

Organic-inorganic materials through first simultaneous frontal polymerization and frontal
geopolymerization

Original

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Materials Letters

Organic-inorganic materials through first simultaneous frontal polymerization and frontal geopolymerization --Manuscript Draft--

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Corresponding Author:	Alberto Mariani, Professor, PhD Universita degli Studi di Sassari Dipartimento di Chimica e Farmacia Sassari, ITALY
First Author:	Valeria Alzari
Order of Authors:	Valeria Alzari
	Elie Kamseu
	Cristina Leonelli, Professor
	Alberto Spinella
	Giulio Malucelli, Professor
	Greta Bianco
	Daniele Nuvoli
	Davide Sanna
	Francesco Armetta
	Mariella Rassu
	Alberto Mariani, Professor, PhD
Abstract:	The first frontal geopolymerization (FGP) took place in the same reaction medium in which the frontal polymerization (FP) of 1,6-hexanediol diacrylate (HDDA) was occurring, thus giving rise to an organic-inorganic hybrid in one step in just a few minutes. Because of their exothermicity, the two reactions support each other and sustain propagating fronts. By contrast, using the classical techniques (prolonged heating) instead of FP, due to large gas formation the reaction is explosive or, if carried out at room temperature, phase separation occurred



uniss

DIPARTIMENTO DI CHIMICA
E FARMACIA

via Vienna, n. 2, 07100 Sassari (Italy)

t +39 079 229535

dip.chimica.farmacia@pec.uniss.it

www.uniss.it

Alberto Mariani

PROFESSORE DI CHIMICA INDUSTRIALE

mariani@uniss.it

tel.: +39 079229556 - +39 3382751583

Sassari, Feb. 2nd, 2021

Prof. Aldo Boccaccini
Editor in Chief
Materials Letters

Dear Prof. Boccaccini,

I am submitting the revised version of our manuscript entitled

Organic-inorganic materials through first simultaneous frontal polymerization and frontal geopolymerization

Valeria Alzari,^{*a} Elie Kamseu,^b Cristina Leonelli,^b Alberto Spinella,^c Giulio Malucelli,^d Greta Bianco,^a Daniele Nuvoli,^a Davide Sanna,^a Francesco Armetta,^e Mariella Rassu,^a Alberto Mariani,^{*a}

** corresponding authors: valzari@uniss.it; mariani@uniss.it*

MLBLUE-D-20-04709

First of all, please notice that **Prof. Giulio Malucelli has been added as a coauthor.**

Indeed, he performed the characterization of the mechanical properties, now included as requested by the referee. All coauthors agree to add him.

Response to the reviewer (in bold):

COMMENTS FROM EDITORS AND REVIEWERS

Reviewer #1: The paper is an original branch belonging to the Geopolymers tree. Interesting paper which deserves publication at Materials letters. However I consider there are a few points should be briefly commented in the paper.

**Nothing is mentioned about the mechanical characteristics of the hybrid material. How the presence of the organic component affect the mechanical development of the Geopolymer component.*

- The mechanical properties have now been added in the new section "3.3

Evaluation of the mechanical properties” and in Table 2.

**Only Al NMR is given in the manuscript. It would help to understand the reactions occurring in these systems if ²⁹Si NMR spectra of MK, Geopolymer and Hybrid, were analysed in the paper*

- ²⁹Si NMR spectra have now been added in section 3.2 MAS NMR and in Figure 4.

**It would be of great help if chemical reactions were described in the traditional way of chemical equations.*

- Figure 1 and eq. 1 have been added on this purpose.

Limitations of space should not be a problem for including all these clarifications.

- This was very appreciated. Indeed, the addition of the new data requested by the reviewer resulted in a number of words exceeding that indicated for the first submission.

