide resin. The materials to bond are metallic wires and a thermoplastic polyurethane matrix. The curing kinetics of the primer and its mechanical properties were analysed by photo-DSC and photo-rheology to optimize the formulation. Adhesion and durability were then tested by pull-out tests before and after hydrothermal aging for several formulations and processing parameters. The proposed UV-curable primer outperformed a conventional surface treatment and a thermally cured silane primer used for comparison in terms of processing time, adhesion and durability.

1 Introduction

In many industrial cases of continuous composite production with metallic wires, the short processing times preclude from using on-line traditional silane primers implying a sol-gel condensation [1] at the composite interfaces as they show rather slow and temperature dependant kinetics. It is however crucial to achieve an optimal adhesion and durability of the interfaces, to ensure a reliable transmission of the mechanical load. An online application could propose improvements compared to an antecedent surface preparation, by protecting the reinforcement surface from dust and grease contamination, or preventing a premature reaction of functional groups during storage, while potentially keeping costs to a minimum. Surface contamination during storage is currently partly resolved by surface activation prior to bonding with heat or solvents, but these are energy consuming and pollutant. A primer that can be deposited and cured on-line, at high processing speed would thus propose an ideal solution.

A main issue to implement primer systems on high-speed processing lines is to reduce the curing time to a minimum (dictated by the desired line speed and length), and an original route to achieve this goal is the use of UV illumination with appropriate photo-curable monomers that initiate cure within a few seconds. In such systems, light intensity rather than thermal energy is used to dissociate active species [2, 3]. In combination with an epoxysilane for adhesion promotion, this system could offer the required level of mechanical performance and robustness (no oxygen inhibition), allowing the formation of chemical bonds between the functional groups of the monomers and both the substrate and the subsequent coating. For instance, a compatibility study of common mono-functional groups with thermoplastic polyurethane at 200 °C [4] demonstrated the reactivity of both epoxide and hydroxyl

functional groups with urethanes. In addition, the coating mechanical properties could be tailored with the adjunction of hydroxyl functional monomers, polyols or hyperbranched polymers (HBP) [5-7].

In previous work, the cationic photo-polymerization of a cycloaliphatic epoxy resin was studied in function of the UV intensity, temperature and time, including dark curing and post-curing effects, to show that it is possible to achieve a high degree of cure with a short UV exposure followed by dark-curing or post-cure. In parallel, the adhesion of thermoplastic polyurethane elastomer to galvanized steel has been characterized for benchmark surface treatments such as surface degreasing and silane primers, and the method to analyse pull-out test results has been established for this material combination[2, 8]. The present research aims to propose a novel class of fast-curing adhesion promotion systems between inorganic substrates and some thermoplastic polymers, using an UV-curable epoxy resin formulation with functional additives to tailor its curing, mechanical, adhesion and durability properties.

2 Experimental

2.1 Primer materials

The base monomer was cycloaliphatic epoxide resin (ECC) for cationic UV curing (Genomer 7210 from Rahn, Switzerland). This monomer is the most used and widely available UV-curable epoxide resin and offers a good balance of toughness and hardness once cured [9]. The photo-polymerizable cationic reactive diluent was trimethylolpropane oxetane (TMPO from Perstorp Specialty Chemicals, Sweden). The photo-polymerizable cationic silane was Beta-(3,4-epoxycyclohexyl)ethyl-tri-methoxysilane (Silquest A-186 from Momentive Performance Materials, Switzerland). This silane was meant to act as an adhesion promoter for the epoxide resin. The polyol (Polyol 3380 from Perstorp Specialty Chemicals, Sweden) and the hydroxyl terminated hyper-branched polymers (HBP) (Boltorn H2004 from Perstorp Specialty Chemicals, Sweden) were meant to serve as chain transfer agents to increase the cross-linking, the flexibility and the chemical resistance of the photo-polymerizable primer. The photo-initiator was an iodonium salt (Irgacure 250 from Ciba, Switzerland) that was photosensitized using an isopropyl thioxanthone (ITX) photosensitizer (Genocure ITX from Rahn, Switzerland).

