

Novel cationic UV-cured hybrid coatings with enhanced mechanical resistance and thermal properties

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Abstract

Cationic photopolymerization of epoxy novolac resins (ENR) formulations were investigated with the aim to develop new UV-Cured coatings characterized by high thermomechanical properties for applications in harsh environments in oil and gas industry. Hybrid coatings were developed by dispersion of inorganic fillers and the properties of UV-cured films were fully characterized in terms of their viscoelastic properties, thermal properties, resistance to heat and adhesion strength.

Keywords

Cationic, photopolymerization, UV-curing, epoxy novolac resin, coating

Introduction

Nowadays, oil and gas industry is still relying on thermally cured epoxy resins as protective coatings for internal pipelines because of the greater performance in terms of adhesion, thermal and chemical resistance of the resulting crosslinked polymer. In fact, these coatings are supposed to withstand great operative temperature and pressure in harsh environments rich in acids (CO₂) and hydrocarbon species, therefore high glass transition temperature and film barrier properties are required^[1]. Usually, amine cured epoxy novolac resins (ENR) with high number of functionalities are employed for these applications as the only resins able to meet these requisites. However, these resins usually need to be cured at high temperature for several hours and are usually solvent based, relying on environmentally unfriendly components such as xylene to reduce the final mixture viscosity. Replacing such formulations with UV curable resins would eliminate the need of dangerous solvents and cut on the cost of ovens for the curing process. In addition, radiation curing would allow polymerization to occur in minutes instead of hours increasing productivity significantly. In particular, cationic photopolymerization is taken into consideration for its better performances in term of absence of oxygen inhibition, better adhesion and chemical resistance^[2]. Cationic process of widely used epoxy-based resins such as diglycidyl ether of bisphenol A (DGEBA) and branched resins is possible and has been observed in diverse studies^{[3][4]}, but little information is provided regarding the resulting thermo-mechanical performances.

In the present work, the possibility to cure a highly functional epoxy novolac resin by means of cationic photopolymerization is studied and the properties of the final coating are compared with another commercially used cationic cycloaliphatic epoxy as well as a thermally cured resin. The highly viscous ENR is photopolymerized using a commercially available sulfonium hexafluorophosphate cationic

photoinitiator and its properties evaluated in terms of temperature resistance, adhesion and mechanical performances. Finally, fillers are introduced in the photocurable formulations to increase scratch resistance and improve surface properties of epoxy coatings.

Experimental section

Materials

Epoxy novolac resin (D.E.N.^(TM) 425) with an EEW of 169-175 gr/eq and a viscosity at 25°C between 9500-12000 cPs was purchased from Olin Epoxy. 1,4-Butanediol diglycidyl ether (BDGE) was purchased from EMS Chemie GmbH (Switzerland). Cationic photoinitiator triarylsulfonium hexafluorophosphate, the cycloaliphatic epoxy 3,4-epoxy cyclohexylmethyl-3',4'-epoxy-cyclohexan (CE) and fumed silica nanoparticles with mean diameter of 5-20 nm were purchased from Sigma Aldrich. Quartz filler Silverbond SA 300 with a particle mean diameter of 6 μm was purchased from Came s.r.l., while benzyl alcohol (BzOH) was purchased from Fluka Chemie GmbH (Switzerland). Thermal epoxy formulation used as a comparison was kindly supplied by MPR/GSC chemicals. Of this formulation, two version were supplied: one complete with fillers and additives (NGF) and the second consisting only in the epoxy novolac binder along with the amine binder (NGT).

