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Fluorescence Study of the Hydrolytic Degradation Process of Polysiloxane Coatings of Basalt Fibers

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Abstract

Surface basalt fibers were modified using different silanes aqueous solutions to generate different polyorganosiloxane coatings. After removing the commercial sizing of the basalt fibers by a calcination and subsequent activation processes looking for a surface silanol regeneration, polysiloxanes were grafted on the fibers surface. Three aqueous solutions were used for the silanization: i) γ -aminopropyltriethoxysilane, APTES; ii) γ -aminopropylmethyldiethoxysilane, APDES, and iii) a mixture them in a proportion of 50% by weight, APTES+APDES. The silanized basalt fibers were chemically labeled with fluorescein isothiocyanate to be afterwards immersed in different aqueous solutions at pH=7 in order to study the hydrolytic degradation of the polysiloxane coatings. The hydrolysis phenomena were monitored by steady state fluorescence at different temperatures to subsequently study the kinetics of the process. Furthermore, the hydrolysis process of the polyorganosiloxane coatings was also studied by monitoring as a function of time the pH of the solution where the silanized basalt fibers are immersed. The data obtained from fluorimetry were well fitted to an integrated expression arising from a first order kinetic process which subsequently allowed estimating the activation energies of the monitored hydrolytic degradations. All the results obtained pointed out that, although the hydrolytic rate of the polysiloxane coatings increased in the order APDES < APDES+APTES < APTES differences in mechanism were not the cause of that order but the initial concentration of siloxane bonds to be hydrolyzed.

Keywords: basalt fibers, polyorganosiloxane, hydrolytic degradation.

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1. INTRODUCTION

It is well known that performance of composite materials are greatly dependent on the interfaces formed between the materials used as the reinforcements and the matrices respectively [1,2]. In fact, properties of composite materials are strongly influenced by the type of adhesion between the reinforcement and the matrix. Therefore, surface modification of reinforcements through especial treatments has been one of the most common strategies to improve the adhesion or interphase properties in composites [3,4].

In particular, when silicic materials are used to reinforce other materials such as plastics and cement based materials, their surface treatments mainly consist in the application of silane coupling agents [5–7]. Among those silanes difunctional organosilicon compounds of general formula $Y-Si(X)_3$, are the most commonly used. X represents a hydrolysable group (such as methoxy, ethoxy or chlorine). These groups, after hydrolyzing to silanol, can react with other silanol groups present on the surface of the silicic material to form siloxane linkages. On the other hand, Y represents a non-hydrolysable organo-functional group (such as amino, mercapto or epoxy) physically or chemically compatible with the matrix [8–10].

Silane coupling agents are usually very effective in improving the interface region generated in the type of composites above mentioned [11–13]. In fact, a chemical bridge between the constituents of the composite is usually formed, creating an interphase with intermediate properties between the reinforcement and the matrix which may help the transmission of loads from the reinforcement to the matrix. Besides, it is generally stated that silane surface treatments of reinforcements provide a relatively water resistant bond [4,14,15]. However, the siloxane linkage is a hydrolysable bond highly dependent on pH [16,17].

In order to have information about possible hydrolytic degradation processes occurring at the interfaces of these composites, a deep study would be necessary in order to fully understand the final performance of the materials. One of the agents that might cause an interface failure is the water that, with a simple hydrolytical process, may lead to a weaker interaction between the reinforcement and the matrix, poorer transmission of

loads between them and consequently higher probability of a catastrophic mechanical failure.

In previous works, studies of the water effect on glass fiber/silane coupling agents interface were shown [14,18]. It was stated that when glass fibers are treated with hydrolyzed silane solution, multi-layers of the silane coupling agent, in particular when a trifunctional silane is used, are deposited on the fiber surface, being the first one achemically reacted layer, the second a chemisorbed layer and the third one a physisorbed layer. It was shown that the chemically reacted layer was characterized by a higher stability to hot water extraction which conferred the silanized substrate high resistance to hygrothermal attack. The chemisorbed layer, mainly consisted of oligomers with higher functionality in terms of siloxane bond formation, and possessed better resistance to hydrolysis than oligomers with lower crosslinking degree. Especially, this second layer could be extracted by boiling water after prolonged immersion. The outer part of the coating, the physisorbed layer, consisted of oligomers that did not form part of the siloxane network and that easily was hydrolyzed, being able to be extracted with water even at room temperature [14,18].

