GEOPOLYMER CAMP 2013

Saint-Quentin, 9th July 2013

Novel Hybrid Organic-Geopolymer Materials

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'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."

Kickelbick, G. (Editor) Hybrid Materials: Synthesis, Characterization, and Applications, Wiley-VCH, 2007

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

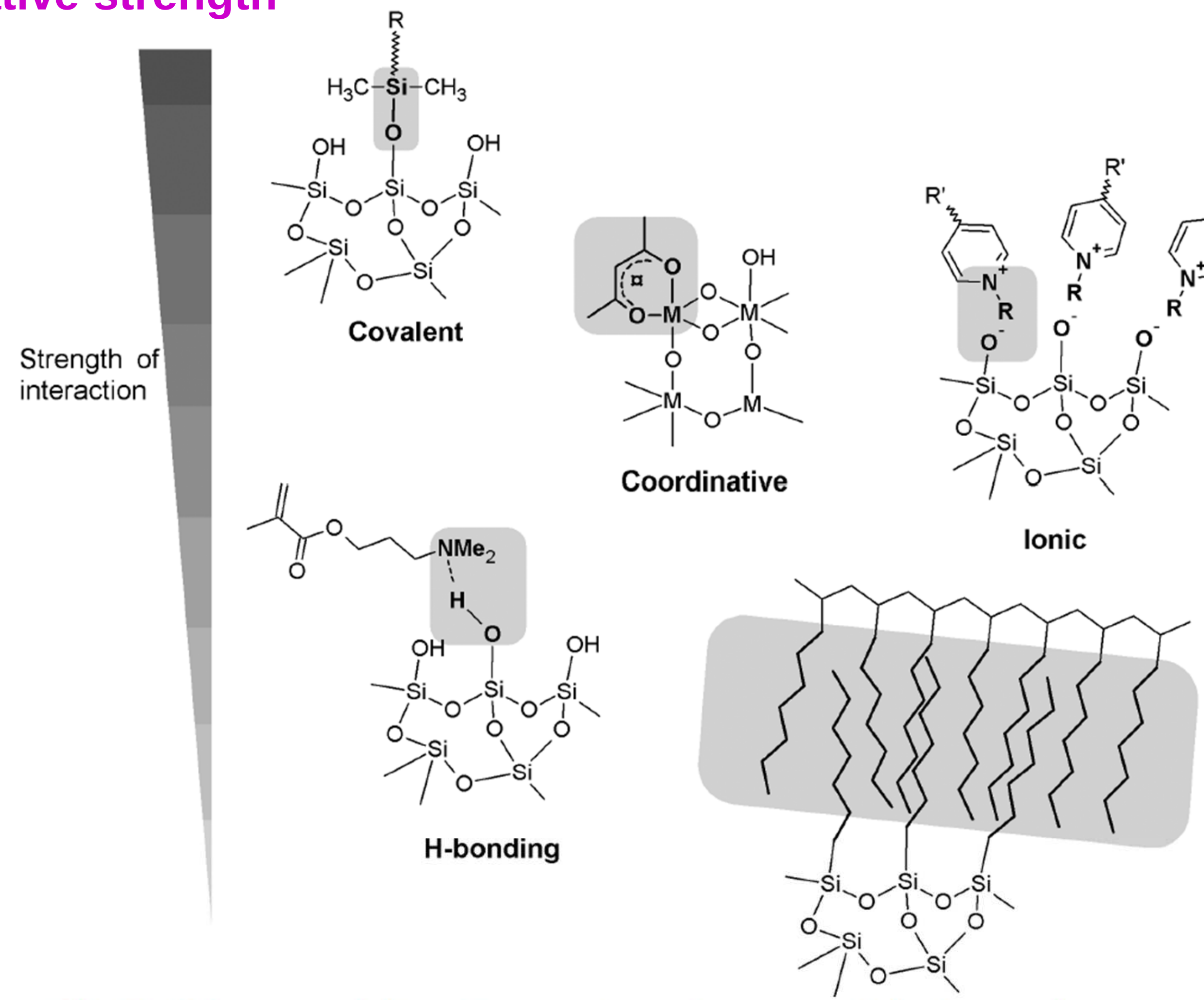
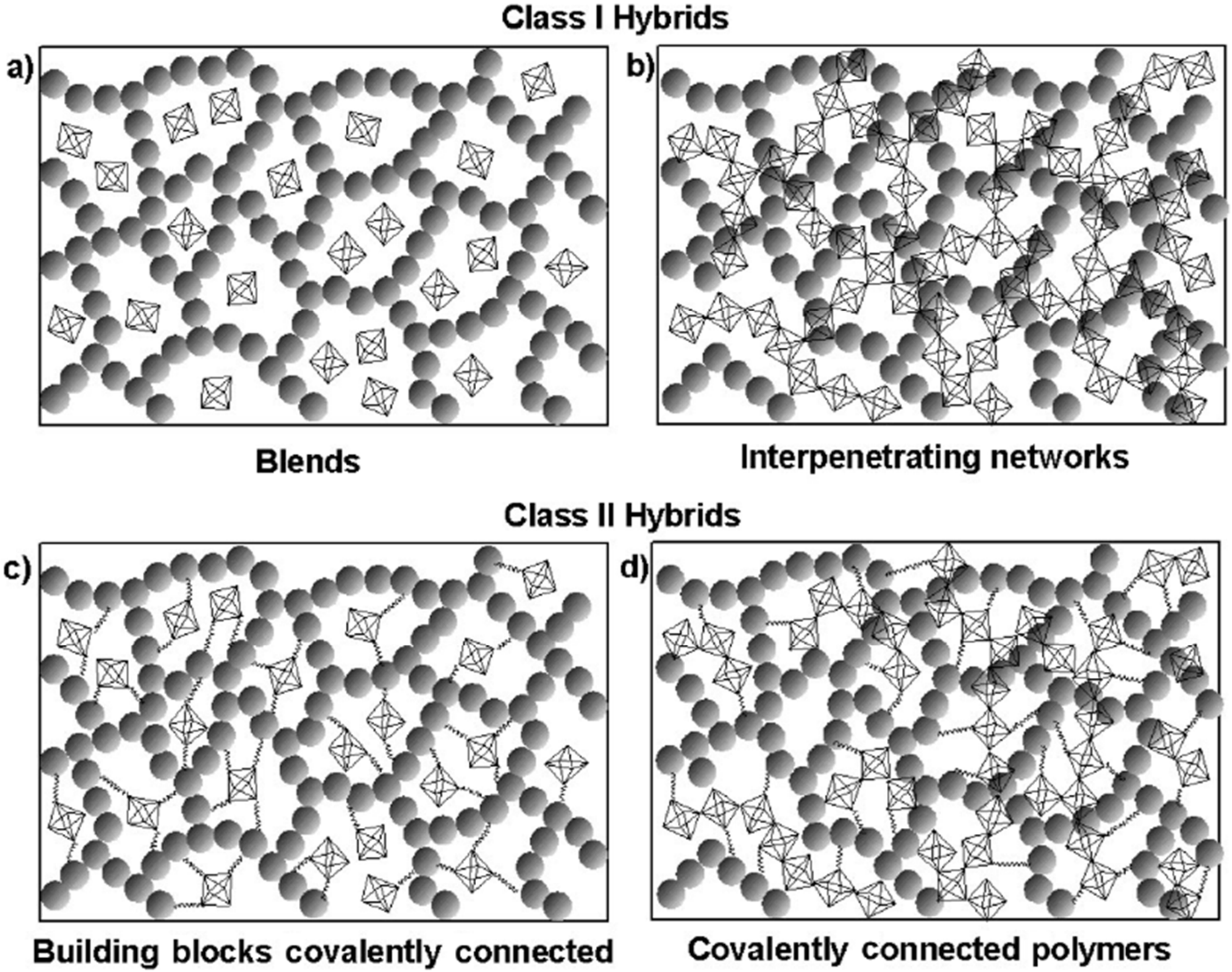


Table 1.1 Different possibilities of composition and structure of hybrid materials.