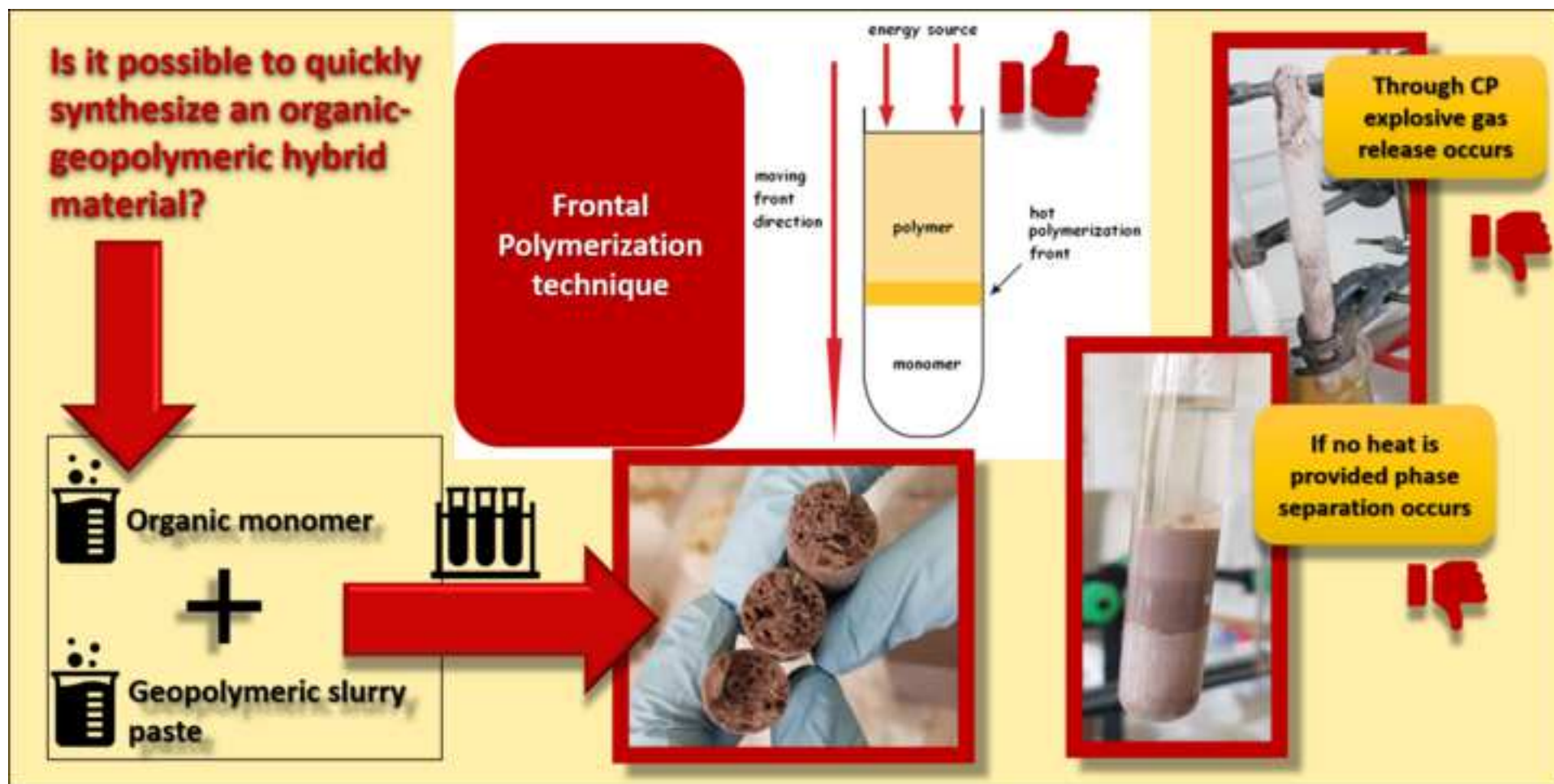
We do hope that present version can be accepted and published on Materials Letters.

Also on behalf of my coauthors, I do thank you, your collaborators and the reviewers for your kind help to improve the quality of the manuscript.

With my best regards



Prof. Alberto Mariani



Highlights

- A MK-based geopolymer paste frontally reacted together with an organic monomer
- The organic monomer sustained polymerizing front in a 90-100 s consolidation process
- Concurrent geopolymerization of MK was proved by solid state NMR
- The hybrid composite showed excellent wettability between inorganic and organic phases

Organic-inorganic materials through first simultaneous frontal polymerization and frontal geopolymerization

Valeria Alzari,^{*a} Elie Kamseu,^b Cristina Leonelli,^b Alberto Spinella,^c Giulio Malucelli,^d Greta Bianco,^a

Daniele Nuvoli,^a Davide Sanna,^a Francesco Armetta,^e Mariella Rassu,^a Alberto Mariani,^{*a}

^{*} corresponding authors: valzari@uniss.it; mariani@uniss.it

^a Department of Chemistry and Pharmacy, University of Sassari, Via Vienna 2, 07100 Sassari, Italy.