Taking into account the above mentioned, it is reasonable to think that the behavior under the effect of water and temperature could be different depending on the different chemical structures. Therefore, controlling the structure of the coating by the use of different silane systems grafted on the fibers may be a way of controlling hydrolysis phenomena. Then it is important to highlight here that, to understand the chemical mechanism of the hydrolytic degradation of a silane based coating should be crucial to help on designing materials in order to improve final performance of them against failure by hydrothermal degradation. All these aspects are especially important in the case of fiber reinforced concrete composites since their manufacture implies the mixture of their components with water.

D. Olmos et al [19] monitored the hydrolytic degradation of different polyorganosiloxanes coatings of silica microfibers by using fluorimetry. The method consisted on labelling the siloxane-based coating with a fluorescent dye and then following the fluorescence emission of an aqueous solution where the microfibers were immersed.

In the present work, basalt fibers (potential reinforcers of cement based materials) were modified with different aminosilanes to generate different polyorganosiloxane coatings. After that, they were labelled with fluorescein isothiocyanate. The high molar absorptivity at the wavelength of the argon laser (488nm), the large fluorescence quantum yield and high photostability of the fluorescein dye points it as a good choice, expecting it to be a very sensitive fluorescent label or probe. It is important to remember that fluorescein in aqueous solution occurs in cationic, neutral, anionic and dianionic forms what makes its absorption and fluorescence properties strongly pH dependent [20]. Once the fibers are fluorescence labeled the hydrolysis degradation of the polysiloxane coatings was monitored by pH variations and fluorimetry respectively. The influence of the pH and temperature on the kinetics of the hydrolytic process was also taken into account.

2. EXPERIMENTAL

2.1 Materials

Basalt continuous filaments with mean diameter 17 μm (Incothelogy GmbH) were used with a length of about 6.4 mm after being chopped. They were supplied with a commercial sizing compatible with cement and natural hydraulic lime (NHL) matrices. Two silanes, γ -aminopropyltriethoxysilane (APTES, chemical structure I) and γ -aminopropylmethyldiethoxysilane (APDES, chemical structure II), supplied by ABCR GmbH & Co.KG, were used to silanize the basalt fibers obtaining different surface coatings. Fluorescein isothiocyanate isomer I (FITC, chemical structure III), supplied by Sigma-Aldrich was used as fluorescent label. To prepare solutions of FITC *N,N*-Dimethylformamide, DMF, (Sigma-Aldrich) was used as solvent. Taking into account that the form of FITC in aqueous solution depends on the pH and therefore its fluorescence response, the experiments were carried out at controlled pH by using a buffer solution of neutral pH (potassium di-hydrogen phosphate, $\text{pH} = 7.0 \pm 0.02$ at 20°C , Scharlau).

2.2 Sample Preparation

Considering that the commercial fibers are already coated with sizing, a cleaning of their surface is necessary before applying a new coating in a controlled way. Indeed, a surface pre-treatment (calcination and activation processes) of the as-received basalt fibers and silanization process were carried out realized according to the methods described in reference [21]. After the silanization with with aqueous solutions of i) APTES, ii) APDES and iii) with a mixture of 50% by weight of APTES and APDES, the coated fibers were labeled as follows: 0.4 g of each sample were immersed in 25 mL of FITC (10^{-4} M) solution in DMF and stirred for 20 min at room temperature.

The isothiocyanate group of the FITC easily reacts with the amino group (NH_2) of the silane coupling agents to form a thiourea bond (Figure 1) [22,23].

FIGURE 1. Aminosilanes coupling agents and their expected reaction with fluoresceine isothiocyanate.

Finally, the labeled samples were washed with dimethylformamide (DMF) to remove all the physisorbed or non-reacted FITC and vacuum dried for at least 3h at 40 °C. [19,24,25]. The surface characterization of the modified basalt fibers was already carried out in reference [21].

2.3 Instrumental techniques

Degradation of the silane coatings was monitored by pH measurements at room temperature by using a Lab 745 pH-meter (SI Analytics). 0.35 g of silanized basalt fibers were introduced in a cellulose paper bag and hanged using a nylon thread to finally be immersed in a beaker with 30 ml of distilled and deionized water. The aqueous solution was continuously stirred while pH values were taken as a function of time for 24 hours. After the experiments, the water was evaporated from the remaining solutions and the residue was analyzed by Fourier-transformed infrared spectroscopy (FT-IR) in the transmission mode using a FTIR Spectrum GX (Perkin-Elmer). Spectra were recorded in the range 400–4000 cm^{-1} from the average of 20 scans with a resolution of 4 cm^{-1} .

On the other hand, the hydrolysis degradation was also studied by steady state fluorescence spectroscopy using an Edinburgh Instruments Co. fluorimeter. However, before monitoring the coatings hydrolysis, spectra of the FITC labeled fibers were taken from front face excitation using a solid sample holder placed at an angle of 15° respect to the excitation beam. Every spectrum was recorded between 500–700 nm, setting the excitation wavelength at 483 nm, with a dwell time of 0.1 s and excitation and emission slits at 10 and 7 nm.