Matrix:	crystalline ↔ amorphous
	organic ↔ inorganic
Building blocks:	molecules ↔ macromolecules ↔ particles ↔ fibers
Interactions between components:	strong ↔ weak

Source: Kickelbick, G, Wiley-VCH, 2007

The different types of hybrid materials.



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 strenght 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 strenght

Limit in their extensive applications as structural material

Geopolymeric composites

Fillers

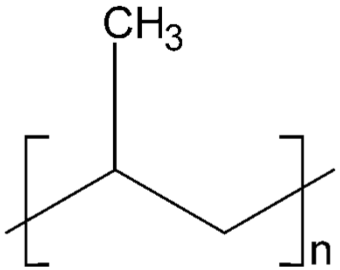
- Particles
- Fibers

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

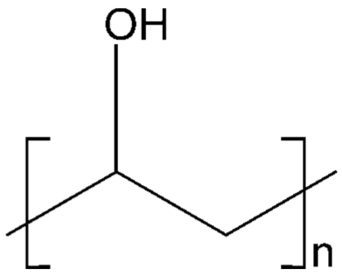
Polymeric Fillers

- Low density
- Chemical stability
- Easy processing
- …
- …
- *Chemical tailoring*

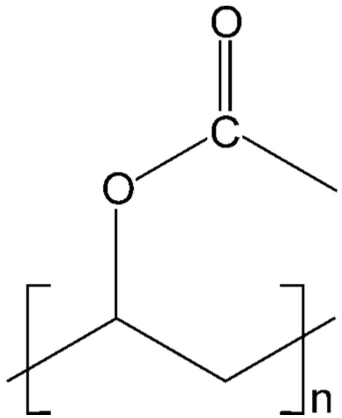