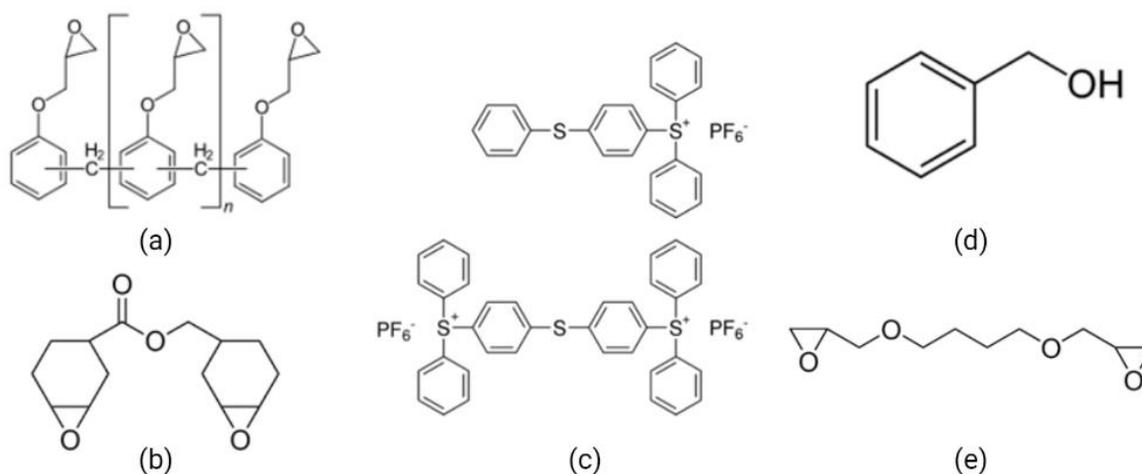


Figure 1. (a) Epoxy novolac resin (ENR); (b) 3,4-Epoxy cyclohexylmethyl-3',4'-epoxy-cyclohexan (CE); (c) Triarylsulfonium hexafluorophosphate (SPF₆); (d) Benzyl alcohol (BzOH); (e) 1,4-Butanediol diglycidyl ether (BDGE).

Testing methods

Fourier Transform Infrared Spectra (FTIR) were obtained using a Thermo Scientific Nicolet iS50 Spectrometer operating in transmission, 32 spectra were obtained for each measurement in the spectral range from 4000 to 600 cm⁻¹ with a resolution of 4 cm⁻¹. Samples were deposited on a silica wafer in a 12 μm thick layer and irradiated with a Dymax ECE 5000 UV flood mercury lamp with wavelength range between 200 and 400 nm and intensity of 130 mW/cm². Spectra were collected after 1, 3, 5, 10, 30, 60, 120, 240 seconds irradiation time. Results here presented are average of at least two different runs. Conversion was calculated comparing the epoxy peak areas obtained from the spectra before and after the irradiation process. By monitoring their decrease over time it was possible to calculate the epoxy degree of conversion (α) using the following equation:

$$\alpha (t) = 1 - \frac{(A_{Et})(A_{R0})}{(A_{E0})(A_{Rt})} \quad (1)$$

Where α is the conversion percentage at time t , A_{E0} and A_{Et} the area of the epoxy peak at time 0 and time t respectively, while A_{R0} and A_{Rt} are the areas of the reference peak at time 0 and time t respectively. The band of C-O bond stretching in the oxirane ring at 915 nm was chosen to evaluate the epoxy concentration in epoxy novolac resin while the C-O-C stretch at 760 nm was used for CE resin, C=C stretch of aromatic ring at 1610 nm was used as reference peak for both resins.

Dynamical mechanical thermal analysis (DMTA) was used to evaluate glass transition temperature and viscoelastic properties of resin mixtures as a function of temperature. A Tritec 2000 DMA equipment from Triton Technology Ltd was used with a temperature ramp of 3°C/min, a frequency of 1 Hz and a total displacement of 20 μ m. Samples of thickness comprised between 100 and 120 μ m were polymerized on polypropylene (PP) substrates using Dymax lamp with intensity of 130 mW/cm² for 120 seconds. Glass transition temperatures presented are average of at least two experiments for each sample.

Thermal gravimetric analysis (TGA) of samples was performed using a Mettler Toledo TGA/SDTA 851e. Samples were polymerized in thin films of 100 – 120 μ m thickness using the Dymax lamp for 120 seconds at 130 mW/cm², 10 mg of film were placed in the pan and heated in N₂ atmosphere (50 mL/min) with a heating rate of 10°C/min from 25°C to 900°C. The onset temperature of degradation ($T_{d5\%}$) was calculated as the temperature at which 5% of mass loss occurred in the sample.

Adhesion tests (pull off test – ISO 4624) of resin formulations were performed on steel substrates, the instrument used was an Elcometer 510 automatic pull-off adhesion gauge. Substrate used were carbon steel panel of 80 x 40 x 4 mm blasted on one side to respect blast-cleaning standard of Sa ½ (ISO 8501-1). Resin formulation was applied on blasted side in two layers of 50 - 60 μ m each and cured for 120 s and 130 mW/cm². Once cured, the surface was sanded and dollies were glued using an epoxy structural adhesive (Scotch-Weld DP 460) to its surface. Dollies were cured for 3 hours at 49°C. Pull off test were performed right after and adhesive curing cycle and strength and type of failure recorder. Adhesion strength was calculated for each formulation as an average of 4 separate pull off tests. Pull off tests were considered invalid if the detachment occurred in the glue instead of the coating layers unless the adhesive strength value recorded exceeded specification. Pull off tests were considered passed if the adhesive strength registered was above 10 MPa.

