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# Epoxy-modified Portland cement: effect of the resin hardener on the chemical degradation by carbon dioxide

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## Abstract

Portland cement employed in $CO_2$ injection wells is strongly susceptible to acidic attacks leading to long-term deterioration. This study investigates the chemical degradation of composites based on an epoxy resin blend (with and without a hardener) and cement paste when exposed to $CO_2$, aiming to provide a new polymer-modified cement with better chemical resistance. $CO_2$ degradation experiments were conducted with dissolved $CO_2$ at 70°C and 50 bar. Results showed that composites containing hardener undergo lower degradation by $CO_2$ when compared to the composites with uncured epoxy resins. Some of these composites present smaller degraded layer than pure Portland cement.

*Keywords:* resin-cement composite; $CO_2$ degradation; Portland cement paste; epoxy resin; hardener.

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## 1. Introduction

Carbon dioxide ($CO_2$) emissions are one of the most significant concerns among all greenhouse gases. An effective method for reducing atmospheric $CO_2$ is to capture and storage this gas in geological reservoirs (e.g. deep saline aquifers, unmineable coal seams, depleted oil/gas reservoirs) [1].

The Portland cement commonly used in $CO_2$ injection and storage wells is strongly susceptible to acidic attacks, causing negative impacts on long-term wellbore integrity. $CO_2$ can diffuse through the cement matrix and depending on the pore structure and water saturation in the pores, it can be very aggressive. When $CO_2$ dissolves in the water inside the pores, it forms carbonic acid ($H_2CO_3$) that reacts most readily with portlandite (calcium hydroxide, $Ca(OH)_2$). $Ca(OH)_2$ carbonation results, in the first step, in calcium carbonate ($CaCO_3$) (low solubility), which can be converted, in the second step, to calcium bicarbonate ($Ca(HCO_3)_2$) (high solubility). Consequently, $Ca(HCO_3)_2$ is able to gradually leach out of the cement matrix, increasing its porosity and permeability, and reducing the mechanical strength with possible loss of structural integrity [2,3,4].

In order to overcome the carbonation issue, polymer-based admixtures can be incorporated into cement paste. The incorporated polymeric phase produces cementitious materials with superior mechanical and chemical properties compared with conventional Portland-cement systems [5,6,7,8]. Two processes take place during the hardening of polymer-modified cementitious materials: cement hydration and formation of polymer bridges or films depending on the polymer content. It is very important that both processes proceed well to yield a monolithic matrix phase with a network structure in which the polymeric phase interpenetrates the cement hydrate phases [5]. Knapen et al. [9,10] described the formation of polymer bridges between layered $Ca(OH)_2$ crystals in the presence of very low water-soluble polymer contents (usually below 4%). Such polymer bridges could act as bonding agents improving the internal cohesion of the cement paste and reducing the crack formation.

Epoxy resins have been widely used as admixtures in the concrete industry due to their high inherent strength, high bond strength and chemical resistant properties. Usually, epoxy resins require a hardener, which are generally amines or organic acids, to initiate curing process and to form crosslinked networks. Jo [11] stressed that epoxy cement mortars with a hardener require a polymer content higher than 40% to achieve good mechanical properties and durability. However, some studies have pointed out that epoxy resin can cure in the presence of hydroxide ions or alkalis (i.e. $Ca(OH)_2$) formed from the hydration of Portland cement [11,12,13]. Hardener-free epoxy-modified cements can provide an auto-healing or self-repairing function for micro cracks [13,14]. It is estimated a degree of crosslinking of epoxy resin (without a hardener) of about 50% with a polymer content of 20% in the cement. The excess of unhardened resin remains initially in the pores of the hardened cement paste. As micro cracks are formed, the resin is gradually released to crosslink and harden with $Ca(OH)_2$ present in the cement. This phenomenon can fill and repair micro cracks [13,14]. Besides the self-repairing property, studies have shown that epoxy cement mortars without a hardener maintain some chemical and mechanical properties that are much better than conventional epoxy cement mortars with a hardener [11,12,13,15]. For instance, carbonation depth of epoxy cement mortars without a hardener, which were exposed to outdoor and indoor environments for a year, is considerably smaller than that with the hardener at the same polymer-cement ratio. With a polymer-cement ratio of 40%, it was found a carbonation depth of approximately 3 mm and 1 mm for epoxy cement mortars with and without a hardener, respectively [11].