Polymeric Fillers



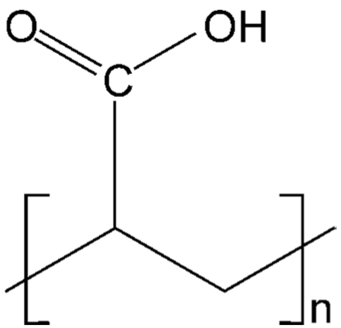
PP



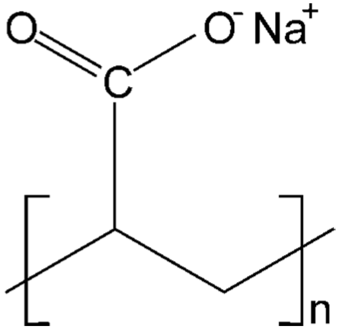
PVA



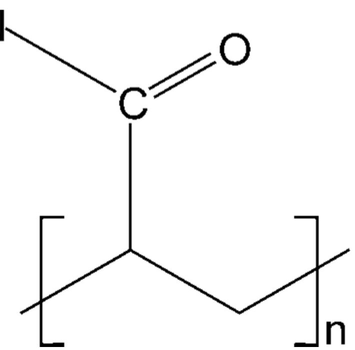
PVAc



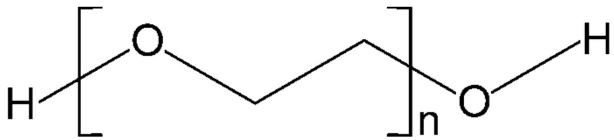
PAA



PAANa

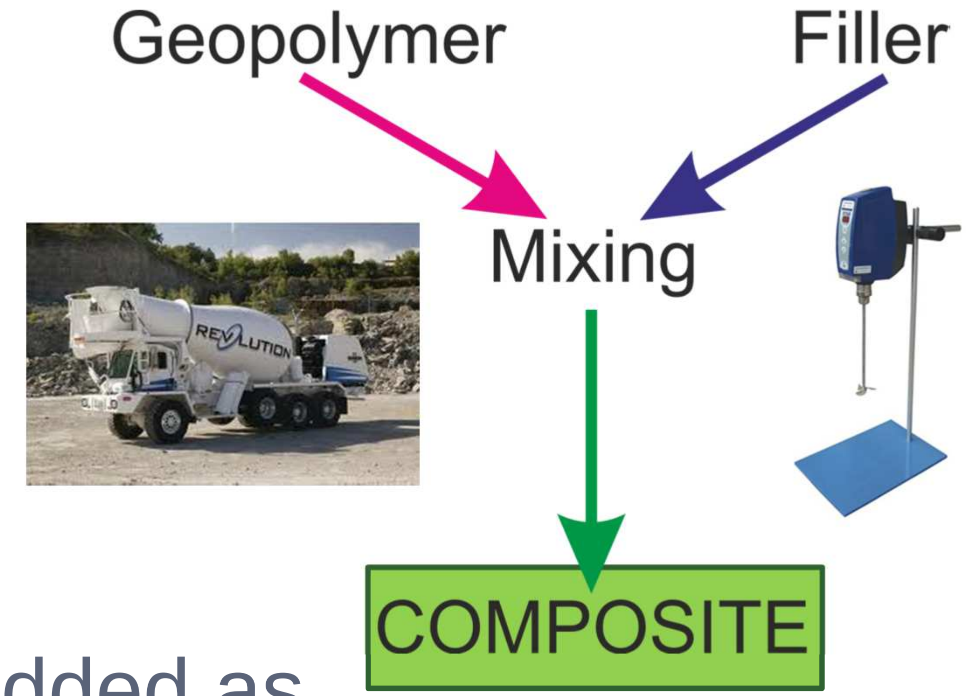


PAm



PEG

Organo-geopolymer compounds



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

No.	w(PP fiber)/%	Fluidity/ cm	Setting time/h		Compressive strength/MPa		Flexural strength/kPa	
			Initial	Final	1 d	3 d	1 d	3 d
PPf1	0	18.0	25	30	32.6	41.5	5.00	5.51
PPf2	0.25	17.5	26	29	54.2	49.6	6.03	8.45
PPf3	0.50	17.0	28	30	54.7	52.3	9.41	7.50
PPf4	0.75	16.5	28	29	36.6	38.3	10.0	9.41

- 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.**

Zhang, Z et al. (2009) J. Cent. South. Univ. Technol. 16:49.