In order to monitor the hydrolytic degradation of the polyorganosiloxane coatings, a thermostated cell holder was used, where a quartz cuvette with the aqueous solution (pH=7) is placed. The FITC labeled fibers were introduced in a very small cellulose paper bag, hanged using a nylon thread to be immersed in the aqueous solution continuously stirred with a magnetic bar. As the hydrolytic degradation is occurring, fragments of the labelled coating are released in solution leading to fluorescence which is recorded as a function of time. The experiments were carried out at different temperatures (25 °C, 35 °C, 40 °C and 45 °C). Fluorescence spectra were recorded for 10

h between 490–700 nm, setting the excitation wavelength at 483 nm, the dwell time at 0.1 s and excitation and emission slits at 4 nm. Finally, the hydrolysis was studied from the representations of the integrated fluorescence intensity (area of the fluorescence spectra) as a function of the immersion time.

In the Figure 2 a scheme of the hydrolytic degradation experiment using fluorescence spectroscopy is shown.

FIGURE 2. Scheme of the hydrolytic degradation experiment using fluorescence spectroscopy.

3. RESULTS AND DISCUSSION

3.1 pH measurements

In order to follow the processes occurring during the immersion of the modified basalt fibers in pure water, the pH of the aqueous solution was measured as a function of the immersion time (Fig. 3). The three plots showed similar profiles although with slope changes occurring at different immersion times depending on the type of aminosilane grafted on the fibers. In general, the plots can be divided in two regions: in the first one

the pH increases due to the amino groups protonation and in the second one the pH decreases due to the siloxane hydrolysis and subsequent silanol generation. Taking into account that both phenomena might occur simultaneously and that they have opposite tendency in terms of pH, the appearance of a maximum should indicate when the pH variation starts being controlled by the hydrolytic process.

Attending the immersion times at the maxima of the pH plots in Figure 3, an order for the hydrolytic degradation rate may be inferred for the coatings under study, APTES > APTES+APDES > APDES. Here it was considered that the faster the hydrolytic process the sooner it will control the pH variation of the solution

FIGURE 3. pH measurements of the silanized basalt fibers immersed in distilled and deionized water solution.

In order to prove that the coatings were removed from the basalt fibers surface due to the hydrolytic fragmentation FT-IR spectra were taken from the three residues remaining after evaporating the water (Fig. 4). The FT-IR spectra show the characteristic absorption bands (Table 1) attributed to the polyorganosiloxane generated on the fiber surfaces. In particular, in the high-energy region of the FTIR spectra ($3800\text{--}2800\text{ cm}^{-1}$) some characteristic bands of the different aminosilanes are present, the N-H stretching of the amino groups and the C-H stretching bands of the methylene, CH_2 , and methyl,

CH₃, groups. These results are in agreement with the FTIR spectra obtained for the three coatings on the fibers and reported in a previous work [21], pointing out that during the immersion of the fibers in the water fragments of the polyorganosiloxane coatings were incorporated to the solution due to hydrolysis.

FIGURE 4. FT-IR spectra of the residues obtained from the pH experiment.

Table 1. Absorption Bands of Aminosilanes [21,26].

ν (cm ⁻¹)	Absorption bands of Aminosilane
3400	ν (O-H)
3400-3300	ν_{as} (N-H)
2970-2960	ν_{as} (C-H) (CH ₃)
2930-2920	ν_{as} (C-H) (CH ₂)
1600	δ (N-H)
1483	δ (CH ₂)
1450	δ (CH ₂)
1440	δ (CH ₃)
1410	δ (Si-CH ₂)
1380	δ (CH ₃)
1260	ν (Si-C)
1160	ρ (CH ₃)
1100	ν_{as} (Si-OSi)
1100	ν_{as} (Si-OC)
1000	ν_{as} (Si-OSi)
950	δ (Si-OH)

However, with this method only a qualitative analysis of the hydrolytic process can be considered since this phenomenon is expected to be dependent on the pH of the solution and, as it was shown, the pH is continuously changing. Due to this, another method to study the hydrolytic phenomena should be taken into account.