The effects of carbonation in polymer-modified cementitious materials are mostly evaluated under mild conditions (e.g. 20% $CO_2$, 20°C, atmospheric pressure) and with polymers in form of coating [16,17,18]. As far as we know, there are few studies that evaluate the effects of polymeric admixtures (incorporation of polymers into cement paste) on the chemical degradation by $CO_2$ under realistic disposal conditions (elevated temperature and pressure) [19,20,21]. Moreover, under these conditions the effects of resin hardeners on the resistance to $CO_2$ acidic attack remain an open issue that should be considered and further investigated. In view of this, an experimental study was conducted to develop composites based on an epoxy resin blend (with and without a hardener) and cement paste. $CO_2$ degradation experiments were performed with $CO_2$ dissolved in water at 70°C and 50 bar to simulate conditions of practical interest. For comparison, unmodified cement paste was also prepared and tested likewise.

**Nomenclature**

| | |
|---|---|
| S1 | composites without hardener |
| S2 | composites with hardener |
| PC | pure cement |
| NDL | non-degraded layer |
| DL | degraded layer |

## 2. Materials and methods

### *2.1. Cement*

Class G Portland cement (LafargeHolcim) was used in this study. The chemical composition of the cement is given in Table 1. The paste, composed of Portland cement and water, was prepared according to API Specification 10A with a water/cement weight ratio of 0.44. The conditions of cement paste preparation were kept constant in all composites in order to evaluate the actual effect of epoxy resin.

Table 1. Chemical composition of class G Portland cement.

| Composition | % |
|---|---|
| $SiO_2$ | 21.25 |
| $Al_2O_3$ | 3.95 |
| $Fe_2O_3$ | 4.57 |
| CaO | 65.07 |
| MgO | 2.31 |
| $SO_3$ | 2.27 |
| $Na_2O$ | 0.25 |
| $K_2O$ | 0.33 |

### *2.2. Polymeric admixture*

A bisphenol A (DGEBA)/phenol-Novolac (EPN) blend system (Huntsman Corporation) was used as epoxy resin in this study. EPN resins can upgrade the performance offered by DGEBA resins, improving their chemical resistance. A waterborne polyamine epoxy hardener was used for preparing the composites containing hardener. The properties of the epoxy resins and hardener are given in Table 2.

Table 2. Properties of epoxy resins and hardener (Huntsman Corporation).

| Component | Epoxy/$H^+$ active equivalent (g $eq^{-1}$) | Viscosity at 25°C | Mix proportion (phr) |
|---|---|---|---|
| DGEBA | 182 – 192 | 12,000 – 16,000 mPa s | 80 |
| EPN | 172 – 179 | 80,000 mPa s | 20 |
| Hardener | 270 | Z – Z4 Gardner Holdt | 144 |

### *2.3. Epoxy resin-cement paste composites*

Composites were prepared using 10%, 20%, 30% and 50% w/w of epoxy resin content with respect to the cement. For the composites containing hardener, firstly the hardener was mixed with the epoxy resin blend (DGEBA + EPN) and then kept at room temperature for 15 min (induction time). Afterwards, cement paste was added to the epoxy resin system (DGEBA + EPN + hardener), well mixed and the final mixture poured into cylindrical molds (h= 2 cm and d=

1 cm) for curing at room temperature during 14 days. For the composites without hardener, cement paste was directly mixed with the epoxy resin blend (DGEBA + EPN), then molded for curing. For comparison, unmodified cement paste (pure Portland cement) was also prepared. In order to simplify, we have denominated the composites without hardener as "S1" and the composites with hardener as "S2".