Modification of geopolymers by using water soluble organic polymers

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

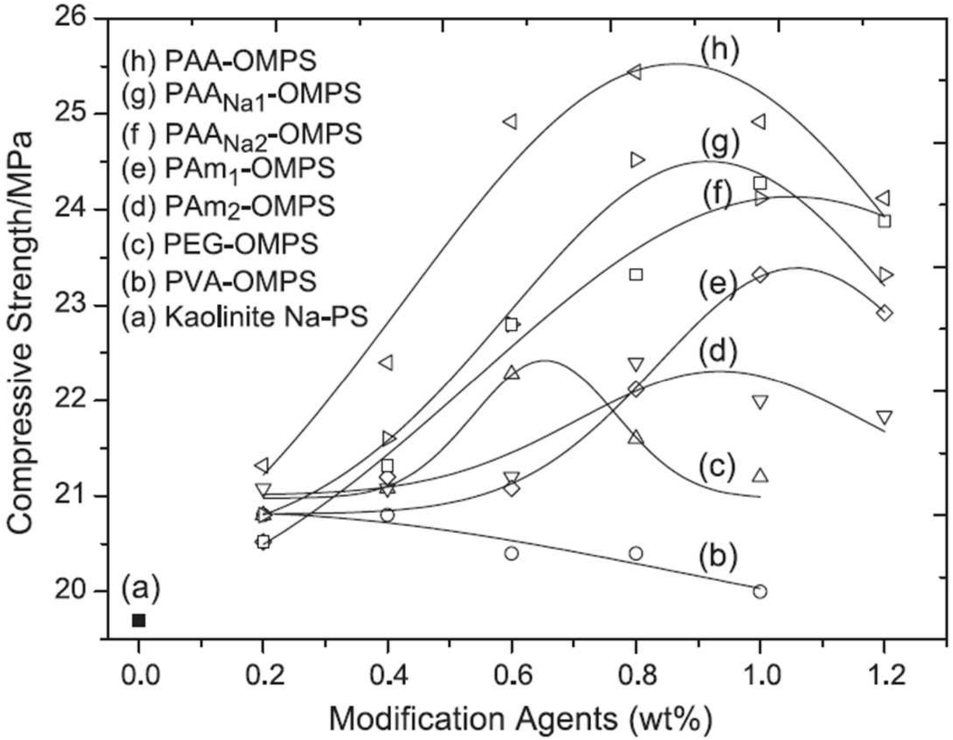
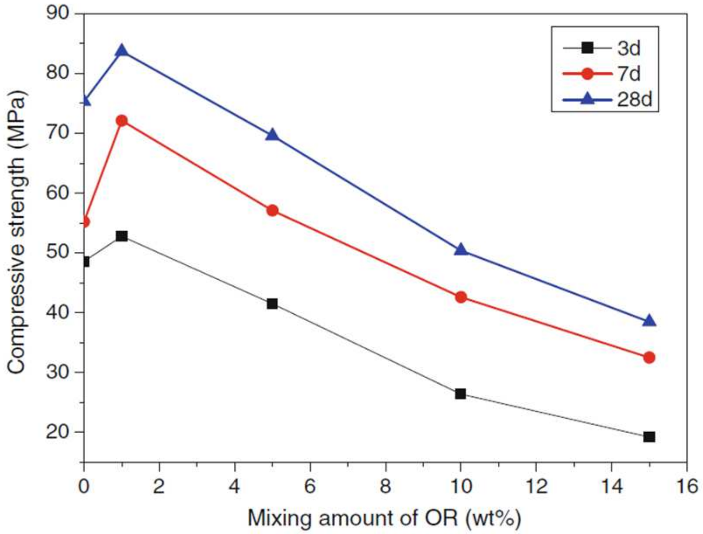


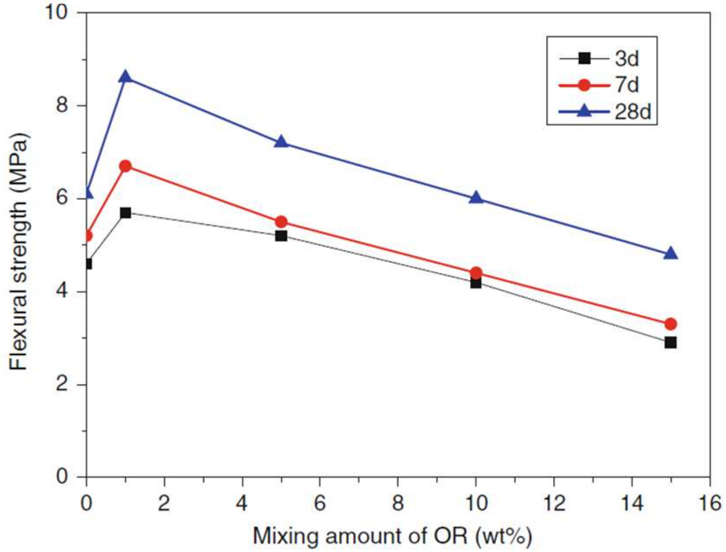
Table 1
Physical and mechanical properties of OMPSs