2.2 Primer formulation

For the preliminary determination of curing and mechanical properties, the concentrations of TMPO, HBP, and A-186 additives were each varied independently at 0, 5, 10 and 20 wt%. All formulations contained 2 wt% of the iodonium salt photo-initiator and 0.5 wt% of the ITX photosensitizer, balance to 100% with the ECC monomer.

The formulations of the primers for the adhesion study were then optimized on the basis of the results from this preliminary study. The HBP was therefore replaced by the tri-functional polyol, which is less branched and viscous (as HBP had a negative impact on photo-polymerization speed). According to the results from the preliminary study, TMPO concentrations were varied at 0, 5, 10 and 15 wt% with a fixed amount of 5 wt% Polyol. Likewise, polyol concentrations were varied at 0, 5, 10 and 15 wt% with a fixed amount of 10 wt% TMPO. These values led to the highest mechanical properties. The silane A-186 was then added to the best resulting adhesion formulation (15 wt% polyol with 10 wt% TMPO) at concentrations of 1, 5, 15, 35 wt%.

All formulations were prepared by dissolution of the photo-initiator and photosensitizer in the monomer with additives upon agitation at 80 °C for 1 min and showed good homogeneity.

2.3 Materials for the adhesion study

The polymer matrix was a thermoplastic poly(ether)urethane (TPU) elastomer Elastollan supplied by BASF. The TPU pellets were stored in a desiccated place and then dried in low vacuum at 80 °C for 1 h prior to processing. The wires used to study the adhesion of the TPU

towards galvanized steel in pull-out tests were high strength electrogalvanized steel 1.0617 (C72D) after DIN EN 10016 from NV Bekaert SA, Belgium. They present a slightly rough surface morphology. The diameters were 175, 190 and 210 μm. The main properties of these materials are given in Table 1.

	Elasticity Modulus E [MPa]	Tensile strength [MPa]	Tg [°C]	Poisson's ratio	Density [g/cm^3]
TPU	51.7	36	-30	0.47	1.15
Steel C72D	210'000	2'750	-	0.31	7.85

Table 1. Datasheet of the high carbon spring wire 1.0617 (C72D) after DIN EN 10016 (music wire ASTM A228) and of the TPU from BASF (data from BASF).

In addition, two other thermoplastics and stainless steel wires were used in single wire pull-out tests for comparison: a polyamide 12 (PA12) Grilamid L16 from EMS-Grivory (Switzerland), a high density polyethylene (PE) 25055E from Dow (USA), and Bekinox stainless steel wires with a diameter of 130 μm from NV Bekaert SA, Belgium.

2.4 Methods

The heat of the photo-polymerization reaction was measured isothermally by means of photo-differential scanning calorimetry (p-DSC, Q100, TA Instruments, USA) connected through two optical fibres guides (as for the sample and the reference) to a 200 W, high pressure Hg lamp (OmniCure S2000, Exfo-Omnicure, Canada) according a previously described procedure [2]. Experiments were conducted under a UV irradiation exposure of 17 mW/cm^2 at 30°C.

The rheological behaviour of the resin during photo-polymerization was measured using a rheometer AR2000ex with UV-curing accessory (TA Instruments, USA) with a parallel plate setup according a previously described procedure [2]. The UV irradiation started during the test after 10 s with an intensity of 500 mW/cm^2 at ambient temperature.

The bulk mechanical properties of the UV-cured resin before and after post-curing at 200 °C for 2 h were studied with a dynamic mechanical analyser (DMA Q800, TA Instruments, USA) according a previously described procedure [2]. The samples for DMA measurements were 60×12.4×3.2 mm^3 rectangular beams cured 15 min at 12.5 mW/cm^2 on each face using a high pressure Hg lamp (PC-2000, Dymax, USA).