^b Department of Engineering "Enzo Ferrari", University of Modena and Reggio Emilia, Via P. Vivarelli
10, 41125 Modena, Italy.

^c ATeN Center, Università degli Studi di Palermo, Via F. Marini 14, 90128 Palermo, Italy.

^d Department of Applied Science and Technology, Politecnico di Torino, and Local INSTM Unit, Viale
T. Michel 5, 15121 Alessandria - Italy

^e Dipartimento Scienze e Tecnologie Biologiche, Chimiche e Farmaceutiche – STEBICEF, Università
degli Studi di Palermo, Parco d'Orleans II, Viale delle Scienze, 90128, Palermo, Italy.

keywords: geopolymer, frontal polymerization, frontal geopolymerization, hybrid

Abstract

The first frontal geopolymerization (FGP) took place in the same reaction medium in which the frontal polymerization (FP) of 1,6-hexanediol diacrylate (HDDA) was occurring, thus giving rise to an organic-inorganic hybrid in one step in just a few minutes. Because of their exothermicity, the two reactions support each other and sustain propagating fronts. By contrast, using the classical techniques (prolonged heating) instead of FP, due to large gas formation, the reaction is explosive or, if carried out at room temperature, phase separation occurred.

1. Introduction

Frontal Polymerization exploits the formation and propagation of a hot polymerization front that converts monomer into polymer thanks to the exothermicity of the reaction itself. [1-6]

Inert components, such as solvents or fillers, can be responsible for unsuccessful FP experiments.

Actually, water can prevent FP because it dilutes the monomer, has a large heat capacity, and has a relatively low boiling point (with further high heat absorption). [5]

For analogous reasons, since polycondensations are generally not sufficiently exothermic, only frontal polyadditions have been reported so far. [1,6]

Geopolymers are crosslinked inorganic materials easily obtained from many common materials by simple and cheap chemical modifications. [7,8] One of the well-known raw materials to produce chemico-mechanically stable geopolymers is metakaolin alkali-activated by a solution of NaOH and Na₂SiO₃ at room temperature, which consolidates to a ceramic-like product in a few hours. [9]

In this work, for the first time, an organic-inorganic hybrid was obtained by simultaneously frontally polymerize an acrylic monomer and a geopolymeric paste, thus in one step resulting in a hybrid composed of two types of materials.

2. Experimental

Materials. HDDA, NaOH were from Sigma-Aldrich; 35% Na₂SiO₃ from Merck; Metakaolin (MK) from Ceske Lupkove Zavody); Trihexyltetradecylphosphonium Persulfate (TETDPPS) was synthesized according to [10].

Frontal Polymerization of HDDA. In a glass test tube, HDDA was mixed with 1wt% of TETDPPS (radical initiator). The tube (1.6 cm x 15 cm) was filled with the mixture. A K-type thermocouple connected to a digital recorder was inserted at about 1-2 cm from the bottom of the tube to record front temperature (T_{max}) and determine front velocity (V_f). FP started by heating the external wall of the tube with a soldering iron in correspondence of the upper surface of the mixture.

Geopolymerization. To the “alkaline activating solution” (AAS: 8M NaOH + 35% Na₂SiO₃, 1:1 v/v) MK was added (MK:AAS=2:1 wt./wt.) and stirred to form a homogeneous paste, which was poured into a silicon mold and keep at room temperature for 24 h.

Simultaneous FP and FGP. HDDA, TETDPPS and MK (up to 44 wt.-%) were mixed vigorously. AAS was added; the obtained paste was transferred into a glass test tube and frontally polymerized (HYBRID sample) as above.

Table 1 Samples, compositions and synthetic parameters

Sample	Composition	Technique & conditions	Notes	T _{max} (°C)	V _f (cm/min)
Poly(HDDA)	Blank sample, the organic polymer	FP	SUCCESSFUL PROCEDURE	192	4.0
GEOPOLYMER	Blank sample made from MK and AAS	r.t., 24 h	SUCCESSFUL PROCEDURE	-	-
COMPOSITE	Poly(HDDA) with MK as a filler (44 wt.-%) – no water present	FP	SUCCESSFUL PROCEDURE <i>No phase separation. MK is inert and dissipates heat.</i>	160	3.8
HYBRID	Poly(HDDA) containing geopolymer (from AAS and MK 44 wt.-%)	FP + FGP	SUCCESSFUL PROCEDURE <i>No phase separation. Even if water dissipates heat, geopolymerization is exothermic and sustains fronts.</i>	119	4.0
HYB-RT	Same starting materials as HYBRID	r.t.	UNSUCCESSFUL PROCEDURE <i>No reaction before phase separation occurrence (3-5 min)</i>	-	-
HYB-CP	Same starting materials as HYBRID	80 °C, 1 h	UNSUCCESSFUL PROCEDURE <i>Explosive gas release. No hybrid formation.</i>	-	-

²⁷Al and ²⁹Si MAS NMR spectra were acquired by a Bruker Avance II 400 spectrometer operating at a frequency of 104.26 and 79.49 MHz for the ²⁷Al and ²⁹Si nuclides respectively.