OMPSs	Optimum loadings (wt.%)	Compressive strength (MPa)	Increment of compressive strength (%)
Na-PS	–	19.7	–
PAA–OMPS	0.8	25.4	29.0
PAA_{Na1}–OMPS	0.8	24.5	24.4
PAA_{Na2}–OMPS	1.0	24.3	23.4
PAm_1–OMPS	1.0	23.3	18.3
PAm_2–OMPS	0.8	22.4	13.7
PEG–OMPS	0.6	22.3	13.2
PVA–OMPS	0.2	20.8	5.6

S. Zhang Materials Letters 58 (2004) 1292– 1296

Organic resins (PVAc+Acrylic resin) reinforced geopolymer composites





- The addition of the organic resin increases the mechanical strenght 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

Zhang YJ et al J Mater Sci (2010) 45:1189–1192

Tailoring the chemical compositions of resins

Fine control of the experimental conditions and procedure

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:

Sodium Silicate solution

Sodium Hydroxide

Alkaline solution:

$Na_2O \cdot 1.4SiO_2 \cdot 10.5H_2O$

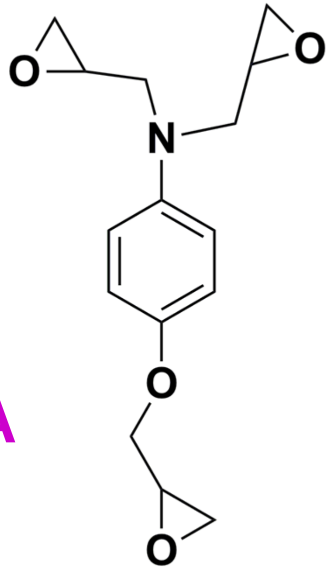
MK

Final composition:

$Al_2O_3\ 3.5SiO_2\ 1.0Na_2O\ 10.4H_2O$

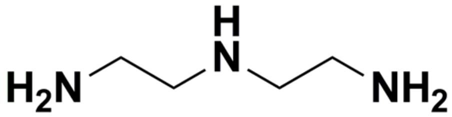
assuming that geopolymerization occurred at 100%.