Steel-TPU single filament pull-out tests were performed to evaluate the interfacial shear strength of galvanized steel wire-reinforced thermoplastics according a previously described procedure [8]. The stress at failure was calculated from the maximal force using a stress transfer model of the pull-out sample to calculate the intrinsic interfacial shear strength τ_0 [10], using the shear-lag parameter defined by Nairn [11]. This analysis assumed an elastic material behaviour and did not account for large strains, but it was shown to offer an accurate estimation of τ_0 for the present system [8]. The following galvanized steel surface treatments and/or primers were applied onto the steel surfaces just before co-moulding with TPU: (i) a corona discharge treatment at 240V 50-60Hz 0.18A applied by a high frequency generator BD-20V (Electro- Technic Products, USA); (ii) an optimized [8] aminosilane solution in ethanol with 1wt% γ-aminopropyltriethoxysilane (γ-APS) (Momentive, USA) adjusted to pH5 with H_3PO_4 and allowed to hydrolyse 1 h at 22°C before use. In that case, the steel wires were dipped in the solution 5 minutes in an ultrasonic bath before drying 1 h at 93°C for condensation; (iii) the UV-cured primer formulations described in section 2.2, photo-polymerized 2.5 min at 12.5 mW/cm^2 successively on the two sides of the steel wires placed horizontally using a high pressure Hg lamp (PC-2000, Dymax, USA).

3 Results and discussion

3.1 Photo-polymerization

In order to study the effects of photo-reactive diluent (TMPO), silane (A-186) or HBP on the photo-polymerization, the induction and α'_{max} time values, the maximum conversion rate α'_{max} value and the final normalized epoxy/oxetane conversion values α after 10 min were determined by p-DSC and the vitrification and gelation time values by photo-rheology, in function of the additives concentration, as shown in figure 1.
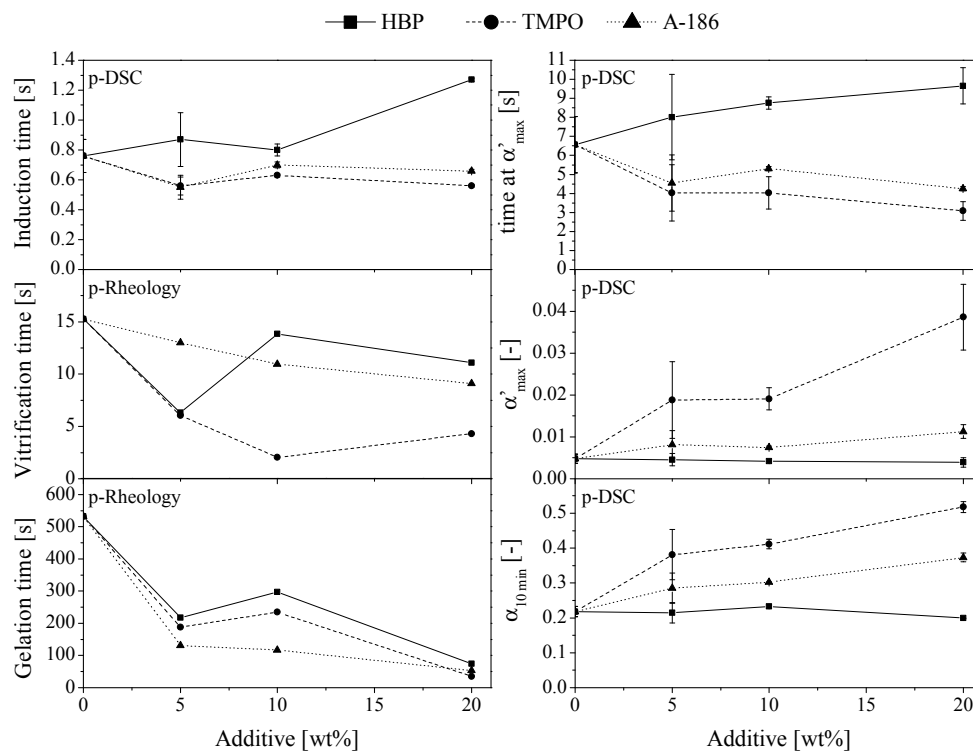
Figure 1. Results of photo-DSC and photo-rheology. Induction, α'_{max}, vitrification and gelation time values, maximum conversion rate α'_{max} value and final normalized conversion values α after 10 min in function of the additives concentration (HBP, TMPO or A-186) for the UV-curable epoxy primer.