²⁷Al MAS NMR experiments were performed by direct polarization using a 2.5 mm MAS probe at a spinning speed of 20 KHz, with a 15° pulse on the ²⁷Al nuclide of 3 μs, 128 scans and a delay time of 3 s.

²⁹Si MAS NMR spectra experiments were performed by direct polarization using a 4 mm MAS probe at a spinning speed of 6 kHz, with a 90° pulse of 4.9 μs, 512 scans and a delay time of 30 s. Spectra deconvolution was performed by pure gaussians and using the Levenberg-Marquardt algorithm for the fitting procedure.

SEM analysis was performed by SEM FEI Quanta 200, High vacuum mode, by mounting a small fractured specimen on SEM holder, using double sided carbon tape. Freshly fractured surfaces were investigated. Compression tests, according to ASTM D695, were performed using a Zwick-Roll Z010 apparatus, equipped with a 100 kN load cell, at 23 ± 2 °C and 50 ± 5% relative humidity. For each material, samples were cut in small cylinders 1 cm high, and at least five tests were repeated for each sample. The standard deviation was always below 5%.

3. Results and discussion

3.1 Syntheses

The scheme of the reactions involved in this work are depicted in Figure 1 and eq 1.

HDDA was selected because of our previous studies on its FP inside stones [11,12] for restorative consolidation. It showed good compatibility and high reactivity.

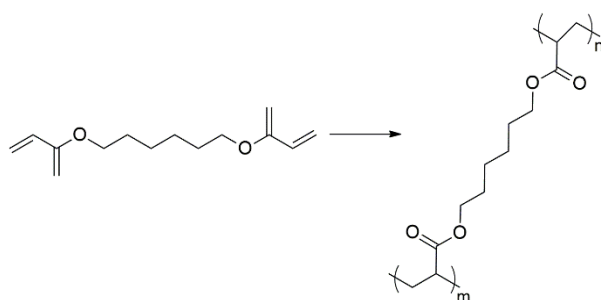
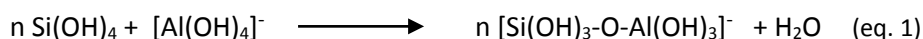


Figure 1 Polymerization of HDDA: crosslinked poly(HDDA) is formed.

By preliminary tests, it was found that both azobisisobutyronitrile and benzoyl peroxide were not compatible enough with the reaction medium; moreover, they were responsible for a large bubble generation due to gas releasing. For these reasons, TETDPPS was used as the radical initiator, which is soluble both in water and HDDA, and supports low temperature fronts. [10]

The whole system is made of two main components: the acrylate monomer HDDA and the inorganic component based on geopolymeric slurry paste (MK+ AAS).

The reaction related to the reticulation of the geopolymeric phase can be summarized as condensation (as in eq. 1) of two (or more) Si(OH)_4 and $[\text{Al(OH)}_4]^-$ tetrahedral units to form an aluminosilicate chain, ring or more complex 3D networks, as in amorphous glass structure.



While FP of HDDA is well known, [11,12] some preliminary experiments were performed to establish the maximum amount of MK allowing it to occur.

It was noticed that (Figure 2): i) front positions as a function of time are straight lines, thus indicating that fronts moved at constant velocity; ii) temperature profiles are constituted of a horizontal line (temperature recorded far from the incoming fronts), followed by a sharpen increase (hot propagating fronts crossing the thermocouple junction).

The above evidences are consistent with the occurrence of “pure” FP: fronts were self-sustaining (no deceleration was observed), and that was most probably the only reaction occurring. Indeed, if it was not the case, a temperature variation before its sudden increase should be observed.

To determine pot lives, temperature profiles of non-ignited mixtures were also recorded. Apart from HDDA, in all other cases temperature did not change up to phase separation occurrence, which typically happened after 3-5 minutes. This confirms that pot lives are long enough for pure FP occurrence.