3.2 Fluorescence experiments

In Figure 5 the normalized fluorescence spectra of the FITC chemically bonded to the silanized basalt fibers are shown. In all the cases a broad band centered at about 530 nm is observed in accordance with the fluorescence emission characteristics of FITC given by the dye supplier with a fluorescence maximum at a wavelength $\lambda_{\text{max}} = 520$ nm at pH = 9. However, slight variations can be observed in the whole profile of the fluorescence spectrum depending on the nature of the coating. It is observed that the higher the functionality of the silane (functionality order: APTES > APTES+APDES > APDES) the broader the fluorescence band is. This result may be explained considering more heterogeneous surroundings for the fluorophore when using a silane with higher functionality. In principle, with a silane with a high functionality regions with different crosslinking degrees can be obtained, leading to different environments to the FITC fluorescent label or more heterogeneity at a molecular scale. In Figure 5 is also added, as a control, the emission spectrum of the activated fibers evidencing an emission that can be considered negligible respect to the fluorescence emission from the silanized fibers modified with FITC.

FIGURE 5. Normalized fluorescence spectra of activated and labelled silanized basalt fibers

3.2.1 Hydrolysis monitoring by fluorimetry

For all the samples under study and at different temperatures in the Figure 6 the integrated fluorescence intensity of the aqueous solutions (pH = 7) where the fibers are immersed is represented as a function of the immersion time. In all cases, the fluorescence intensity quickly increases and then is stabilized reaching a plateau. On the other hand, it is observed that, at the beginning of the process, the slopes of the curves are different depending on the nature of the polyorganosiloxanes and the temperature. In terms of the coatings nature those slopes increase in the following order $APDES < APDES+APTES < APTES$. If a higher slope is associated to a faster hydrolytic process the fluorescence results are in accordance with the results obtained from the pH measurements. However, in this case the measurements are done at constant pH because a buffer solution was used. Besides, a higher temperature is translated into a higher hydrolytic rate as expected.

As it is described before, when the fibers surfaces are treated with hydrolyzed silane solution, in principle, three layers of silane coupling agents could be formed. Probably,

the effect of the increase of the temperature, in addition to produce the hydrolysis of the outer part of the coating, also is responsible of the hydrolysis of the second layer of oligomers deposited on the fibers surface.

Considering more amino groups susceptible of being reacted with FITC in the case of the APTES coating, one would expect more fluorescence intensity in the aqueous solution after hydrolysis during the fluorescence experiments. However, just the opposite was observed. Apart from considering that total fluorescence can be dependent on several external factors such as intensity of the lamp, a possible explanation may be the consideration of lower yield in the thio-urea formation due to steric hindrance. A high crosslinking degree in the polysiloxane coating may lead to lower accessibility to the amino groups and therefore less FITC attachment. In fact, that is what is expected taking into account the γ -aminopropyltriethoxysilane chemical structure proposed by Wang et al. after being reacted on silica based surfaces [27,28]. As those authors described, the structure of the γ -aminopropyltriethoxysilane is characterized by three different layer with different functionality in terms of cross-linking degree. The outer part, that consists in a small molecular oligomers is presumably the most accessible to allow the reaction between the amino groups and the isothiocyanate group of the fluorescent moiety. On the contrary, a more linear and open chemical structure expected for the difunctional silane, APDES, should allow easier reaction with the fluorescent moiety. Therefore, the results in terms of total intensity may be interpreted simply attending the FITC concentration. Higher amount FITC fluorophores should give higher fluorescence intensity after hydrolysis but without influencing the hydrolysis mechanism which only should depend on the nature of the siloxane coating and pH.

FIGURE 6. Integrated fluorescence intensity as a function of immersion time of the aqueous solution where the modified fibers are immersed: a) APTES, b) APTES+APDES and c) APDES.

3.2.2 Kinetic study of the hydrolytic degradation process

In order to carry out a kinetic study of hydrolytic degradation process of the basalt fibers coatings, the following equilibrium reaction is assumed for the hydrolysis of the siloxane bonds in the poliorganosiloxanes:

where Si-O-Si is the hydrolysable siloxane bond, and Si-OH is the silanol group formed after the hydrolysis.

Furthermore, another assumption is to consider that the direct and reversed reactions of the equilibrium represented by the equation (1) are first order reactions. On the other hand, if the initial concentration of the reactant is named “a” or $[\text{Si-O-Si}]_0 = a$ and the amount of siloxane reacted “x” then, the concentration of the siloxane groups at a given reaction time will be $[\text{Si-O-Si}]_t = (a - x)$ and the concentration of silanol groups generated will be $[\text{Si-OH}]_t = 2x$.