Results and discussion

Photocuring investigation of different epoxy-based formulations

In order to study the effect of the concentration of the photoinitiator on the photopolymerization process, different resins mixtures of CE and ENR were prepared containing 0.5, 1, 2 and 3 wt % of photoinitiator, the conversion of epoxide groups was calculated for each time step. The FTIR conversion as a function of irradiation time are reported in Figure 1 for the investigated formulations. Epoxy conversion of the amine cured formulation (NGF) calculated after curing in oven at 90°C for 2 hours was found to be 78% and was used as a term of comparison. Both CE and ENR resins exhibited an increase in conversion of epoxy groups with increasing concentration of photoinitiator, reaching maximum values at the concentration of 3 wt%. As observed in Figure 2, CE resin showed significantly faster kinetics, reaching maximum conversion in few seconds. When the concentration of photoinitiator was just 1 wt% a conversion of 78%, equal to the one of the amine-cured formulation, was reached, while at 2 and 3 wt % respectively, a conversion as high as 85% and 91% could be achieved after an irradiation of 60 seconds. On the other

hand, ENR resin showed lower values of conversion and required longer time to reach them as shown in Figure 2.

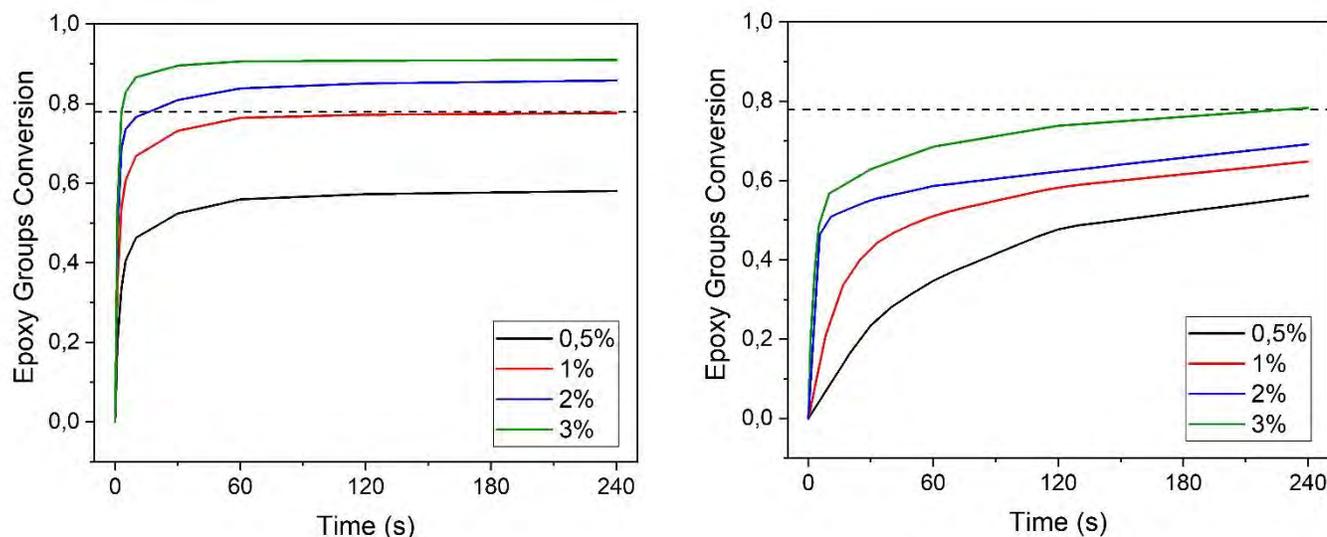


Figure 2. Effect of Photoinitiator on epoxy groups conversion of CE resin (a) and ENR (b).

Conversion plateau were not as well-defined as the one showed in CE conversion curves and kinetics was visibly slower. After 60 seconds at 1 wt % photoinitiator, the conversion reached was 51% and 65% after 240 seconds of irradiance. ENR maximum conversion was equal to 78% and could only be obtained after 240 seconds irradiance at 3 wt % of photoinitiator. Cycloaliphatic epoxy higher reactivity compared to bisphenol-based resins is well known from former studies [5]. In addition, CE resin has a viscosity of 400 cPs, considerably lower compared to ENR (10150 cPs). In fact, viscosity plays a major role in cationic polymerization mechanism allowing monomer and oligomers species to diffuse more easily during the propagation step of the process. Introducing a larger concentration of photoinitiator has been showed to be an easy way to increase epoxy groups conversion and accelerating kinetics. However, the introduction of a higher photoinitiator content may result in the formation of too many propagating polymers with lower molecular weight and thus shorter chains, leading to a detrimental effect on the mechanical properties of the final coating. For this reason, and because of the high price of the photoinitiator, a concentration of 1 wt % was used in further experiments.

