Novel Hybrid Organic-Geopolymer Materials

Dr. Giuseppina Roviello
Dipartimento di Ingegneria
Università degli Studi di Napoli Parthenope
'Hybrids'

- Broadly used term
- It is used to define different systems:
  - Crystalline highly ordered coordination polymers
  - Sol-gel compounds
  - Materials with and without interactions between the inorganic and organic units
  - … …
Hybrid material

"a material composed of an intimate mixture of inorganic components, organic components, or both types of component. The components usually interpenetrate on scales of less than 1 µm."
IUPAC, 1997

"a hybrid material is a material that includes two moieties (organic and inorganic) blended on the molecular scale."
Hybrid materials

- A more detailed definition takes into account the possible interactions between the inorganic and organic species.
  - **Class I** ➔ Van der Waals, Hydrogen bonding, weak electrostatic interactions
  - **Class II** ➔ Strong chemical interactions ( coordinative, covalent ... )
Selected interactions typically applied in hybrid materials and their relative strength

<table>
<thead>
<tr>
<th>Strength of interaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>Covalent</td>
</tr>
<tr>
<td>Coordinative</td>
</tr>
<tr>
<td>Ionic</td>
</tr>
<tr>
<td>H-bonding</td>
</tr>
</tbody>
</table>

Table 1.1 Different possibilities of composition and structure of hybrid materials.

| Matrix:                  | crystalline ↔ amorphous  |
|                         | organic ↔ inorganic      |
| Building blocks:        | molecules ↔ macromolecules ↔ particles ↔ fibers |
| Interactions between components: | strong ↔ weak |
The different types of hybrid materials.

Class I Hybrids

a) Blends

b) Interpenetrating networks

Class II Hybrids

c) Building blocks covalently connected

d) Covalently connected polymers

Source: Kickelbick, G., Wiley-VCH, 2007
Geopolymeric Hybrid materials

It is possible to expect very interesting characteristics that are not found in the organic polymer or in the inorganic material independently:

° Features such as being flexible like a plastic but have excellent thermal stability and mechanical strength

Novel Hybrid Organic-Geopolymer Materials
Geopolymers vs OPC

Advantages

- Lower manufacturing energy consumption
- Ecofriendly synthetic procedures starting from inexpensive raw materials (fly ashes or furnace slags, ...)
- Develop higher strength in a shorter period at room temperature
- Superior acid resistance
- Superior fire resistance
- Lower shrinkage, ...

Disadvantages

As in the case of ceramics or OPC:

- Brittle behaviour
- Low flexural strength

Limit in their extensive applications as structural material
Geopolymeric composites

Fillers

- Particles
- Fibers

- Inorganics
- Polymers
- Natural fibers
- Particulate
- Carbon fibers
- Basalt
Polymeric Fillers

- Low density
- Chemical stability
- Easy processing
- ...
- ...
- Chemical tailoring
Polymeric Fillers

- PP
- PVA
- PVAc
- PAA
- PAANa
- PAm
- PEG
Organic polymer added as
- powder
- emulsion
- presence of compatibilizers

'Organo-geopolymer compounds result from the mixing or impregnation of compatible organic polymers to mineral geopolymers'

J. Davidovits, Geopolymer Chemistry & Application, Chapter 14
Polypropylene fiber reinforced geopolymers

Table 4 Effects of PP fiber content on slurry and geopolymer

<table>
<thead>
<tr>
<th>No.</th>
<th>w(PP fiber)/%</th>
<th>Fluidity/cm</th>
<th>Setting time/h</th>
<th>Compressive strength/MPa</th>
<th>Flexural strength/kPa</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Initial</td>
<td>Final</td>
<td>1 d</td>
</tr>
<tr>
<td>PPF1</td>
<td>0</td>
<td>18.0</td>
<td>25</td>
<td>30</td>
<td>32.6</td>
</tr>
<tr>
<td>PPF2</td>
<td>0.25</td>
<td>17.5</td>
<td>26</td>
<td>29</td>
<td>54.2</td>
</tr>
<tr>
<td>PPF3</td>
<td>0.50</td>
<td>17.0</td>
<td>28</td>
<td>30</td>
<td>54.7</td>
</tr>
<tr>
<td>PPF4</td>
<td>0.75</td>
<td>16.5</td>
<td>28</td>
<td>29</td>
<td>36.6</td>
</tr>
</tbody>
</table>

- PP containing geopolymers have higher strength than pure ones.
  - The **compressive strength** of PPF3 is increased by 67.8% and 19.5% for 1 and 3 d;
  - **Flexural strength and impacting energy**, the direct toughness indicating parameters, are increased by 36.1% and 6.25% for 3 d.
  - Though flexural strength and impacting energy of PPF4 are higher, its compressive is lower even than that of pure ones

- **Excessive PP fiber may have a negative effect on the structural integrity of geopolymer.**

Modification of geopolymers by using water soluble organic polymers

Polyacrylic acid (PAA), Sodium polyacrylate (PAANa), Polyethylene glycol (PEG), Polyvinyl alcohol (PVA), Polyacrylamide (PAm)

Organic resins (PVAc+Acrylic resin) reinforced geopolymer composites

- The addition of the organic resin increases the mechanical strength substantially.