Consequently, for a first order reaction, the direct reaction rate could be expressed by $v_1 = k_1 [\text{Si-O-Si}]_t = k_1(a - x)$ while the reversed reaction rate would be $v_2 = k_2[\text{Si-OH}]_t = k_2 2x$ and therefore, the hydrolysis rate should be described by the difference between the direct reaction rate and the reversed reaction rate, $v_1 - v_2$. If that hydrolysis rate is expressed as the variation of the silanol production as a function of time, $d[\text{SiOH}]/dt$, the expression for the hydrolysis rate would be described by the equation (2)

$$v = \frac{1}{2} \frac{d[\text{Si-OH}]_t}{dt} = v_1 - v_2 = k_1(-x) - 2k_2x_t \quad (2)$$

Taking into account that when the equilibrium is reached there is not change in the silanol production, $d[\text{SiOH}]/dt = 0$, and that the siloxane reacted is named as x_e , the equation 2 could be written as

$$\frac{1}{2} \frac{d[\text{Si-OH}]_t}{dt} = 0 = k_1(-x_e) - 2k_2x_e \quad (3)$$

Rearranging the equation (3) an equilibrium constant. K_c , could be obtained as the ratio between the direct reaction rate and the reversed reaction rate, k_1/k_2 :

$$\frac{k_1}{k_2} = \frac{2x_e}{[\text{Si-O-Si}]_0 - x_e} = K_c \quad (4)$$

Besides, using equations (2) and (4) it can be written:

$$\frac{dx_t}{dt} = k_1 \frac{a}{2x_e} (x_e - x_t) \quad (5)$$

and, after variables separation in equation (5) and the corresponding integration equation 6 is obtained:

$$k_1 \cdot t = \frac{2x_e}{a} \ln \frac{x_e}{x_e - x} \quad (6)$$

If the fluorescent intensity, I, is proportional to the number of fragments released from the coating by the hydrolysis, and these fragments are proportional to the concentration of siloxane groups that have been reacted at a certain time, x, then I should be proportional to x.

$$x = D \cdot I \quad (7) \text{ where "D" is a constant.}$$

Introducing this relation in the expression (6) it will be obtained

$$k_1 \cdot t = \frac{2x_e}{a} \ln \frac{x_e}{x_e - D \cdot I} \quad (8)$$

After taking exponentials in Eq. (8) and rearranging an expression for fluorescent intensity as a function of reaction time is obtained:

$$I = \frac{x_e}{D} - \frac{x_e}{D} e^{-\frac{aK_1 t}{2x_e}} \quad (9)$$

Since for every sample x_e is a constant then eq. 9 can be simplified by

$$I = I_e - I_e e^{-ct} \quad (10).$$

Where I_e and c are constants that only depend on temperature

$$I_e = \frac{x_e}{D} \text{ and } c = \frac{aK_1}{2x_e} \quad (11)$$

To see the goodness of the mechanism proposed the data of the fluorescence intensity as a function of reaction or immersion time were fitted by the use of the equation (10).

Regardless of the sample and temperature, the fitting was quite good as can be seen in the Figure 7 where, as an example, the fits for the samples at the temperature of 25°C are shown. Therefore, as a first approximation, under the presence of water the degradation process of the three coatings studied can be described by a hydrolytic equilibrium reaction where both the direct and reversed reactions are first order reactions..

FIGURE 7. Examples of fluorescence data fitting by the integrated rate equation (9).

From here and accepting the mechanism proposed for the hydrolytic degradation, an estimation of the required time to reach the equilibrium can be done. The criterion chosen might be to take the time for which the fluorescence intensity of the fitted curve does not change more than 1%. Using this criterion, for different temperatures, the degradation times when the equilibrium is reached for all the samples were obtained (Table 2).

If faster hydrolytic degradation is translated to shorter time to reach the equilibrium, the hydrolytic degradation rates of the coatings could be ordered as follows: APTES > APDES+APTES > APDES. In principle, this result might have two possible explanations : i) different mechanism of the hydrolytic process as a function of the polyorganosiloxane structure and ii) differences in the initial concentration of the Si-O-Si bonds susceptible of being broken down by hydrolysis. The last explanation is based on the consideration that concentration of Si-O-Si bonds is expected to be dependent on the amount of attached silane and especially the crosslinking degree which, in fact, will be favored with the functionality of the silane. Therefore, when APTES is used to coat the fibers more amount of material and crosslinking degree is expected (Figure 8). On the contrary, when APDES (with a lineal structure) solution is applied to the basalt fibers less amount of attached material and siloxane bonds are expected (Figure 8). Results that can be found elsewhere from a deep characterization of the modified basalt fibers with APTES and APDES agree the above mentioned [21].

FIGURE 8. Expected chemical structures of the basalt fibers coatings after the treatments with APTES a) and APDES aqueous solutions b).

Table 2. Hydrolytic degradation times when the equilibrium is reached.