Effect of different diluents on epoxy groups conversion

Once the exact concentration of photoinitiator was selected, three different reactive and non-reactive diluents were added to the ENR resin with the purpose of both decreasing the mixture viscosity and increasing the epoxy group conversion. The chosen diluents were CE resin, having a significantly lower viscosity and higher reactivity compared to ENR, the reactive diluent BDGE and BzOH as a chain transfer agents. The diluents were added in concentrations of 5, 10 and 20 wt% and the conversion of epoxy groups was studied as a function of the irradiation time. For each concentration viscosity values were recorded and a range between 2000 and 4000 cPs was selected as optimum to achieve in the final resin mixture. When a percentage as low as 10 wt% of BDGE was added it was possible to reduce ENR viscosity

from 10150 cPs to 2200 cPs, similar results were obtained when 10 wt% of BzOH was added, reducing the viscosity of the mixture to 25% of the original. On the other hand, a greater concentration of CE was required to reach a similar reduction in viscosity, with 30 wt% of cycloaliphatic epoxy needed to decrease to 2130 cPs the viscosity of the mixture.

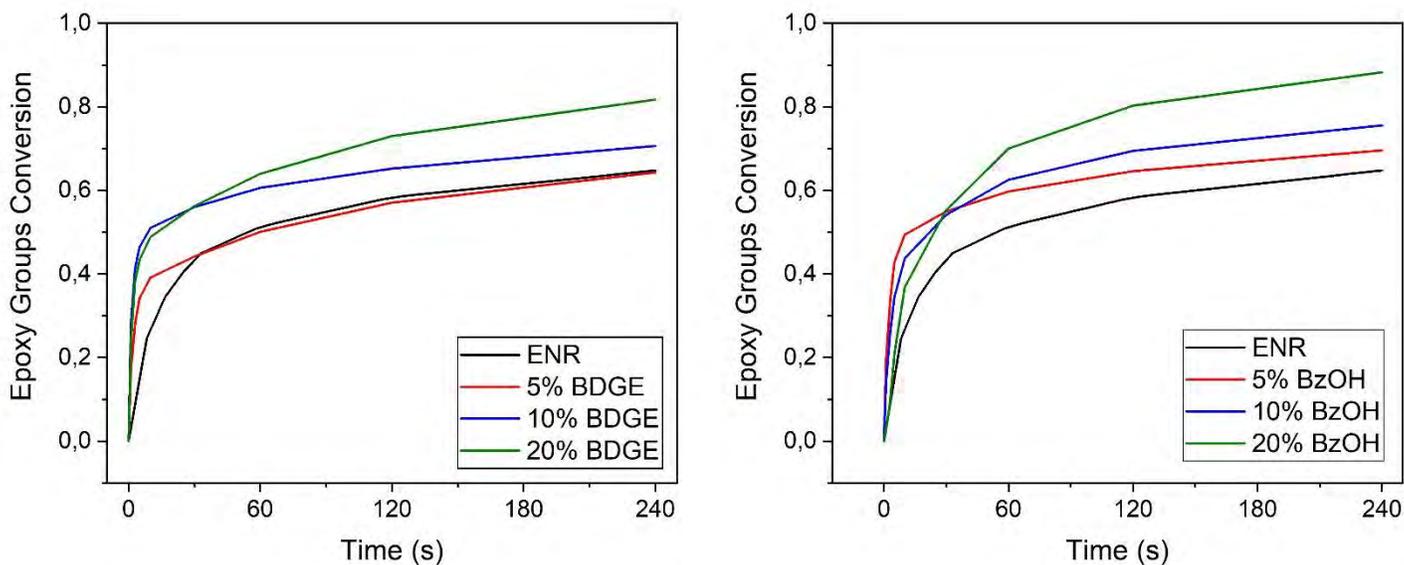


Figure 3. Effect of different concentrations of BDGE (a) and BzOH (b) on ENR epoxy groups conversion.