- The optimal amount of hydrophilic organic polymer is around 1%.

- Higher polymer concentration causes a tremendous decrease in the mechanical properties.

Limited compatibility between organic and inorganic phases.

Incorporation of an appreciable amount of organic epoxy resin to geopolymeric matrix, significantly improving the mechanical properties.

Novel hybrid organic-inorganic materials.
Claudio Ferone, Giuseppina Roviello, Francesco Colangelo, Raffaele Cioffi, Oreste Tarallo
Applied Clay Science 73 (2013) 42-50
Strategy

Organic epoxy resin
MK-based geopolymer

co-reticulation

freshly prepared geopolymeric suspension.
partly crosslinked epoxy resins
Phases that, in principle, are *dramatically incompatible* became highly compatible up to micrometric level.
Geopolymer:

Alkaline solution:
\[ \text{Na}_2\text{O} \cdot 1.4\text{SiO}_2 \cdot 10.5\text{H}_2\text{O} \]

MK

Final composition:
\[ \text{Al}_2\text{O}_3 \ 3.5\text{SiO}_2 \ 1.0\text{Na}_2\text{O} \ 10.4\text{H}_2\text{O} \]
assuming that geopolymerization occurred at 100%.
Epoxy organic resins 1 and 2

Resin 1: A (82%) + B (18%)
Resin 2: A (79.6%) + B (4.4%) + C (16.0%)

% in weight

The organic component of resins are selected in order to produce numerous hydroxyl tails during the epoxy ring opening reaction.
The organic phase became ‘temporarily hydrophilic’ and well-mixable with the aqueous inorganic phase.

Possible formation of hydrogen bonds (class I hybrid)
Epoxy organic resins 1 and 2

The organic component of resins are selected in order to produce:
- numerous hydroxyl tails during the epoxy ring opening reaction.
- a thermally stable polymer.

In this way, the organic phase became ‘temporarily hydrophilic’ and well-mixable with the aqueous inorganic phase.

Resin 1: A (82%) + B (18%)
Resin 2: A (79.6%) + B (4.4%) + C (16.0%)

% in weight
Co-reticulation method

Geopolymer suspension ↔ Not fully reticulated organic resin

Simultaneous crosslinking of the two components

test tube tilting method
Resin content: up to 25% w/w

High compatibility (without the formation of agglomerates) just by hand mixing.

Homogeneous and stable in time dispersion of the organic microdomains into the inorganic phase, without addition of external additives.

Hybrid I  $\rightarrow$ MK-GEO:Resin 1 (80:20)

Hybrid II  $\rightarrow$ MK-GEO:Resin 2 (80:20)
SEM micrographs

Geopolymer
SEM micrographs

Hybrid I

b

b'

200 µm

20 µm

Hybrid II

C

C'

200 µm

20 µm
Chemical characterization obtained by energy-dispersive X-ray spectroscopy (EDS) in the regions indicated by white rectangles. All results are in weight %.

<table>
<thead>
<tr>
<th>Spectrum</th>
<th>In stats.</th>
<th>C</th>
<th>O</th>
<th>Na</th>
<th>Al</th>
<th>Si</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spectrum 1</td>
<td>Yes</td>
<td>65.54</td>
<td>29.15</td>
<td>1.49</td>
<td>1.48</td>
<td>2.35</td>
<td>100.00</td>
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<tr>
<td>Spectrum 2</td>
<td>Yes</td>
<td>25.14</td>
<td>42.93</td>
<td>6.11</td>
<td>8.68</td>
<td>17.13</td>
<td>100.00</td>
</tr>
<tr>
<td>Spectrum 3</td>
<td>Yes</td>
<td>20.73</td>
<td>49.67</td>
<td>6.64</td>
<td>8.09</td>
<td>14.87</td>
<td>100.00</td>
</tr>
</tbody>
</table>

SEM micrographs (amplification $5\times10^3$) of the hybrid II cured at room temperature.
## Thermal properties

<table>
<thead>
<tr>
<th></th>
<th>Curing Temperature (°C)</th>
<th>Weight loss starting temperature (°C)</th>
<th>Temperature at 10% weight loss (°C)</th>
<th>Weight loss ending temperature (°C)</th>
<th>Combustion residual at 800°C (weight %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Geopolymer</td>
<td>25</td>
<td>30</td>
<td>101</td>
<td>450</td>
<td>72</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>30</td>
<td>120</td>
<td>450</td>
<td>76</td>
</tr>
<tr>
<td>Resin 1</td>
<td>25</td>
<td>260</td>
<td>342</td>
<td>700</td>
<td>0</td>
</tr>
<tr>
<td>Resin 2</td>
<td>25</td>
<td>290</td>
<td>349</td>
<td>670</td>
<td>0</td>
</tr>
<tr>
<td>Hybrid I</td>
<td>25</td>
<td>30</td>
<td>109</td>
<td>750</td>
<td>53</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>30</td>
<td>140</td>
<td>670</td>
<td>57</td>
</tr>
<tr>
<td>Hybrid II</td>
<td>25</td>
<td>30</td>
<td>112</td>
<td>640</td>
<td>54</td>
</tr>
<tr>
<td></td>
<td>60</td>
<td>30</td>
<td>154</td>
<td>655</td>
<td>59</td>
</tr>
</tbody>
</table>

The graph shows the weight loss (%) and heat flow (W/g, exo down) as a function of temperature (°C) for different materials. Continuous lines represent Hybrid I cured at RT, while dashed lines represent Hybrid I cured at 60°C.
Average Compressive strength, average stress at a 0.015 strain ($\sigma_{0.015}$) and average stress at a 0.018 strain ($\sigma_{0.018}$) of specimens.