Temperature	t_{APTES} (min)	$t_{APTES+APDES}$ (min)	t_{APDES} (min)
25 °C	115 min	144 min	156 min
35 °C	117 min	140 min	170 min
40 °C	113 min	125 min	166 min
45 °C	103 min	122 min	137 min

In order to evaluate if a change of the mechanism is the main contribution to the variation in the hydrolytic degradation rate, the activation energy (E_a) values were estimated as a fitting parameter from the curve fittings as follows.

From equation (7) it can be said that

$$x_e = D \cdot I_e \quad (12)$$

Where I_e is the fluorescence intensity at the equilibrium that depends on temperature, $I_e(T)$. On the other hand, the k_1 can be assumed to be an Arrhenius like kinetic constant

$$k_1 = A e^{\frac{-E_a}{RT}} \quad (13)$$

where A is the pre-exponential factor, R the general gas constant, T the absolute temperature and E_a the activation energy of the process. Taking the equations 11, 12 and 13 it can be written:

$$c(T) = \left(\frac{a}{D}\right) \frac{1}{I_e(T)} A e^{\frac{-E_a}{RT}} \quad (14)$$

Since $c(T)$ and $I_e(T)$ values can be obtained as fitting parameters by using the fitting function (10), activation energies can be obtained from the ratios between expressions like the equation (14) at two different temperatures, T_i and T_j respectively.

$$\frac{c(T_i)}{c(T_j)} = \frac{I_e(T_i)}{I_e(T_j)} e^{-\frac{E_a}{R} \left(\frac{1}{T_i} - \frac{1}{T_j} \right)} \quad (15)$$

$$E_a = \frac{R}{\left(\frac{1}{T_i} - \frac{1}{T_j} \right)} \ln \left[\frac{I_e(T_i)}{I_e(T_j)} \cdot \frac{c(T_j)}{c(T_i)} \right] \quad (16)$$

Taking into account that four temperatures were studied for each sample, six combinations of pairs of temperatures in expression (16) can be used to obtain six activation energies. Therefore an apparent activation energy should be obtained from the average of those six values obtained. Table 3 gathers the average values of the average activation energies obtained for the hydrolytic degradation of the three coatings under study.

In principle, all the results are in agreement with other reported in previous studies where an activation energy of 23.6 kcal/mol was obtained for the hydrolysis of siloxane bonds [16].

Table 3. Averaged activation energy (E_a) values for the hydrolytic degradation of the three coatings under study.

	E_a (kcal/mol)
<i>APTES</i>	24
<i>APDES</i>	29
<i>APTES + APDES</i>	22

Taking into account the error in the values of the Table 3 it can be concluded that for the three coatings the activation energy of the hydrolytic process is the same and suggesting

therefore that the corresponding chemical mechanism is the same. Therefore other seems to be the reason of the different hydrolytic degradation rates observed for the three coatings.

In general, regardless of the reaction order a reaction rate increases with the initial concentration of the reactants; therefore it is reasonable to assume that the rate of the hydrolytic process was dependent on the initial concentration of siloxane bonds. From the thermogravimetric Analysis (TG) performed in a previous work for the same systems under study [21], it was possible to estimate the number of moles of siloxane bonds, $n_{\text{SiO-Si}}$, susceptible of being hydrolyze (Table 4) using the weight loss and molecular weight of the silane used (in the case of the mixture, APTES + APDES, an mean value between the molecular weights of the two silanes was used).. The estimated values of the number of mole values obtained form results are shown in the Table 4.

Table 4. Estimated values for the number of moles of Si-O-Si hydrolyzed bonds.

	<i>$n_{\text{Si-O-Si}}$</i> (mol)
<i>APTES</i>	4.7×10^{-5}
<i>APTES+APDES</i>	3.5×10^{-5}
<i>APDES</i>	4.5×10^{-6}

Assuming a first order reaction for the direct reaction of the hydrolytic process, at a hydrolytic reaction time, $t = 0$, the initial reaction rate, v_o , must be directly proportional to the initial concentration of siloxane bonds or the initial number of moles at constant volume.

$$v_o = \left(\frac{dl}{dt} \right)_{t=0} = \text{Constant} \cdot [\text{SiOSi}]_o \quad (17)$$

Where the values of v_o can be obtained from the initial slope of the curves of integrated fluorescence intensity as a function of immersion time and the values of the initial number of moles of siloxane bonds can be taken from the Table 4. If there were a clear dependence between the initial concentration of siloxane bonds and the hydrolytic rate one would expect the same values for the ratios between the initial reaction rates for two coatings and the ratios between the corresponding initial number of moles of siloxane bonds.

$$\frac{v_o(APTES)}{v_o(APDES)} = \frac{n_{SiOSi}^o(APTES)}{n_{SiOSi}^o(APDES)} \quad (18)$$

Where $n_{SiOSi}^o(coating)$ represents the initial number of moles of siloxane bonds of a particular polysiloxane coating.