However, it was found that MK amounts > 44 wt.% resulted in an excessive heat dissipation, which prevented fronts to self-sustain.

It was found that HDDA frontally polymerized if:

i) water (alone or in AAS) was not present: the large amount of heat that water absorbs hardly allows fronts to self-sustain; namely, only poly(HDDA) and COMPOSITE, both synthesized in absence of water, were obtained.

ii) AAS was present together with MK, giving rise to HYBRID sample. In fact, if only AAS is present, no reaction occurs. This indicates that only in the presence of both MK and AAS - which mutually react to give the geopolymer - the polymerizing front of HDDA can self-sustain, even in aqueous medium. This is

a first evidence that FP occurs simultaneously to FGP, both contributing to whole exothermicity needed for the two fronts to propagate.

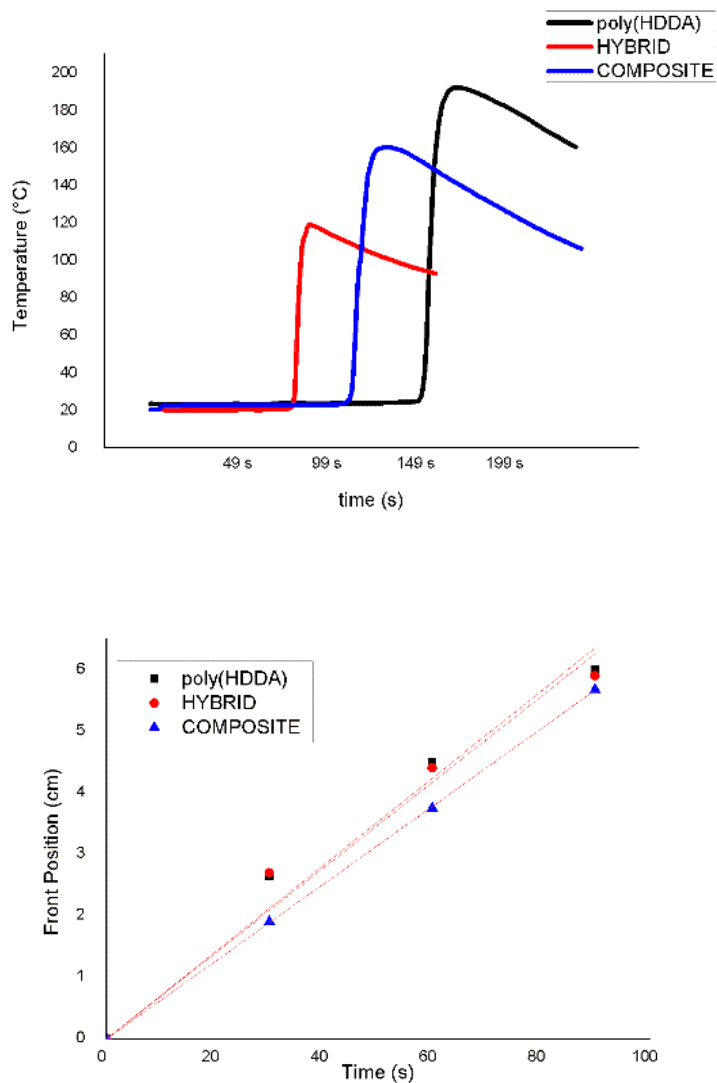


Figure 2 Temperature profile of FP runs (top); Front positions as a function of time (bottom).

These experiments confirm that it is possible to obtain the HYBRID sample only through simultaneous FP and FGP, because in other conditions (for example, by classical polymerization, CP, or keeping the mixture at room temperature) no reaction occurs, also because of phase separation occurrence. Besides, the exothermicity of the FP reaction of HDDA is necessary to support the simultaneous FGP, and this latter contributes to the overall heat release thus allowing the organic FP to occur.

3.2 MAS NMR

²⁷Al MAS NMR spectra are reported in Figure 3.