### *2.4. $CO_2$ degradation experiments*

The cured composites were exposed to a $CO_2$/water system at 70°C with $CO_2$ pressure of 50 bar (high purity, 99.9%, White Martins) for 7 days under static conditions. At the end of the experiments, the composites were characterized by field emission scanning electron microscopy (FESEM), universal attenuated total reflectance-Fourier transform infrared spectroscopy (UATR-FTIR) and thermogravimetric analysis (TGA) in order to evaluate their chemical degradation.

## 3. Results and discussion

The results showed that the S1 composites undergo higher degradation when exposed to dissolved $CO_2$ than S2 composites, as shown in Fig. 1. FESEM analysis evidenced that S2 composites with 10%, 20% and 30% of epoxy resin content have a smaller degraded layer (up to 665 µm) when compared to the pure cement (~ 1000 µm). For the S1 composites, the degraded layer of the samples containing 10% (~ 1220 µm) and 20% (~ 1040 µm) of resin content is similar to the pure cement, being higher with 30% (~ 2385 µm). Both S1 and S2 composites showed significantly greater degradation with 50% of resin in the cement. Overall, the degraded layer tends to increase with increasing epoxy resin content. It is known that the early hydration of cement is modified with increased polymer content. This reflects changes in the nature of the hydration products (i.e. degree of compaction, average grain size, crystal orientation) and in the pore structures that ultimately can affect the resistance of the composites to $CO_2$ acidic attack [9,22,23].

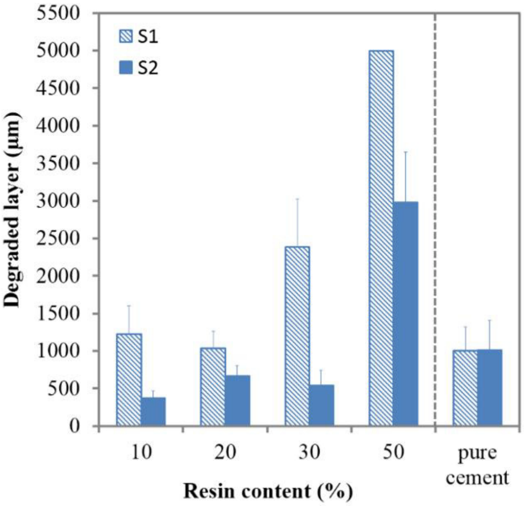

Fig. 1: Degraded layer for S1 (without hardener) and S2 (with hardener) composites at different epoxy resin contents and for pure cement paste.

The literature indicates the possibility of curing the resin in the presence of hydroxide ions or alkalis (e.g. $Ca(OH)_2$) formed from the hydration of Portland cement, however the same was not observed for the S1 composites in our experimental conditions. In fact, a part of the epoxy resin in the S1 composites was leached out of the cement matrix into the aqueous phase after 7 days of reaction. This phenomenon could favour the formation of pathways for $CO_2$ diffusion in the cement paste, rendering these composites more susceptible to carbonation as evidenced in the Fig. 1.

In the S2 composites, leaching of the epoxy resin was not verified due to formation of crosslinked epoxy networks in the presence of hardener. Fig. 2 clearly shows that the S2 composites exhibit a much less porous structure than the S1composites after carbonation reaction.

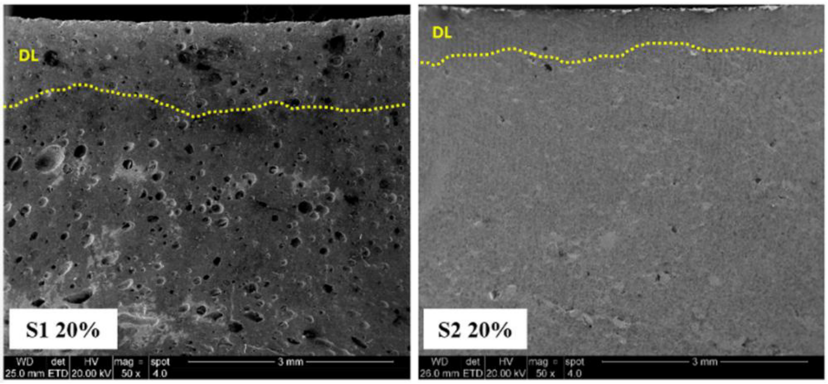

Fig. 2: FESEM images of the S1 (without hardener) and S2 (with hardener) composites with 20% of epoxy resin content. Dotted line demarcates degraded layer (DL).

