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FRONTAL POLYMERIZATION AND GEOPOLYMERIZATION, THE FIRST EXAMPLE: ORGANIC-INORGANIC HYBRID MATERIALS

C. Leonelli¹, G. Malucelli², A. Mariani³, D. Nuvoli³, A. Spinella⁴

¹ Dipartimento di Ingegneria "Enzo Ferrari", Università di Modena e Reggio Emilia,
Via P. Vivarelli 10, 41125 Modena, Italy

² Dipartimento di Scienza Applicata e Tecnologia, Politecnico di Torino,
Viale T. Michel 5, 15121 Alessandria, Italy
e-mail: giulio.malucelli@polito.it

³ Dipartimento di Scienze Chimiche, Fisiche, Matematiche e Naturali, Università di Sassari,
Via Vienna 2, 07100 Sassari, Italy

⁴ ATeN Center, Università di Palermo, Via F. Marini 14, 90128 Palermo, Italy

Introduction

Frontal polymerization (FP) is a technique that exploits the formation of a hot polymerization front, capable of self-sustaining and self-propagating, to convert the monomer into a polymer.[1-3] The presence of inert fillers, low boiling solvents and high heat capacity (e.g., water) often cause the front to extinguish due to excessive heat dissipation. For similar reasons, usually only the polyaddition reactions, and not the polycondensation ones, lead to obtaining complete FP polymerizations.

Geopolymers are cross-linked inorganic polymers based on aluminosilicates. One of the most commonly used systems for obtaining geopolymers is that consisting of metakaolin activated by an alkaline solution composed of NaOH and Na₂Si₂O₃, in which the formation of the geopolymer takes place within a few hours, through polycondensation at room temperature [4,5].

In this work, for the first time, an organic-inorganic hybrid polymer is obtained through simultaneous frontal polymerizations of an acrylic and geopolymer system.

Results and Discussion

For the organic system, the monomer 1,6-hexanedioldiacrylate (HDDA) was chosen since it has high reactivity and shows good compatibility with the geopolymer system. In addition, the HDDA has already been used in previous works concerning the application of the FP for the consolidation of stone materials [6].

As for the initiator, triethyltetradecylphosphonium persulfate (TETDPPS) was used, since it has good solubility in HDDA and in water, it does not provide gaseous decomposition products that can lead to the formation of bubbles in the final material and ensures the self-protection of the front faces at relatively low temperatures.

As far as the geopolymer formation reaction is concerned, this can be schematized as follows:



two or more tetrahedral units of Si (OH)₄ and Al (OH)₃ condense to form linear, ring or three-dimensional aluminosilicates.

The final system is therefore made up of two main components: acrylic monomer HDDA and the geopolymer mixture composed of metakaolin (MK) and activating solution (SA).

The maximum amount of MK capable of guaranteeing a complete FP is 44 wt% compared to the HDDA. For higher quantities, excessive heat dissipation determines the extinction of the polymerization fraction.

Table 1 shows the samples synthesized with the polymerization technique used and the observations on the characteristics of the material obtained. On the basis of the results obtained, it can be stated that the FP of the hybrid system occurs if:

1. water (alone or in the activating solution) is not present: the large amount of heat that the water absorbs prevents self-sustaining of the front; only the systems consisting of the organic polymer and the composite, both synthesized in the absence of water, allow the achievement of a complete FP
2. the activating solution is present together with the metakaolin. Only in the presence of MK and SA, which react with each other to form the geopolymer, the polymerization front of the HDDA is capable of self-sustaining, even in the presence of water. This means that the FP of the HDDA occurs simultaneously with the frontal geopolymerization (FGP) and that both exothermic reactions contribute to the propagation of the polymerization front. Furthermore, from the data in Table 1 it is clear how it is possible to obtain the hybrid material only by means of the simultaneous FP and FGP: in other conditions (classical polymerization, CP or polymerization at room temperature) the polymerization does not occur, due to the separation of phase between the two systems or of the development of gaseous products that determine the quenching of the front. In order to study the effect of the geopolymer phase on the mechanical behavior of prepared hybrids, some preliminary compression tests were carried out.

Table 1: Samples, compositions and synthetic parameters

Sample	Composition	Technique & conditions	Notes	Tmax (°C)	Vf (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	FP	SUCCESSFUL PROCEDURE No phase separation. MK is inert and dissipates heat.	160	3.8
HYBRID	Poly(HDDA) containing geopolymer (from AAS and MK 44 wt%)	FP + FGP	SUCCESSFUL PROCEDURE No phase separation. Even if water dissipates heat, geopolymerization is exothermic and sustains fronts.	119	4.0
HYB-RT	Same starting materials as HYBRID	r.t.	UNSUCCESSFUL PROCEDURE No reaction before phase separation occurrence (3–5 min)	–	–
HYB-CP	Same starting materials as HYBRID	80 °C, 1 h	UNSUCCESSFUL PROCEDURE Explosive gas release. No hybrid formation.	–	–

The results are collected in Table 2. It should be noted that the combination of organic and inorganic phases result in a significantly higher modulus, as compared to that of each of them taken separately.

Table 2: Compression moduli of some of the investigated materials.

Sample	Compression modulus (MPa)
Poly(HDDA)	815
Geopolymer	30
Composite	1510
Hybrid	1148

However, such an increase is greater in COMPOSITE than in HYBRID. This could be due to several factors that require more in-depth investigation, such as: presence of residual water, optimization of the ratio between organic and inorganic phase, wettability at the organic-inorganic paste interface.

Conclusions

Then the first frontal polycondensation was carried out thus obtaining an organic-inorganic hybrid. FP and FGP occurred simultaneously by mutual assistance: i) FGP was obtained only thanks to the exothermicity of the simultaneous frontal polymerization of HDDA, ii) HDDA FP occurred in water only due to the simultaneous heat released during frontal geopolymerization.

The same result was not achieved using classical polymerization procedures. In fact, operating at low temperature, the two polymerizations take hours (or even days), a time too long to avoid phase separation between the organic and the inorganic phases. These first results open the door to the easy, economical and ecological preparation of composites /

hybrid materials made of an organic part and a ceramic part in one step, overcoming the inherent drawbacks of FP with respect to heat dissipation. The occurrence of FGP and its indispensable contribution to the whole reaction can be a starting point to establish a frontal geopolymerization that occurs even in the absence of the organic counterpart, thus expanding the possible applications of the technique, with a particular focus on practical on-site applications, including (self) repairable, chemical, artistic and additive anchor bolts and spacecraft manufacturing.

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