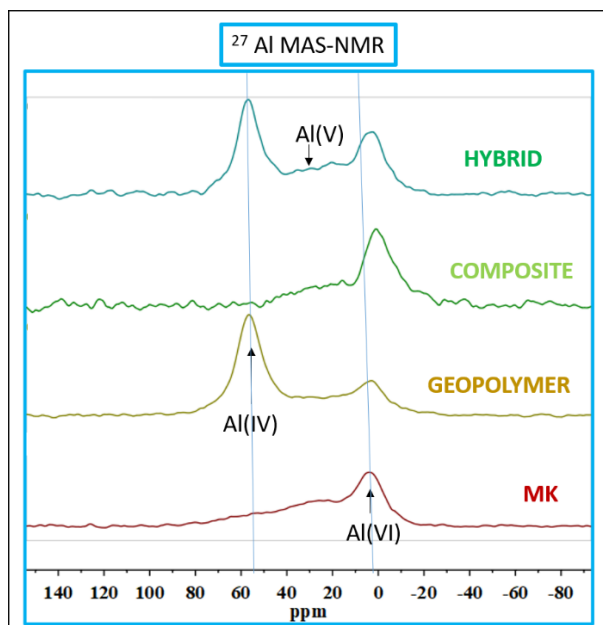


Figure 3 ^{27}Al MAS NMR spectra of the synthesized samples.

In the MK spectrum, three signals are present. The intense resonance at 2.5 ppm is due to aluminum in octahedral coordination. The two broad signals at 28 and 58 ppm indicate pentacoordinated and tetraordinated aluminum, respectively. The spectrum of GEOPOLYMER shows a very intense resonance at 58 ppm due to the tetraordinated aluminum and a residual signal at 2.5 ppm due to unreacted MK. This indicates undoubtedly the geopolymerization occurrence. [15] These coordination changes, although to a lesser extent, were observed by comparing the spectra of MK and HYBRID samples, thus confirming that FGP took place.

In order to corroborate the previous evidences and deeply understand the reactions occurring in these systems, ^{29}Si MAS NMR spectra were acquired for the MK, GEOPOLYMER and HYBRID materials.

It is well known that ^{29}Si spectra of the aluminosilicate materials are constituted by resonances due to silicon atoms in tetrahedral environment ($\text{Q4}(\text{nAl})$ species). This latter notation indicates the number of -OAl species that substitute an -OSi around a silicon atom [16]. Thus, in such spectra there will be five signals indicated as $\text{Q4}(\text{0Al})$, $\text{Q4}(\text{1Al})$, $\text{Q4}(\text{2Al})$, $\text{Q4}(\text{3Al})$, $\text{Q4}(\text{4Al})$ in a range from -80 to -110 ppm. The higher is the number of -OAl species the higher chemical shift will be.

^{29}Si MAS NMR spectra of geopolymers show very broad resonances and the lack of resolution can be overcome by signal deconvolution [17].

²⁹Si MAS NMR spectra obtained for the MK, GEOPOLYMER and HYBRID samples are reported in Figure 4.

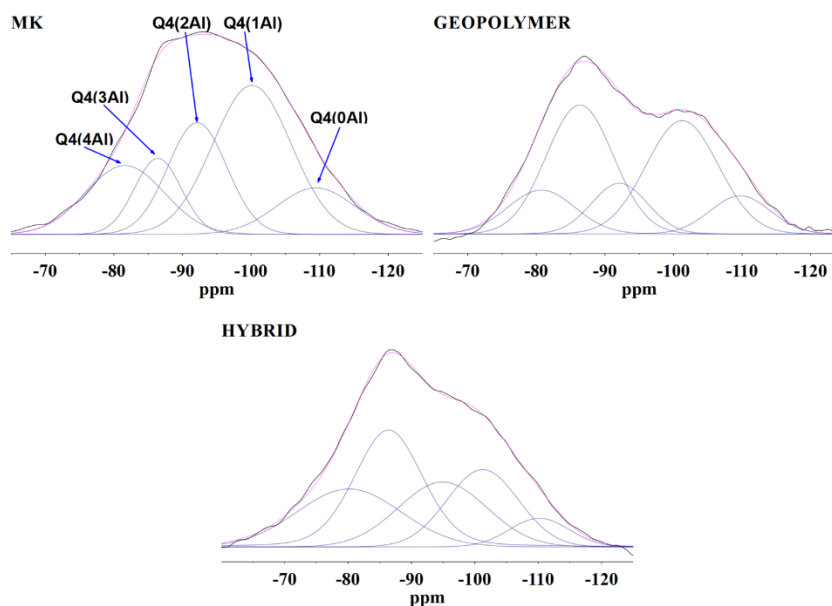


Figure 4 ²⁹Si MAS NMR spectra of the MK, GEOPOLYMER and HYBRID samples together with signal deconvolution.