Regarding the microstructure of the composites, polymer films were found throughout the cement matrix for all S1 composites as well as for S2 composites with 50% of resin content. In contrast, polymer bridges between layered $Ca(OH)_2$ crystals were identified in the S2 composites containing up to 30% of resin content (Fig. 3). The composites containing these polymer bridges have proven to be the most efficient system against the $CO_2$ acidic attack, as it showed smaller degraded layer than pure cement.

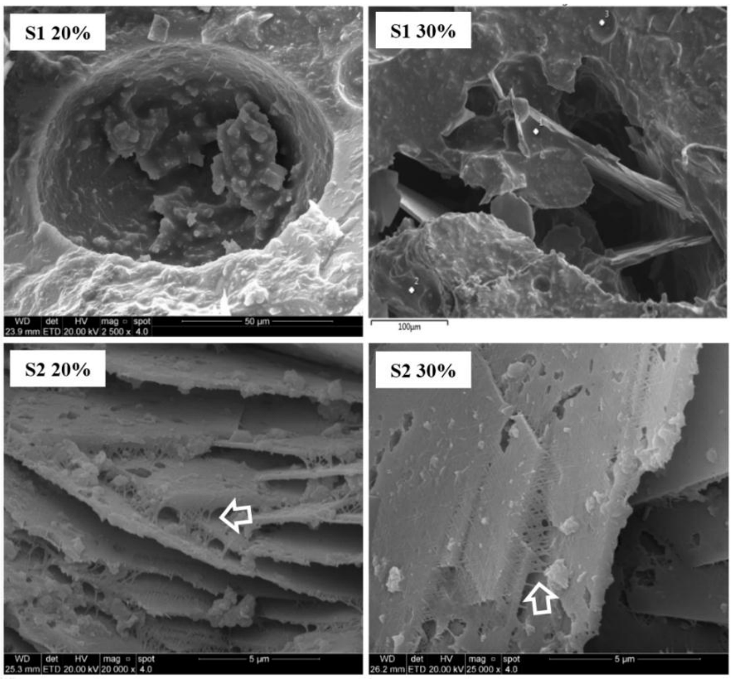

Fig. 3: Polymer bridges (indicated by arrows) and films in S1 (without hardener) and S2 (with hardener) composites with 20% and 30% of epoxy resin content. FESEM images taken from the non-degraded layer.

Fig. 4 shows UATR-FTIR spectra for the pure cement, S1 and S2 composites with 20% of epoxy resin content before and after the $CO_2$ exposure. The samples not exposed to $CO_2$ are referred as initial, whereas the samples exposed to $CO_2$ are differentiated in two layers: the degraded layer (DL) where $CO_2$ has penetrated and reacted (complete reaction of $Ca(OH)_2$), and the non-degraded layer (NDL) where $CO_2$ has not yet penetrated (no reaction with $Ca(OH)_2$). Note that $CO_2$ diffuses through the DL towards the NDL.