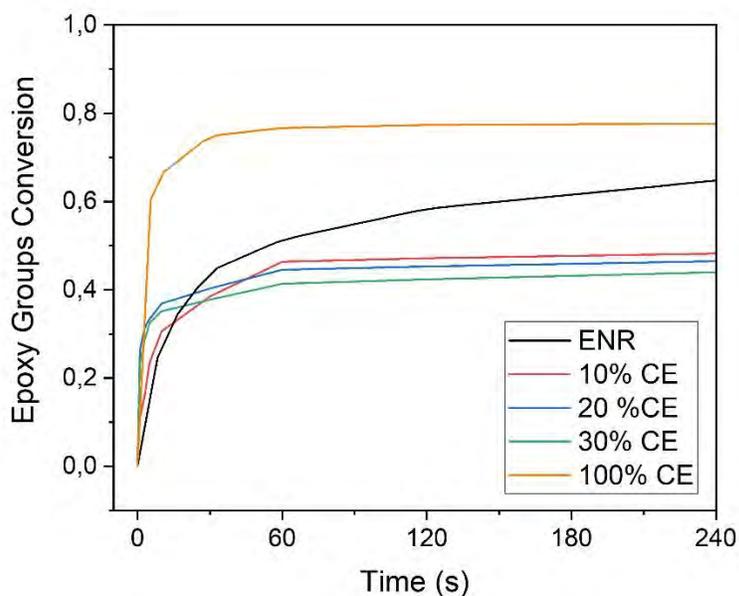


Figure 4. Effect of different concentrations of CE resin on ENR epoxy groups conversion.

The effect on conversion of the different diluents depended on their nature and the interaction with the epoxy monomers. The addition of 10 to 30 wt% of CE resin did not affect positively the epoxy group conversion. In fact, even if an faster rates could be seen in the first seconds of irradiation, the final conversion plateau remained below 50%, resulting in less conversion compared to the one obtained with only ENR (Figure 4). This could be attributed to the different reactivity of the two species inducing CE monomers to consume fast in the first seconds of the reaction increasing viscosity and reducing ENR epoxies accessibility to the propagating chains. On the other hand, the addition of 20 wt% of BDGE resulted in an increase in conversion from 59 to 74% after 120 seconds of irradiation (Figure 3a). The introduction of a resin with lower epoxy functionalities such as BDGE had two opposite effect on the final conversion: the first was that of conversion reduction because of the dilution of the oxirane rings number per mass of resin, the second of conversion increase because of the reduction of the mixture viscosity leading to a better diffusion of the propagating chains and availability of epoxy functionalities for the reaction. The two effects balanced each other when 5 wt% of BDGE was added, therefore the conversion was not affected significantly and the two curves appear almost identical, while with 10 wt% BDGE conversion was increased to 65% after 120 seconds because of the bigger role played by diffusion reduction.

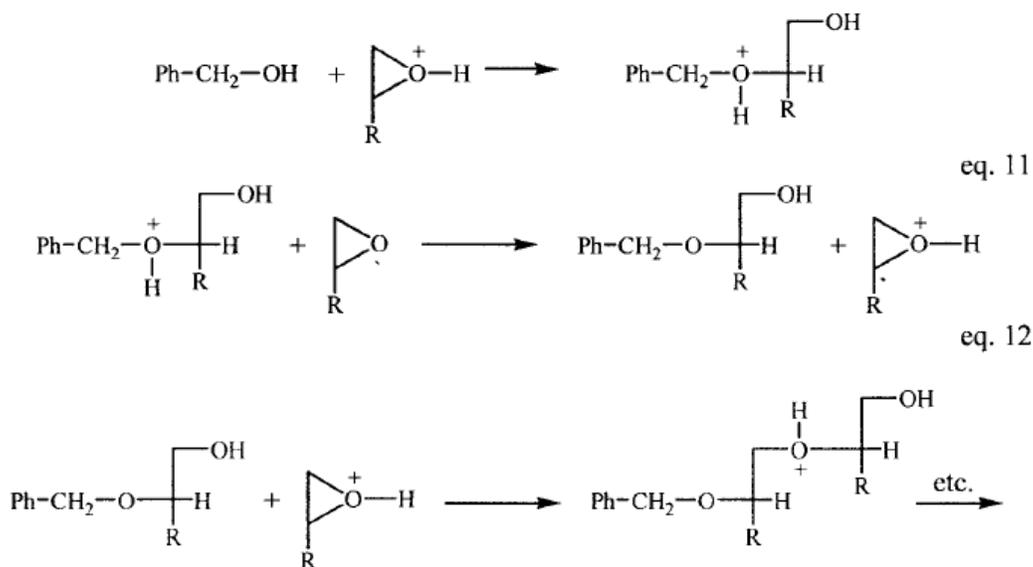


Figure 5. Activated monomer mechanism.