The spectrum of the MK starting material is characterized by the main resonance at 100 ppm due to the Q4(1Al) species (38.5%) typical of metakaolin. Furthermore, less intense signals due to the other silicon species are also present (Q4(4Al), Q4(3Al), Q4(2Al) and Q4(0Al)). This latter is probably due to residual quartz belonging to the starting kaolinite.

In the spectra of the GEOPOLYMER and HYBRID samples the most abundant species is the Q4(3Al) (29.6 and 26.1% respectively) confirming the geopolymerization occurrence. In both samples Q4(4Al), Q4(3Al) and Q4(2Al) signals due to silicate oligomers not bonded to the geopolymeric gel are still present. This indicates a not quantitative geopolymerization and confirms the results of the ²⁷Al MAS NMR analysis.

It is worth noting that FP allows the geopolymer network formation in just a few minutes leading to results similar to the CP ones. This represents an absolute novelty in geopolymerization, which is generally characterized by much longer reaction times (typically, hours).

3.3 Morphological Analysis

SEM analysis was performed on all samples (Figure 5). While poly(HDDA) presents a homogeneous and

very smooth surface, GEOPOLYMER shows the typical powdery aspect of metakaolin crystals interconnected by aluminosilicate gel. On the other hand, COMPOSITE surface is very regular and homogeneous, thus indicating that MK is well dispersed in poly(HDDA) matrix. In HYBRID a certain degree of homogeneity is well visible, indicating that the organic and inorganic components are well mixed and dispersed, without any phase separation. We remind that the latter happened in all cases the organic-inorganic mixture was reacted by the conventional methods.

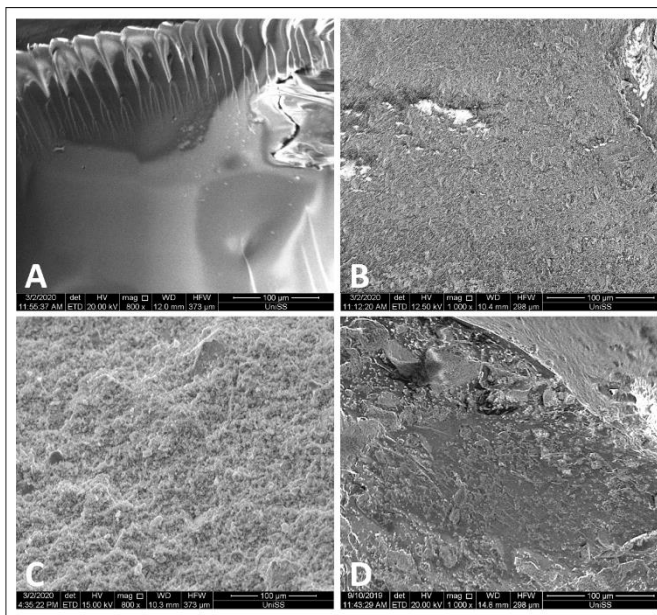


Figure 5 SEM images: A) poly(HDDA); B) COMPOSITE; C) GEOPOLYMER; D) HYBRID.

3.3 Evaluation of the mechanical properties

Aiming at investigating the effect of the geopolymeric phase on the mechanical behavior of the prepared hybrids, some preliminary compression tests were performed. The results are collected in Table 2. It is worthy to note that the combination of the organic and inorganic phases results in a significantly higher modulus as compared with that of each of them taken alone.

However, such an increase is larger in COMPOSITE than in HYBRID. This might be due to several factors that require an additional thorough investigation, such as: presence of residual water, optimization of the ratio between organic and inorganic phases, wettability at the interface organic-inorganic pastes.

Table 2: Compression moduli of some of the investigated materials

Sample	Compression modulus (MPa)
Poly(HDDA)	815
GEOPOLYMER	30
COMPOSITE	1510
HYBRID	1148

Conclusions

The first frontal polycondensation was performed thus allow obtaining an organic-inorganic hybrid. FP and FGP simultaneously happened by mutual assistance: i) FGP was obtained only thanks to the exothermicity of the concurrent frontal polymerization of HDDA, ii) FP of HDDA occurred in water only because of the exothermicity of the simultaneous frontal geopolymerization.

The same result was not reached by using the classical polymerization procedures. Actually, by operating at low temperature, the two polymerizations need hours (or even days) to occur, a time too long to avoid the phase separation between the organic and the inorganic phases. On the other hand, by increasing temperature an explosive reaction occurs.