For a better comparison the ratios between initial reaction rates and the ratios between initial number of moles are gathered in Table 5. As can be seen the ratios are quite coincident, suggesting that the initial concentration of siloxane bonds is the main reason of the different hydrolytic degradation rates observed for the coatings under study. which

Table 5. Dependence of the concentration Si-O-Si bonds and the hydrolytic degradation rate

	$n_{Si-O-Si}/n_{Si-O-Si}$	$(dI/dt)_{Silane\ i}/(dI/dt)_{Silane\ j}$
<i>APTES/APDES</i>	10.4	9.2
<i>APTES+APDES/APDES</i>	7.8	4.2
<i>APTES/APTES+APDES</i>	1.3	1.9

4. CONCLUSIONS

The use of fluorescence of the fluorescein isothiocyanate is a good method to evaluate the hydrolytic degradation of very small concentration of polyorganosiloxanes coatings, grafted on the basalt fibers. The kinetic mechanism of the hydrolysis process proposed in this work, allowed to obtain information about the activation energy of the three systems studied. Besides, an evaluation of the equilibrium degradation times for the different polyorganosiloxanes is determined. The results obtained with different measurements systems are in agreement..

The results demonstrate that the mechanism of the hydrolytic process is very similar for the three systems studied. Nevertheless, some differences are observed in the rate of the hydrolytic degradation process. Indeed, the hydrolytic degradation rate is related to the initial concentration of the Si-O-Si bonds and consequently to the number of the hydrolyzed siloxane bonds. This number is higher when a silane with a cross-linked structure is used. Furthermore, the hydrolytic degradation of the silane coupling agents is faster, depending on the increase of the siloxane crosslinking degree.

It could be assumed that a way to reduce the rate of hydrolytic degradation at the interface in the composite reinforced concrete would be to minimize the degree of coating. A polyorganosiloxane with a lower crosslinking degree and so with a lower amount of Si-O-Si bonds, like the APDES coating, could be the more effective to resist an a possible water attack.

References:

- [1] Y.-W.M. and Y.-W.M. Jang-Kyo Kim, Engineered Interfaces in Fiber Reinforced Composites, 1st Editio, 1998. doi:<https://doi.org/10.1016/B978-008042695-2/50000-2>.
- [2] M.J. Salkind, The Role of Interfaces in Fiber Composites, in: Surfaces Interfaces II, 1968: pp. 417–445. doi:10.1007/978-1-4757-0178-4_14.
- [3] A.T. DiBenedetto, Evaluation of fiber surface treatments in composite materials, Pure Appl. Chem. 57 (1985) 1659–1665. doi:10.1351/pac198557111659.
- [4] N. Suzuki, H. Ishida, A Review on the Structure and Characterization Techniques of Silane/Matrix Interphases, 108 (1096) 19–53.
- [5] Y. Xie, C.A.S. Hill, Z. Xiao, H. Militz, C. Mai, Composites : Part A Silane coupling agents used for natural fiber / polymer composites : A review, Compos. Part A. 41 (2010) 806–819. doi:10.1016/j.compositesa.2010.03.005.
- [6] S.J. Park, J.S. Jin, J.R. Lee, Influence of silane coupling agents on the surface energetics of glass fibers and mechanical interfacial properties of glass fiber-reinforced composites, J. Adhes. Sci. Technol. 14 (2000) 1677–1689. doi:10.1163/156856100742483.
- [7] S. Shokoohi, A. Arefazar, R. Khosrokhavar, Silane coupling agents in polymer-based reinforced composites: A review, J. Reinf. Plast. Compos. 27 (2008) 473–485. doi:10.1177/0731684407081391.
- [8] Plueddemann E.P., Chemistry of Silane Coupling Agents, in: Silane Coupling Agents, Springer, Boston, MA, 1991: pp. 31–54. doi:https://doi.org/10.1007/978-1-4899-2070-6_2.
- [9] G.L. Witucki, BACK TO BASICS A Silane Primer : Chemistry and Applications of Alkoxy Silanes, A J. Coatings Technol. Repr. (1992).
- [10] Y. Xie, C.A.S. Hill, Z. Xiao, H. Militz, C. Mai, Silane coupling agents used for natural fiber/polymer composites: A review, Compos. Part A Appl. Sci. Manuf. 41 (2010) 806–819. doi:10.1016/j.compositesa.2010.03.005.
- [11] J.G. Iglesias, J. González-Benito, A.J. Aznar, J. Bravo, J. Baselga, Effect of

Glass Fiber Surface Treatments on Mechanical Strength of Epoxy Based Composite Materials, *J. Colloid Interface Sci.* 250 (2002) 251–260. doi:10.1006.