Mechanical properties

- Higher compressive strength than neat geopolymer
- Reduction of the brittle behavior (a sort of "pseudo-plasticity")
Synthesis and characterization of novel epoxy geopolymer hybrid composites
Giuseppina Roviello, Laura Ricciotti, Claudio Ferone, Francesco Colangelo, Raffaele Cioffi, Oreste Tarallo
submitted to Materials, 2013

The same synthetic approach has been applied using commercial bi-component resins aiming at obtaining of geopolymer composite useful for massive applications.

Advantages:
- moderate cost availability
- easily handling in massive amounts
Epoxy resins produced by MAPEI S.p.a. (www.mapei.it)

selected on the basis of:
- chemical-physical properties
- chemical composition (similar to that of previously described synthetic ones, designed in order to obtain a good incorporation in the geopolymeric matrix).

Epojet®
EpojetLV®
Epojet®

Component A:
glycidylester of neodecanoic acid

diglycidyl ether hexanediol

Component B:
3,6-diazaoctane-1,8 diamine  
m-xililen-diamine

EpojetLV®

Component A:
glycidylester of neodecanoic acid

Component B:
m-xililen-diamine  
3-azapentane-1,5 diamine
Epojet

\[ R = \text{[-CH}_2\text{-O-}(\text{CH}_2)_6\text{-O-CH}_2\text{-]} \]

Geopolymeric aqueous suspension
Geo-Epojet5 (geopolymer:resin 95:5 w/w)
Geo-Epojet20 (geopolymer:resin 80:20 w/w)

@ Department of Structural Engineering, University of Naples “Federico II”
SEM micrographs

a) neat geopolymer;
b) and d) GeoEpojet20
c) GeoEpojetLV20
Compressive strength

![Graph showing compressive strength vs. resin content]

- GeoEpojet
- GeoEpojet LV
- Geo

![Graph showing compressive strength vs. strain]

- GeoEpojetLV20
- GeoEpojet20
- Geo
SEM micrographs of heat treated samples

GeoEpojet20 kept for 24 h at 800°C in air
Hg intrusion porosimetry

Cumulative pore volume vs pore radius

- a) neat geopolymer,
- b) GeoEpojet20,
- c) GeoEpojet20 after 24 h at 800°C.
X-ray powder diffraction patterns of
(a) GeoEpojet20 sample after 24 h at 800°C after subtraction of background;
(b) nepheline (PDF n° 04-012-4977);
(c) residual.
Heat treated geopolymer based hybrid composite

Possible applications:

- **sieves** for the filtration of particulate or as lightweight heat and acoustic insulating materials.
- production of **adsorbents** for the removal of contaminants (such as arsenate) from water by impregnation of this porous materials with ion exchange resins or inorganic salts.
- development of new inert and low cost **scaffolds** for the cell growing and the controlled release of active guest molecules with biological or pharmaceutical properties.
Conclusions

- Novel hybrid (class I) organic-inorganic materials were prepared through an innovative synthetic approach based on a co-reticulation in mild conditions of epoxy based organic resins and a MK-based geopolymer inorganic matrix.

- A high compatibility between the organic and inorganic phases, even at appreciable concentration of resin (25% w/w), was realized.

- A good and homogeneous dispersion (without the formation of agglomerates) of the organic particles was obtained (even just by hand mixing).

- These new materials show good technological properties: in respect to the neat geopolymer, they present significantly enhanced compressive strengths and toughness and higher deformation before cracking.
Conclusions

- In agreement with the expectations of **Green Chemistry**, in the proposed synthetic procedure the use of solvents is completely avoided.

- Possible use of wastes instead of metakaolin could further reduce the environmental impact of the material we are studying.

- From an environmental point of view this means that it is possible to save material, to use smaller section for the same load condition, to reduce the number of cracks obtaining more durability and so a longer service life ➔ towards an **Environmental Friendly Material**.
Conclusions

Design of new materials

- Quality
- Reproducibility
- Knowledge of the system

- … providing a deep knowledge of the chemical composition and of the interactions in order to have a good knowledge of the system under examination.
- … tailoring the chemical composition to modulate properties
Università di Napoli Parthenope
Department of Engineering

Material Science for Sustainable Engineering Group
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Dr. Giuseppina Roviello
Department of Engineering
University of Naples ‘Parthenope’
Tel. +39 081 547 6781 Fax +39 081 547 6777
E-mail: giuseppina.roviello@uniparthenope.it

Thank you very much for your kind attention....