The induction time and time at α'_{max} increased with HBP content, while the epoxy conversion rate peak α'_{max} and the final conversion remained quite constant. TMPO and epoxysilane had little effect on the induction time and even allowed accelerating the reaction by decreasing the time at α'_{max}. Most of these effects find an explanation in the different monomer molecular weights and viscosities impacting the cationic photo-initiators and photo-sensitizers mobility during induction and then the reactants' mobility during the auto-acceleration phase of the polymerization. In the case of TMPO, this is associated to the smaller polymerization enthalpy of oxetane (443.1 J/g) in comparison to epoxy (689.8 J/g), which was reflected by an increase of the epoxy conversion rate peak α'_{max}. TMPO also had the largest effect on the final conversion and appeared to be an efficient conversion enhancer for a given duration. Only 5 wt% of TMPO almost doubled the conversion. The epoxysilane also increased conversion but this was less pronounced than with TMPO. Both of these molecules are single functional epoxy or oxetane, allowing termination without generating unreacted sites.

Photo-rheology results were used to monitor the gelation (defined as the crossover of $G'=G''$ or identically to tanδ=1), and the onset of vitrification corresponding to the increase of storage shear modulus. This early vitrification corresponded to a freeze in a diffusion controlled state with low mechanical properties, the mechanical vitrification being then concomitant with the

onset of gelation when *G'=G'' [2]*. HBP, TMPO and A-186 additives all reduced the time to vitrification and gelation, which can be related to the preceding p-DSC observations with the HBP polyol molecule providing a higher reactive site density for percolation, while smaller and less viscous additive molecules (TMPO and A-186) increased the conversion rate. Most additive concentrations reduced the gelation time by a factor of two or more. The optimum additive concentrations to reach the fastest vitrification were 5 wt% for the HBP polyol with the vitrification time going from 15 s to 6 s, or 10 wt% for the TMPO with the vitrification time going from 15 s to 2 s, the TMPO again showing the largest effect.