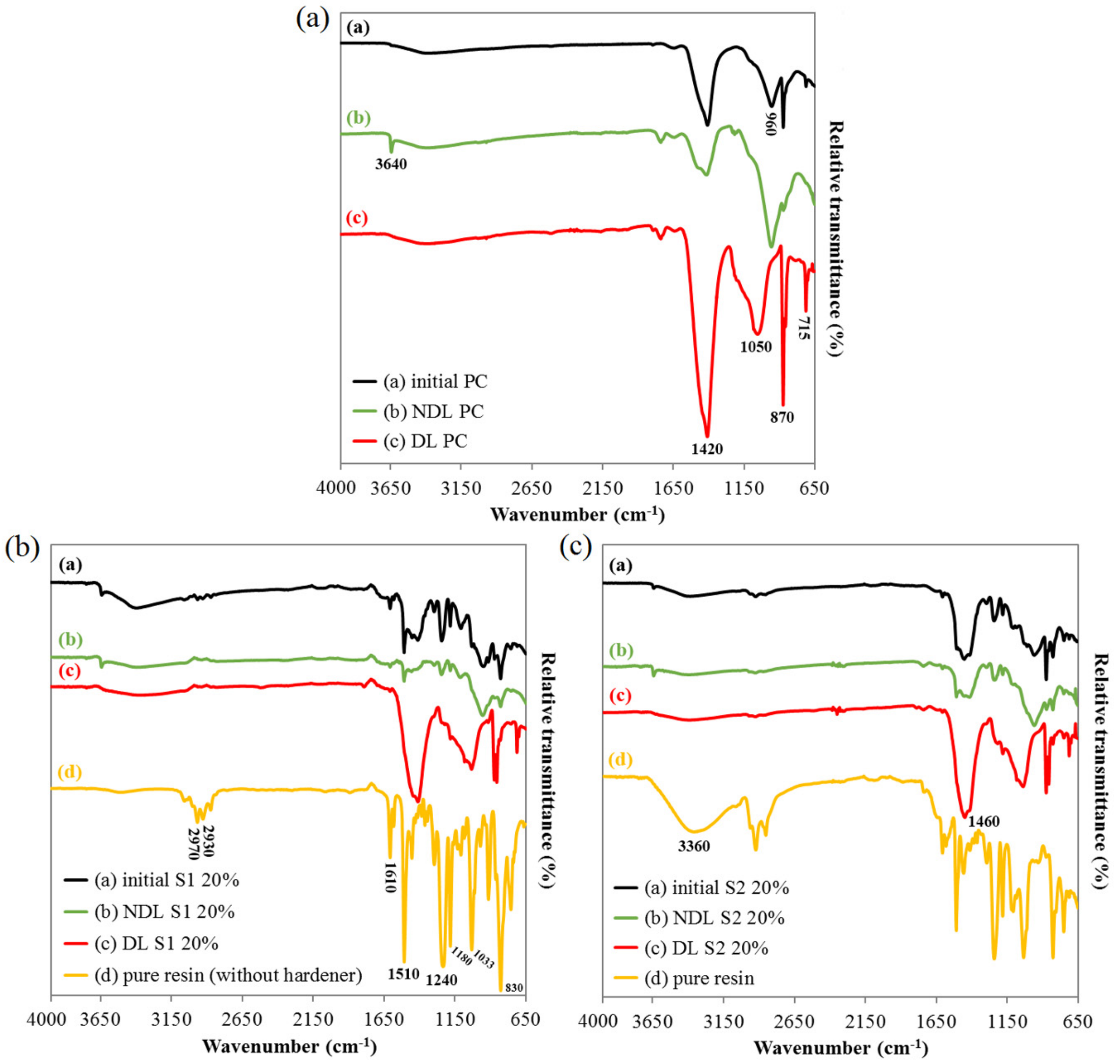

Fig. 4: FTIR spectra for pure cement (PC) (a); S1 composite, without hardener (b); and S2 composite, with hardener (c) containing 20% epoxy resin. Non-degraded layer (NDL) means no penetration of $CO_2$, whereas degraded layer (DL) means penetration of $CO_2$ and reaction with $Ca(OH)_2$. Note that pure resin was not exposed to $CO_2$.