BzOH effect on conversion was more visible, concentration of 10 wt% and 20 wt% increased epoxy conversion to 70% and 81% respectively after 120 seconds irradiation time (Figure 3b). Differently from BDGE and CE, BzOH interacted with the propagating cationic species via an activated monomer mechanism (Figure 5) in which a rapid proton transfer from the growing chain end to the alcohol took place with a chain transfer character resulting in the incorporation of the alcohol species that participate in the chain-transfer reaction. The activated monomer mechanism occurs more rapidly than the usual ring opening mechanism leading to increased polymerization rates and higher conversions^[6]. The effect on conversion induced by the presence of BzOH could be observed already at low concentrations, 5% BzOH addition to the resin mixture resulted in an increase in conversion from 59 to 65% comparable to the addition of 10% BDGE, while conversion as high as 88% could be reached after 240 seconds irradiation in mixtures with 20 wt% BzOH.

Thermal stability and glass transition temperature of different resin mixtures

The effect of the addition of increasing concentrations of different diluents on the mechanical and thermal properties of the final UV-Cured coatings was studied by means of DMTA on samples of 100 μm thickness. High concentrations of diluents were expected to negatively influence Tg because of the weakening of the crosslinking network introduced by new species in the polymer structure. Glass transition temperature (Tg) reduction as a function of diluent concentration is showed in Figure 5.

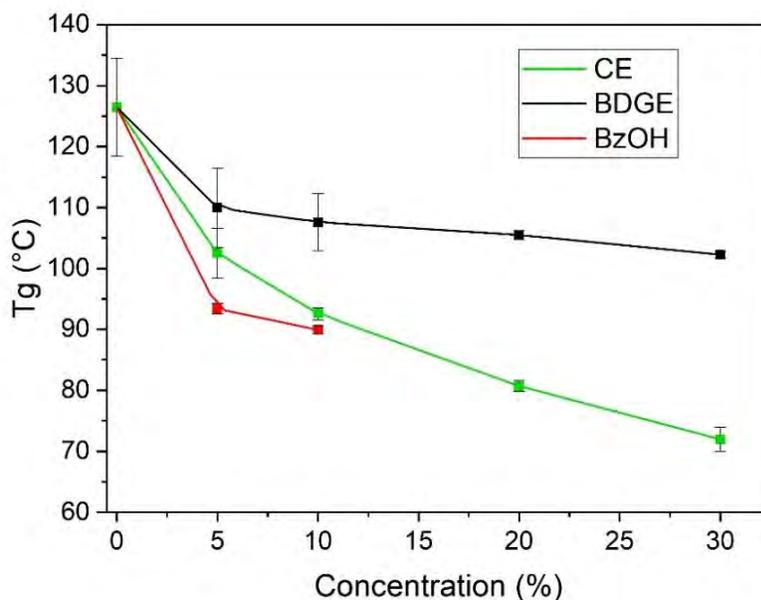


Figure 6. Effect of diluents concentration on final coating Tg.

As expected, all the three diluents affected negatively the glass transition temperature of the final coating. BzOH had the most detrimental effect on the mechanical properties, when a concentration as little as 5 wt% was added to the ENR the Tg decreased from 124 °C to 94 °C, at 10 wt% the reduction was of more than 30 °C. When increasing even more the BzOH concentration the cured sample was sticky and not crosslinked enough to perform a DMTA test. This result may be caused by the too fast consumption of epoxy monomers during the acceleration by activate monomer mechanism. In fact, BzOH induced a fast chain transfer mechanism blocking the growth of the propagating chains and hindering the network formation resulting in a sample where polymeric chains had increased mobility and thus decreasing final glass transition temperature. On the other hand, CE could be added in higher concentrations in the resin mixture without causing important flexibilization of the cured coating. Nonetheless, Tg of ENR/CE mixtures decreased of almost 10°C less for each 10 wt% of CE resin added, when 20% of CE was used the Tg obtained was of 82 °C while when CE concentration was increased to 30 wt% the Tg obtained was of 73 °C. The best result was obtained with BDGE, concentration as high as 30 wt% could be added without decreasing Tg below 100 °C. With 10 wt% of BDGE the final polymer had a reduction in Tg of less than 14% compared to pristine ENR.

Thermal stability of the UV-Cured coatings was evaluated by means of Thermal gravimetric analysis (TGA) and compared with thermal cured coating. As shown in figure 6, all samples have similar

degradation profiles with a localized change in weight corresponding to the decomposition of the polymeric backbone.