Even if a systematic study concerning all parameters is mandatory (to be reported in a next paper), these first results pave the way to the easy, low-cost and eco-friendly preparation of composite/hybrid materials made of an organic and a ceramic part in one step, overcoming the inherent drawbacks of FP as regard heat dissipation. The occurrence of FGP and its indispensable contribution to the overall reaction may be a starting point for the setup of a frontal geopolymerization occurring even in absence of the organic counterpart, thus enlarging the possible applications of the technique, with particular aim to practical, in-situ applications, including (self-)healing, chemical anchor bolts, artistic and additive and spacecraft manufacturing.

Acknowledgements

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References

- [1] J. A. Pojman, Frontal Polymerization, in: K. Matyjaszewski, M. Möller (Eds.), Polymer Science: A Comprehensive Reference, Elsevier BV, Amsterdam, 2012, pp. 957–980.
- [2] I. D. Robertson, M. Yourdkhani, P. J. Centellas, J. E. Aw, D. G. Ivanoff, E. Goli, E. M. Lloyd, L. M. Dean, N. R. Sottos, P. H. Geubelle, J. S. Moore, S. R. White, Nature, 557 (2018) 223.
- [3] D. Nuvoli, V. Alzari, J. A. Pojman, V. Sanna, A. Ruiu, D. Sanna, G. Malucelli, A. Mariani, ACS Appl. Mater. Interfaces, 7 (2015) 3600.
- [4] V. Alzari, D. Nuvoli, S. Scognamiglio, M. Piccinini, E. Gioffredi, G. Malucelli, S. Marceddu, M. Sechi, V. Sanna, A. Mariani, J. Mater. Chem., 21 (2011) 8727.
- [5] P. M. Potzmann, F. G. Lopez Villanueva, R. Liska, Macromolecules, 48(24) (2015) 8738.
- [6] S. P. Davtyan, A. O. Tonoyan, Rev. J. Chem., 8 (2018) 432.
- [7] P. Duxson, A. Fernández-Jiménez, J. L. Provis, G. C. Lukey, A. Palomo, J. S. J. Van Deventer, J. Mater. Sci., 42(9) (2007) 2917.
- [8] F. Pacheco-Torgal, J. A. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasirt in: F. Pacheco-Torgal, J. Labrincha, C. Leonelli, A. Palomo, P. Chindaprasit (Eds.), Handbook of Alkali-Activated Cements, Mortars and Concretes, Woodhead Publishing, 2015.
- [9] J. Cai, X. Li, J. Tan, B. Vandevyvere, J. Build. Eng., 30 (2020) 10130.
- [10] A. Mariani, D. Nuvoli, V. Alzari, M. Pini, Macromolecules, 41 (2008) 5191.
- [11] S. Vicini, A. Mariani, E. Princi, S. Bidali, S. Pincin, S. Fiori, E. Pedemonte, A. Brunetti, Polym. Adv. Technol., 16 (2005) 293.
- [12] A. Mariani, S. Bidali, P. Cappelletti, G. Caria, A. Colella, A. Brunetti, V. Alzari, V. e-Polymers, 9 (2009) 1.
- [13] C. Ponzoni, I. Lancelotti, L. Barbieri, A. Spinella, M. L. Saladino, D. C. Martino, E. Caponetti, F. Armetta, C. Leonelli, J. Hazard. Mater., 286 (2015) 474.
- [14] Z. Aly, E. R. Vance, D. S. Perera, J. V. Hanna, C. S. Griffith, J. Davis, D. Durce, J. Nucl. Mater., 378 (2008) 172.
- [15] P. S. Singh, T. Bastow, M. Trigg, J. Mater. Sci., 40(15) (2005) 3951.
- [16] G. Engelhardt, D. Hoebbel, M. Tarmak, A. Samoson, E.Z. Lippmaa, Anorg. Allg. Chem. 484 (1982) 22.
- [17] S. K. Lee, J.F. Stebbins, Am. Miner. 84 (1999) 937.

Declaration of interests

☒ The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

☐ The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

On behalf of all the authors of the manuscript

A handwritten signature in black ink, appearing to read 'O. Meric', is written over a light gray grid background.

CRedit authorship contribution statement

VA, GB, AS, GM, DN, DS, FA, EK, MR: Investigation. VA, CL, AS, AM: Writing - original draft and review & editing. AM: Conceptualization, Supervision, Resources.