3.2 Mechanical properties

The thermo-mechanical behaviour of the UV-cured resins is presented in figure 2 for dynamic storage and loss modulus. The storage and loss modulus of the pure resin from isothermal DMA tests at 25°C was determined to be 1530 ±180 MPa and 220 ±70 MPa respectively before post-curing, and 1920 ±120 MPa and 50 ±10 MPa respectively after post-curing 2 h at 200°C (for samples initially cured 15 min at 12.5 mW/cm^2 on each face). The T_g of the pure resin was determined at the peak of tanδ form temperature ramp DMA tests to 99 ±2 °C before post-curing and 128 ±17 °C after post-curing.
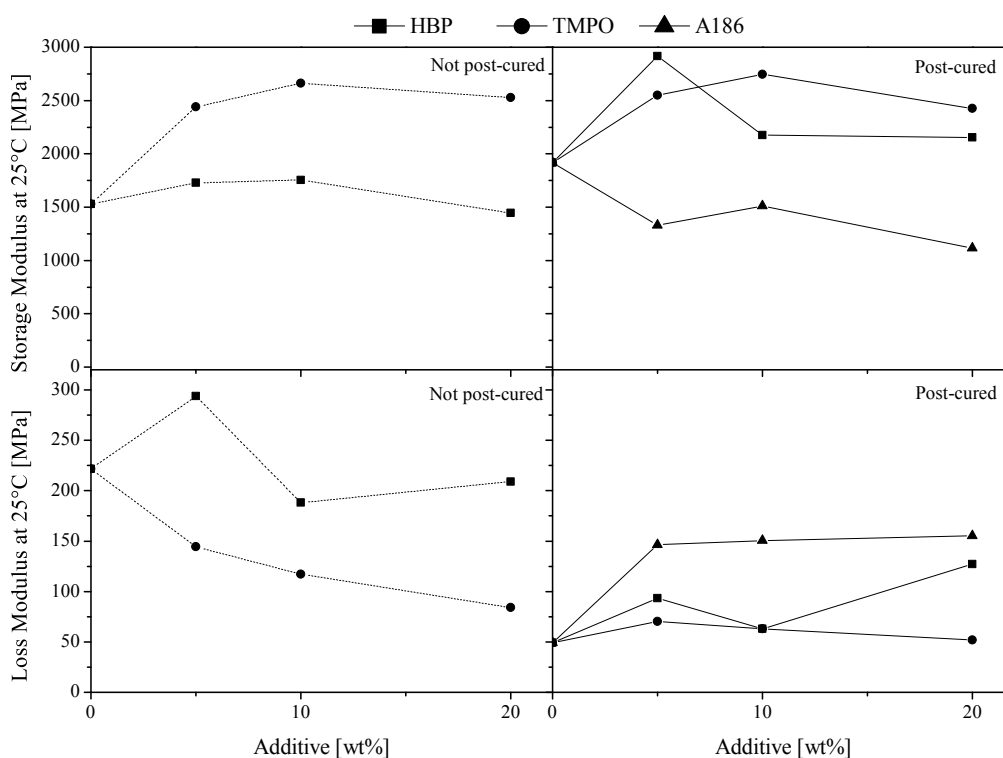
Figure 2. Dynamic storage and loss modulus by DMA of the bulk UV-cured epoxy in function of the additives concentration (HBP, TMPO, or A-186), before and after post-curing 2h at 200°C.

The effects of additives and post-curing on mechanical properties reflected well the observations from the photo-polymerization study: conversion increase was correlated to an increase of storage modulus. The storage modulus of samples containing HBP was therefore slightly impacted with the exception of a maximum near 3 GPa around 5 wt% after post-curing, with the loss modulus remaining quite unaffected. The addition of TMPO resulted in a notable increase of storage modulus with a maximum of 2.5 GPa around 10 wt% that remained constant after post-curing. This indicates that the elevation of temperature above T_g during post-curing at 200°C did not allow the polymerization reaction to continue much further, which could be attributed to the abundance of hydroxyl termination brought by the

mono-functional additive. The addition of TMPO also resulted in a notable decrease of loss modulus tending to the value of post-cured samples.

Samples containing the epoxysilane A-186 were too fragile to be measured in bulk by DMA without the sol-gel condensation allowed by the post-curing. The epoxysilane then led to a significant decrease of storage modulus and increase of loss modulus indicating that this mono-functional epoxy decreased the overall cross-linking density without creating a sufficient amount of reciprocal sol-gel linkages.