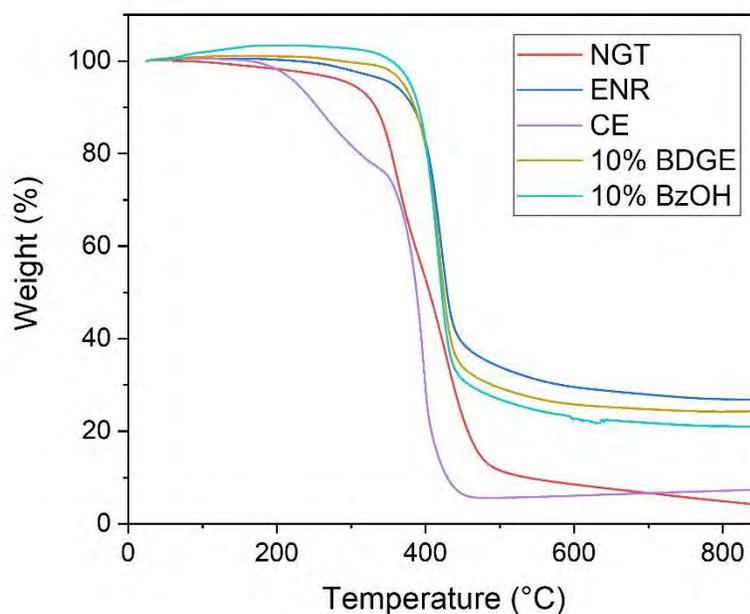


Figure 7. TGA curves of different cured resin formulations.

The onset temperature of degradation ($T_{d5\%}$) was calculated for each sample and used as value to determine the beginning of the decomposition process. Sample which showed lower thermal stability was CE resin with a degradation onset of 213 °C, far lower compared to the amine-cured ENR onset of 300 °C, this could be explained by a weaker bonded polymeric network and less stable structure. On the other hand, UV cured resins in which ENR was used alone or in combination with other diluents had higher $T_{d5\%}$, respectively 356 °C for ENR, 370 for ENR/BDGE (90:10) and 379 °C for ENR/BzOH (90:10). These UV cured formulations showed a higher content of non-degradable ashes that remained from the initial amount of mass tested compared to the other samples. The higher thermal onset of the UV cured ENR indicates the formation of a more rigid and strongly bonded crosslinked network compared to the one formed in the presence of the amine crosslinking agent. Despite the higher conversion reached by other resin mixtures, ENR/BDGE (90:10) formulation was chosen for further experiments with the addition of filler, because of its higher temperature of degradation and glass transition temperature.

Effect of filler on thermomechanical properties of epoxy UV-cured coatings

Two fillers with different particle average size were added to the ENR/BDGE (90:10) mixture in order to study their effect on curing and final mechanical properties. Crystalline silica (quartz) and amorphous silica were added in concentration of 5, 10, 25 and 50 wt% with respect to the resin and dispersed using an ultrasonic bath for 15 minutes. In Figure 8, the effect of filler concentration on the glass transition temperature can be observed. Depending on the positive or negative interactions between particles and matrix the glass transition temperature can respectively increase or decrease. The addition of amorphous silica resulted in a significant decrease in T_g , when concentration as small as 5 wt% was added the T_g

decreased more than 30 °C, from 108 °C to 72 °C suggesting a bad interaction between resin and nanoparticles that could lead to the formation of voids around filler particles with the subsequent decrease in mechanical properties of the final coating.

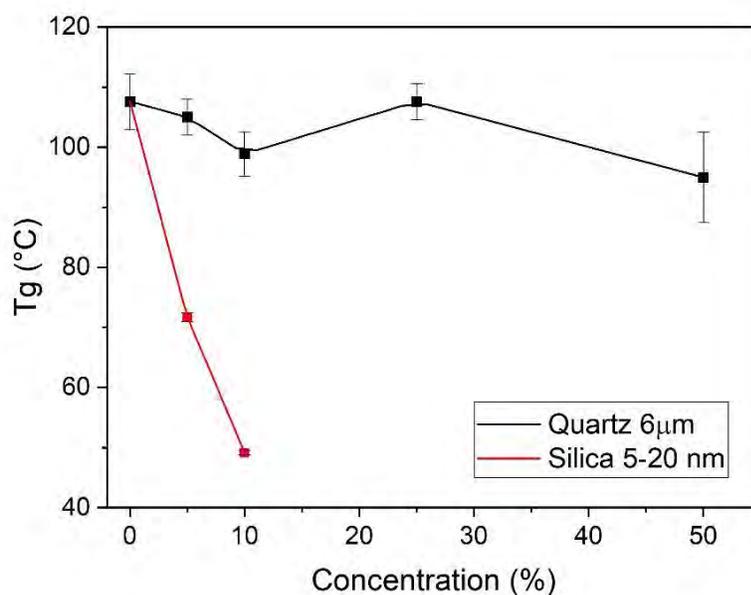


Figure 8. Effect of filler concentration on final coating Tg.