- [12] D. Olmos, J. González-Benito, Visualization of the morphology at the interphase of glass fibre reinforced epoxy-thermoplastic polymer composites, *Eur. Polym. J.* 43 (2007) 1487–1500. doi:10.1016/j.eurpolymj.2007.01.004.
- [13] M. Afroz, I. Patnaikuni, S. Venkatesan, Chemical durability and performance of modified basalt fiber in concrete medium, *Constr. Build. Mater.* (2017). doi:10.1016/j.conbuildmat.2017.07.153.
- [14] H. Ishida, J.L. Koenig, A Fourier-Transform Infrared Spectroscopic Study of the Hydrolytic Stability of Silane Coupling Agents on E-Glass Fibers, *J. Polym. Sci. Polym. Phys. Ed.* 18 (1980) 1931–1943.
- [15] C.C. Le-huy, L.G. Britcher, J.G. Matisons, The effect of silane concentration on the adsorption of poly (vinyl acetate-co-maleate) and γ -methacryloxypropyl-trimethoxysilane onto E-glass fibers, (2002) 195–196.
- [16] H. Ishida, J.L. Koenig, The reinforcement mechanism of fiber- glass reinforced plastics under wet conditions: A review, *Polym. Eng. Sci.* 18 (1978) 128–145. doi:10.1002/pen.760180211.
- [17] H. Ishida, J.L. Koenig, Effect of Hydrolysis and Drying on the Siloxane Bonds of a Silane Coupling Agent Deposited on E-Glass Fibers, 18 (1980).
- [18] K. Jang-Kyo, M. Yiu-Wing, M. Yiu-Wing, SURFACE TREATMENTS OF FIBERS AND EFFECTS ON COMPOSITE PROPERTIES, in: *Eng. Interfaces Fiber Reinf. Compos.*, Ltd, Elsev, 1998: pp. 171–237. doi:https://doi.org/10.1016/B978-008042695-2/50006-3.
- [19] D. Olmos, A.J. Aznar, J. Baselga, Hydrolytic damage study of the silane coupling region in coated silica microfibres : pH and coating type effects, 144 (2003) 82–86. doi:10.1016/S0924-0136(03)00325-X.
- [20] R. Sjback, J. Nygren, M. Kubista, Absorption and fluorescence properties of fluorescein, 51 (1995).
- [21] M. Iorio, M.L. Santarelli, G. González-gaitano, J. González-benito, Applied Surface Science Surface modification and characterization of basalt fibers as

- potential reinforcement of concretes, *Appl. Surf. Sci.* 427 (2018) 1248–1256.
doi:10.1016/j.apsusc.2017.08.196.
- [22] G.T. Hermanson, *Fluorescent Probes, Bioconjugate Tech.* (Third Ed. (2013) 395–463. doi:<https://doi.org/10.1016/B978-0-12-382239-0.00010-8>.
- [23] A. Imhof, M. Megens, J.J. Engelberts, D.T.N. De Lang, R. Sprik, W.L. Vos, *Spectroscopy of Fluorescein (FITC) Dyed Colloidal Silica Spheres*, (1999) 1408–1415. doi:10.1021/jp983241q.
- [24] D. Olmos, A.J. Aznar, J. Baselga, J. González-Benito, Kinetic study of epoxy curing in the glass fiber/epoxy interface using dansyl fluorescence, *J. Colloid Interface Sci.* 267 (2003) 117–126. doi:10.1016/S0021-9797(03)00620-9.
- [25] J. González-Benito, A. Aznar, J. Baselga, Solvent and Temperature Effects on Polymer-Coated Glass Fibers . Fluorescence of the Dansyl Moiety, *J. Fluoresc.* 11 (2001).
- [26] C.-H. Chiang, H. Ishida, J.L. Koenig, The structure of γ -aminopropyltriethoxysilane on glass surfaces, *J. Colloid Interface Sci.* 74 (1980) 396–404. doi:[https://doi.org/10.1016/0021-9797\(80\)90209-X](https://doi.org/10.1016/0021-9797(80)90209-X).
- [27] D. Wang, F.R. Jones, P. Denison, Surface analytical study of the interaction between γ -amino propyl trethoxysilane and E-glass surface-Part I Time-of-flight secondary ion mass spectrometry, *J. Mater. Sci.* 27 (1992) 36–48.
- [28] D. Wang, F.R. Jones, Surface analytical study of the interaction between γ -amino propyl trethoxysilane and E-glass surface-Part II X-ray photoelectron spectroscopy, *J. Mater. Sci.* 28 (1993) 2481–2488.