Weak bands near 3640 $cm^{-1}$ are assigned to OH vibrations of the $Ca(OH)_2$ present in the cement paste (Fig. 4a,b,c) [24,25,26,27]. This band is only found in the initial samples and in the NDL of the carbonated samples. As the intensity of this band can be related with the $Ca(OH)_2$ content, a complete carbonation (reaction of $Ca(OH)_2$ with dissolved $CO_2$) was evidenced in the DL of the pure cement (Fig. 4a) and composites (Fig. 4b,c). Indeed, the intense band in the region of 1460-1420 $cm^{-1}$ confirms the presence of carbonate phases, mainly aragonite and calcite. The two lower frequency carbonate bands — particularly the out-of-plane bend (~870 $cm^{-1}$) and the in-plane bend (~715 $cm^{-1}$) — were also observed [25,27,28]. Silicate phases (i.e. calcium silicate hydrate, C-S-H) were identified by the band near 960 $cm^{-1}$, which shifts to higher wavenumbers (~1050 $cm^{-1}$) in the DL of the pure cement (Fig. 4a) and composites (Fig. 4b,c) due to C-S-H chain polymerization promoted by carbonation [25].

For the pure resin (with or without hardener), two characteristic bands were observed at 2970 $cm^{-1}$ and 2930 $cm^{-1}$ corresponding to C-H bond stretching mode of the aromatic ring and epoxide group, respectively. C=C bond stretching mode of the aromatic ring is evidenced by the bands at 1610 $cm^{-1}$ and 1510 $cm^{-1}$. The intense band at 1240 $cm^{-1}$ is associated with an asymmetric vibration of the C-O-C ether group. The C-C stretching mode of the saturated aliphatic structure was found at 1180 $cm^{-1}$. The absorption band at 1033 $cm^{-1}$ is attributed to the C-O-C symmetric vibration and at 830 $cm^{-1}$ to the asymmetric vibration of the epoxide group [29]. It was verified a broad band at 3360 $cm^{-1}$ in the pure resin with hardener (Fig. 4c) that can be related to OH vibrations of absorbed water molecules.

TG/DTG curves of the pure epoxy resins as well as initial and carbonated samples are presented in Figs. 5 and 6, respectively. For the pure epoxy blend without hardener (Fig. 5a,b; dash-dot lines), the first decomposition step is attributed to degradation of the polymeric chains of DGEBA epoxy resin, with an exothermic signal near 355°C (Fig. 5b). The second decomposition step at ca. 440°C, less intense, unveils the degradation of the polymeric chains of EPN epoxy resin, which is present in smaller amount in the blend and exhibits higher thermal resistance compared to DGEBA epoxy resin. For the pure epoxy blend with hardener (Fig. 5a,b; solid lines), the first decomposition step was observed around 135°C, being attributed to the moisture loss and degradation of oligomers or unreacted hardener (Fig. 5b). The second decomposition step at ca. 385°C unveils the degradation of the polymeric chains of both DGEBA and EPN epoxy resins [30,31].