Concentration higher than 10 wt% could not be added because of the increase in viscosity caused by the high oil absorption of the filler. Differently, crystalline silica effect on Tg was slight, with reduction of maximum 10 and 13 °C when 10 wt% and 50 wt% quartz was added respectively. Quartz effect on Tg was not linear with concentration and the measures presented higher standard error, this may be due to a not throughout dispersion of the particles in the matrix leading to small agglomerates in the coating sample. The effect of the two fillers in term of viscosity increase was also different. In fact, quartz could be added in concentration as high as 50 wt% without affecting too much viscosity, while amorphous silica viscosity increase was more significant, not allowing concentration higher than 10 wt% to be added without resulting in sample embrittlement. The reason to the different effect on viscosity depends on the nature of the particles, crystalline silica has a far less specific area compared to amorphous silica (0.7 m²/g compared to more than 200 m²/g) resulting in a lower oil absorption and thus increased loading factor.

Adhesion to steel substrate – pull off tests

Ultimately, the formulations were applied to blasted steel substrates and cured in two layers of 50 µm thickness each. Adhesion strength was evaluated for each coating, including the two amine-cured ENR with and without fillers (NGF and NGT) which were used as comparison. Results are obtained from an average of 4 separate pull off tests and are collected in Table 1. All UV cured coating presented good to excellent adhesive properties, in particular UV-cured ENR adhesion strength was of 16.76 MPa, comparable with the adhesion strength obtained from NGF coating which was of 16.81 MPa. This result suggests that similar resin properties can be obtained with two different curing techniques, as adhesion is mainly influenced by the epoxy groups conversion and crosslinking density. In fact, the increased network

strength caused by the absence of amine groups in the polymeric chains might compensate the lower conversion of epoxy groups observed in UV-cured ENR (Figure 2b).

Sample	Adhesion Strength [MPa]	Adhesive Failure
NGF	16,81 ± 2,27 (SE)	100% BC
NGT	21,10 ± 0,65 (SE)	30% Y/Z + 70% -Y
ENR	16,76 ± 2,7 (SE)	100% A/B
ENR/BDGE (90:10)	13,20 ± 2,03 (SE)	100% A/B
ENR/BzOH (90:10)	13,64 ± 0,81 (SE)	100% A/B
ENR/BDGE +10% quartz	8,88 ± 0,63 (SE)	100% A/B
ENR/BDGE +25% quartz	14,92 ± 2,59 (SE)	100% A/B
ENR/BDGE +50% quartz	7,48 ± 1,26 (SE)	100% A/B

Table 1. Pull off test of different coatings obtained via UV and thermal cure. Adhesive failure types are classified as: A/B = adhesive failure between first coat and substrate; BC = adhesive failure between first coat and second coat; Y/Z = adhesive failure between adhesive and dolly; -Y = adhesive failure between final coat and adhesive.

Similarly, pull off tests of ENR mixed with 10 wt% of BDGE and BzOH gave adhesion strength values of 13.20 MPa and 13.64 MPa respectively, both higher than the 10 MPa limit. Differently, the addition of 10 wt% and 50 wt% of quartz particles resulted in a significant decrease in adhesion strength, while coatings with 25 wt% of the same filler had higher adhesion strength. These results follow the same profile of glass transition temperature reduction observed in Figure 10, with reduction in pull off test observed for formulations that had lower glass transition temperatures. This non-linear behavior might be the result of the higher UV absorbance caused by quartz nanoparticles, which hindered the photoinitiation step of the polymerization reaction. Another major difference between thermal and UV cured formulation was the type of adhesive failure, which in all UV cured coatings occurred by adhesive failure between substrate and first layer of coating, while in NGF coating occurred by adhesive failure between the first and second layer. In this case, the reason could reside in the presence of adhesion promoter additives in the NGF formulation.

Conclusions

A commercially available epoxy novolac resin (ENR) was successfully cured in short time using an UV-induced cationic photopolymerization mechanism and by using a low concentration of sulfonium salts as photoinitiator. The properties of the resulting coating were found to be comparable to the ones obtained from amine-cured epoxy resins in terms of thermal stability and mechanical resistance. In addition, it was demonstrated that it is possible to increase epoxy groups conversion by adding a reactive diluent (BDGE) or by using a chain transfer agent (BzOH) without significantly affect the curing behavior of the resin or the glass transition temperature of the final coating. Adhesion to a steel substrate of formulations with

and without fillers was found to be comparable to the one obtained with thermal cured resins suggesting a possible use of UV-cured ENR on steel piping in in harsh environments.

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