3.3 Adhesion

The results of the maximum interfacial shear strength τ_0 for the different cationic UV-cured primer formulations before and after aging treatments are presented in figure 3.
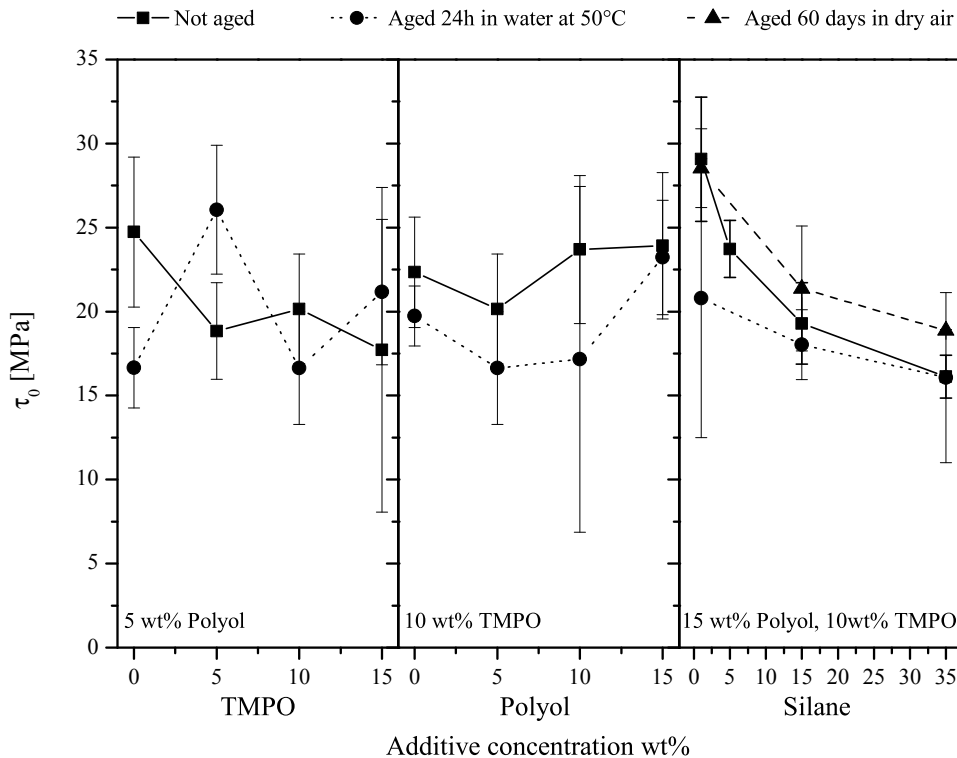
Figure 3. TMPO, UV curable silane and polyol effects on the maximum interfacial shear strength before and after aging.

The addition of TMPO had no significant effect on adhesion but it was chosen to keep it at a value of 10 wt% to benefit from the increased curing kinetics that it provided. At this TMPO concentration, the polyol improved adhesion, especially at 15 wt%, which was selected to further optimize the formulation. This effect could be explained by the chain transfer cross-linking and flexibility offered by polyols, increasing the toughness [7]. The best UV-cured primer formulation resulted in a tremendous adhesion and durability, with τ_0 close to 30 MPa. The most notable formulation characteristic of this optimized primer is the presence of a low level of inorganic content with only 1 wt% of epoxysilane. Other UV-cured primer formulations kept adhesion values comparable to other silane treatments (in the range of 15 MPa to 25 MPa) and still superior to other surface treatments [8]. Hydrothermal aging treatments slightly decreased the adhesion by a few MPa comparably to what was observed with the best aminosilane, demonstrating the high durability of the UV-cured primer in environmental conditions. An increasing adjunction of photo-reactive epoxysilane decreased τ_0 in a non-linear manner. At the highest silane concentration (35wt%), the τ_0 loss reached 45%. This loss of adhesion may be due to several factors. First of all, it was previously shown