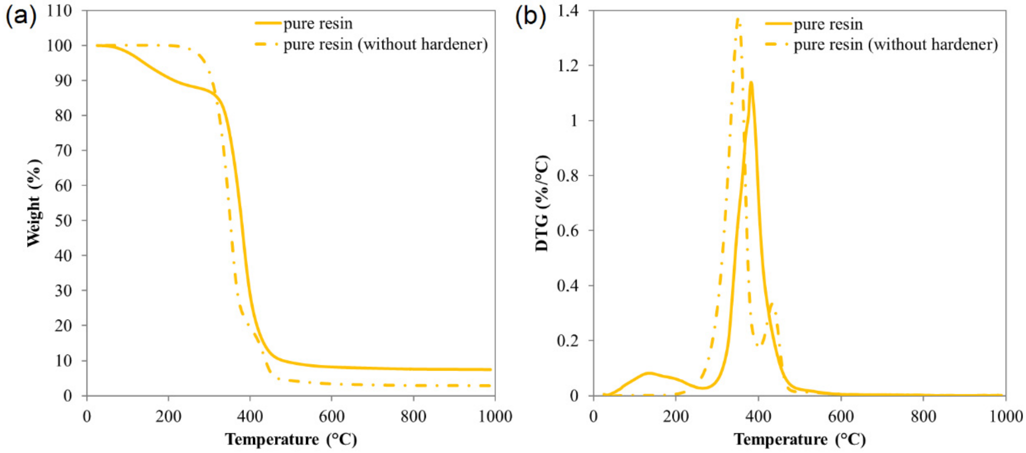

Fig. 5: TG/DTG curves for pure epoxy resins with (solid lines) and without (dash-dot lines) hardener. Note that pure resin was not exposed to $CO_2$.

TG/DTG curves for the initial pure cement (before $CO_2$ exposure) exhibit the first decomposition step attributed to the evaporation of adsorbed water at ca. 87°C (Fig. 6a,b). The second decomposition step, less intense, is associated with the initial dehydration of the C-S-H phase, being observed at 350°C [32]. The third decomposition step at 440°C is attributed to the dehydroxylation of $Ca(OH)_2$ [33]. The last decomposition step shows an overlapping of two exothermic peaks, the first one associated with the final stage of C-S-H dehydration, starting at ca. 480°C [32], and the second one at 715°C attributed to the decomposition of $CaCO_3$, which was probably formed due to exposure of the sample to air [32,34,35].

It is important to note that for the S1 and S2 composites (Fig. 6c,d,e,f), in both initial and NDL samples, temperatures are very close for degradation of the polymeric chains as well as initial dehydration of the C-S-H and dehydroxylation of $Ca(OH)_2$, in the 210°C-460°C temperature range. In addition, final stage of C-S-H dehydration and decomposition of $CaCO_3$ (formed by natural carbonation) are identified by the large peak at around 690°C.