in section 3.2 that increasing the amount of inorganic phase reduced the mechanical properties of the coating. On the other hand, alcohol by-products of the sol-gel reaction may also stay in the cured polymer network and reduce its mechanical properties [12, 13]. The increase of adhesion after dry aging observed for formulations with high inorganic phase contents can thus be explained by an increased sol-gel condensation with aging time and by the evaporation of the alcohol sol-gel reaction by-products plasticizing the primer. As a result, a small amount of silane (~1 wt%) seems to improve adhesion by allowing the creation of covalent bonds with the substrate while high amounts of silane lead to a drastic decrease of mechanical properties detrimental to adhesion. This led to the choice of the formulation containing 15 wt% polyols, 10 wt% TMPO and 1 wt% silane as an optimized UV-curable primer formulation. Adhesion results for this optimized UV-curable primer formulation are presented together with the results for the corona discharge surface treatment and an optimized aminosilane primer [8]. The results of τ_0 before and after dry aging at 22°C in a desiccator or hydrothermal aging in deionized water at 50°C for 24h are presented in figure 4.
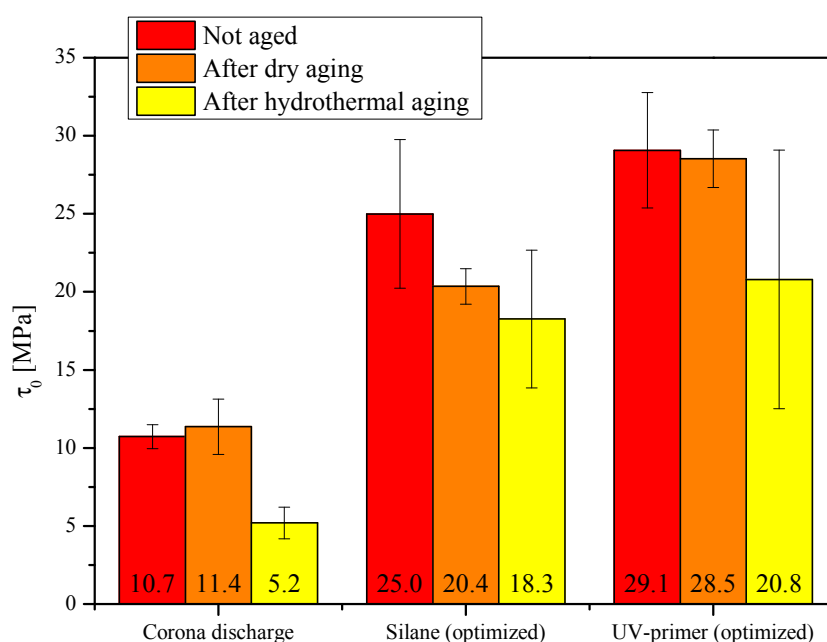
Figure 4. Maximum interfacial shear strength values with the optimized UV-cured epoxy primer before and after aging 60 days in a desiccator at 22°C and after a hydrothermal aging in deionized water at 50°C for 24h. For comparison, values for the corona discharge treatment and the optimized silane treatment are also shown.

The optimized cationic UV-curable primer resulted in overall excellent adhesion and durability with no significant loss after dry aging. After the much more aggressive hydrothermal aging, results demonstrated the durability of adhesion with the cationic UV-curable primer: hydrothermally aged samples with the optimized UV-curable primer had values close to that of the optimized silane after dry aging. For comparison, τ_0 of the non-optimized cationic UV-curable primers after hydrothermal aging was still two to three times higher than with the corona discharge surface treatment.

Alterative measurements with stainless steel wires instead of galvanized steel wires showed similar results with significant improvements of adhesion provided by the UV-cured primer. In addition, single wire pull-out tests results with different thermoplastic matrices (PA12 and PE) and the corona discharge treatment or the UV-cured epoxy primer without additives (not optimized) showed that the primer also significantly improved the adhesion with PA12, which had polar groups in its polymer chains like TPU, but not with PE that had inert polyolefin polymer chains.

4 Conclusion

The cationic UV-curable epoxy primer formulated in the present work outperformed the tested benchmark surface treatment and silane primer in term of adhesion and durability for the TPU-steel composite interface, and demonstrated a fast-curing capability for high processing speed applications. Indeed, curing is achieved within seconds by comparison to an hour of thermal curing typically required for the sol-gel condensation of silanes. The UV-cured epoxy primer however required appropriate formulation parameters to be really efficient and to attain an optimum curing speed. These aspects have been assessed by studying curing kinetics, mechanical properties and adhesion. Correlations were found between the obtained properties, improving the understanding of this new primer material and defining optimum additives concentrations of polyols, trimethylolpropane oxetane, and a UV-curable epoxysilane. In extension, the primer also showed promising results with PA12 or stainless steel and is expected to apply between most polar thermoplastics and metallic surfaces.

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