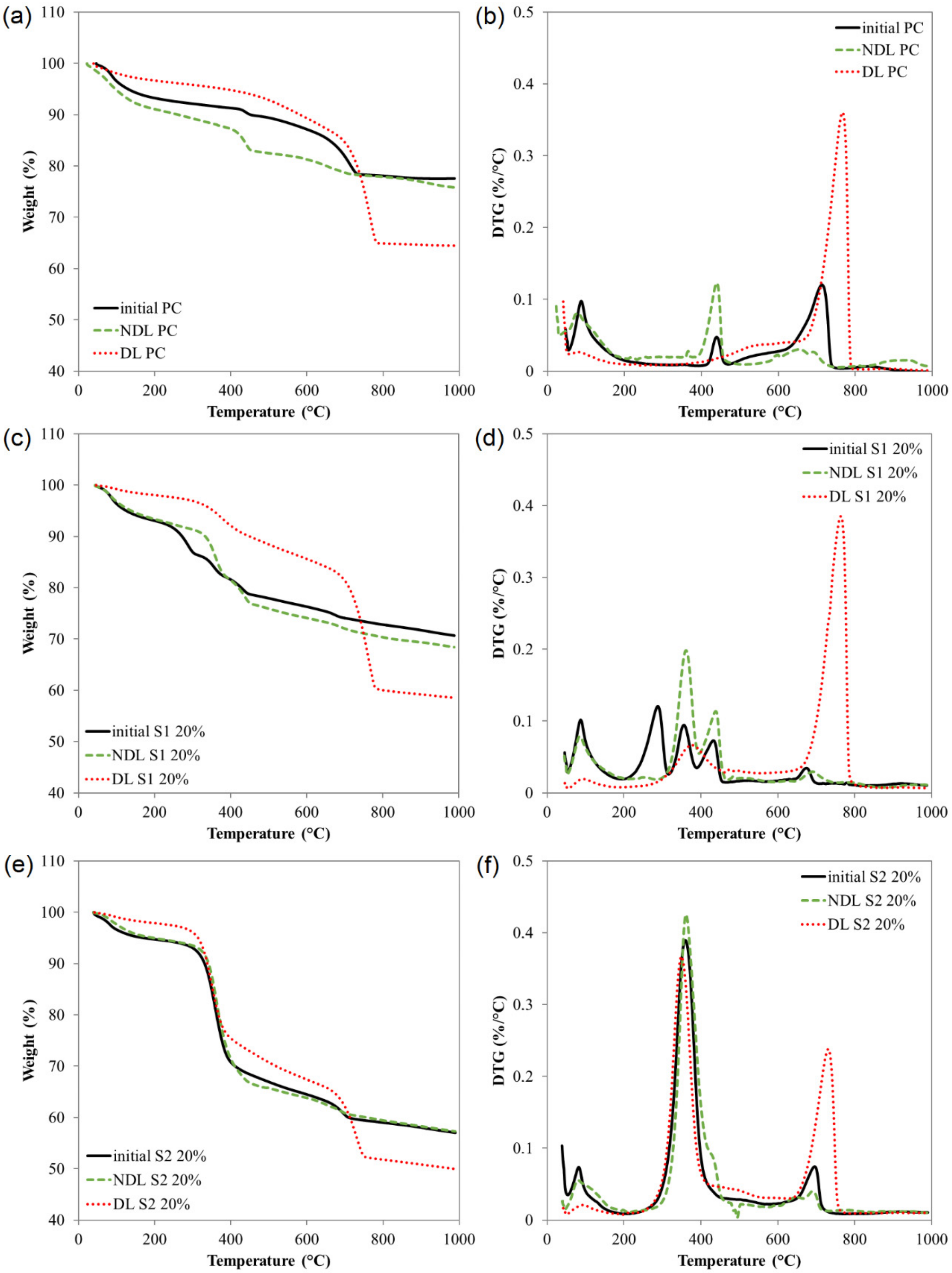

Fig. 6: TG/DTG curves for pure cement (PC) (a & b); S1 composite, without hardener (c & d); and S2 composite, with hardener (e & f) containing 20% epoxy resin. Non-degraded layer (NDL) means no penetration of $CO_2$, whereas degraded layer (DL) means penetration of $CO_2$ and reaction with $Ca(OH)_2$.

After $CO_2$ exposure, by comparing the thermograms for the pure cement, it is observed that TG/DTG curves for the NDL are similar to those of the initial sample: loss of water at 80°C, initial dehydration of C-S-H at 365°C, dehydroxylation of $Ca(OH)_2$ at 440°C and final stage of C-S-H dehydration near 650°C (Fig 6b) [32]. As verified for the initial pure cement, the NDL was also slightly affected by environmental $CO_2$ due to exposure to air, showing an exothermic signal around 695°C attributed to decomposition of $CaCO_3$. For the DL, loss of water is observed at 80°C and the peak associated to the degradation of $Ca(OH)_2$ is no longer identified. Indeed, an intense peak near 765°C attributed to degradation of $CaCO_3$ is well evidenced in this sample, confirming the formation of carbonate by the reaction of $Ca(OH)_2$ with dissolved $CO_2$ [32,34,35].

For both S1 and S2 composites (Fig. 6c,d,e,f), after exposure to $CO_2$, it is found in the DL a weight loss step between 240°C and 470°C associated with the degradation of the polymeric chains. Note that this thermal event is less intense in the S1 composite due to leaching of the epoxy resin. As for DL of the pure cement, dehydroxylation of $Ca(OH)_2$ is not observed. The intense exothermic signal around 750°C in the DL of both composites is attributed to the decomposition of $CaCO_3$ (Fig 6d,f).

## 4. Conclusions

Our results show that the S1 composites did not have satisfactory performance under common conditions encountered in deep $CO_2$ disposal. The epoxy resin can leach out of the cement matrix in the absence of a hardener, undermining the chemical resistance of cementitious materials. However, in the presence of a hardener, the S2 composites have shown an improvement on the resistance against $CO_2$ acidic attack compared to unmodified cement paste. The optimal epoxy resin content in the S2 composites was found to be up to 30% in order to reduce the cement degradation.

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