Epoxy organic resins 1 and 2



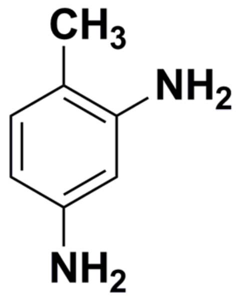
A

N,N-diglycidyl-
4-glycidyl-oxyaniline



B

bis-(2-aminoethyl)amine



C

2,4-diamino-toluene

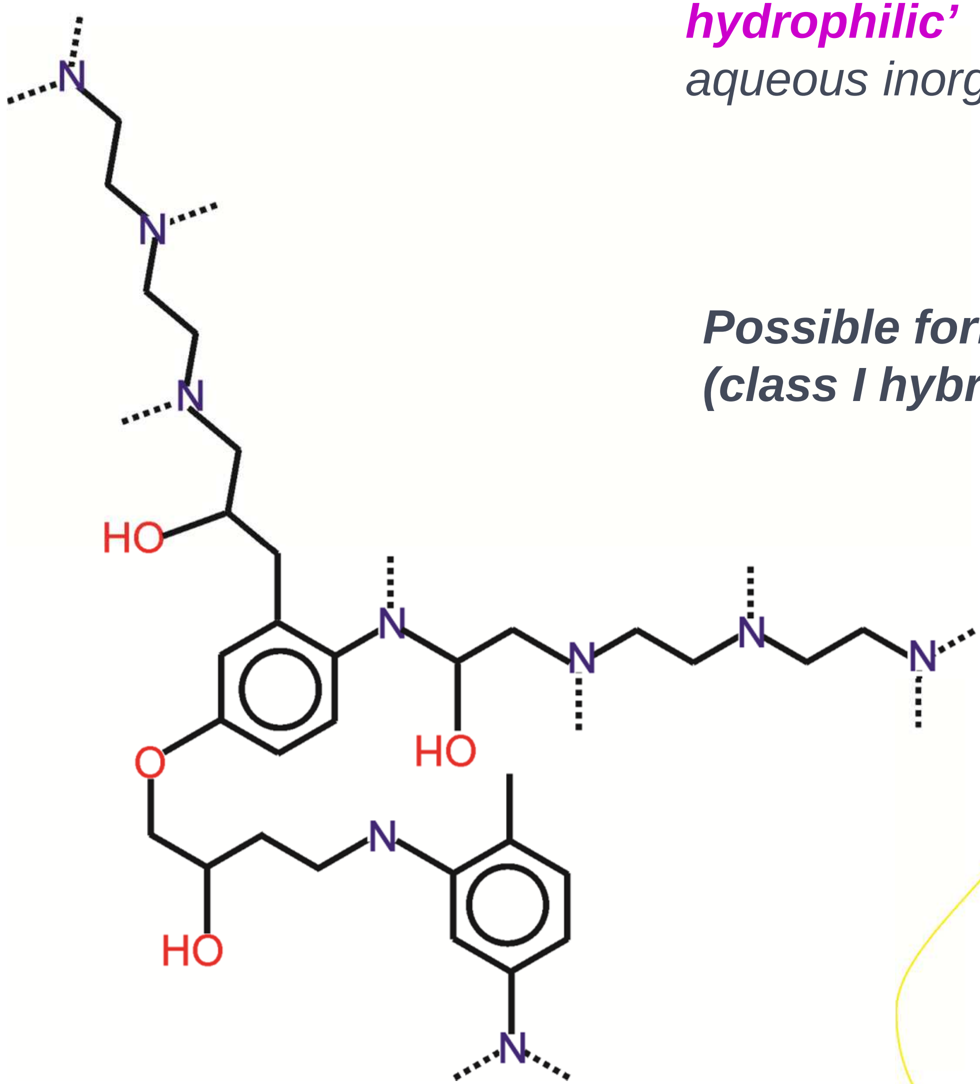
The organic component of resins are selected in order to produce numerous **hydroxyl tails** during the epoxy ring opening reaction.

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

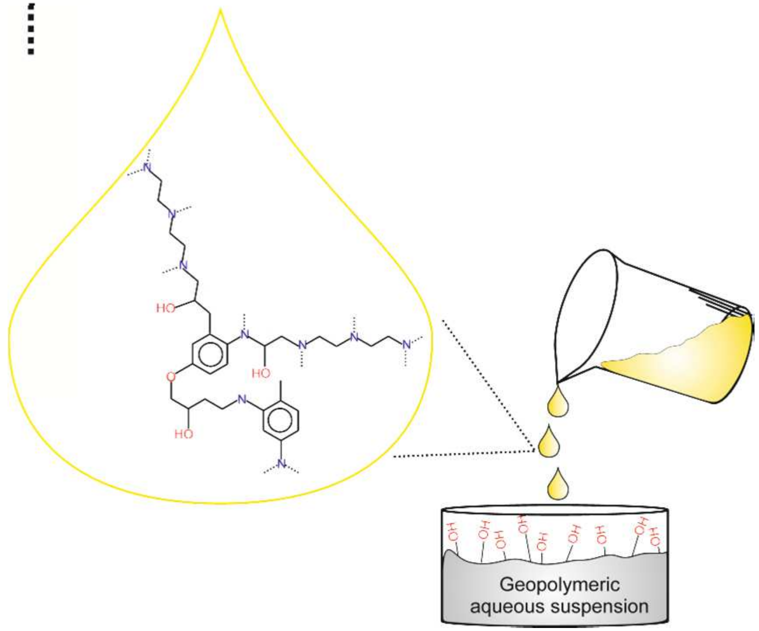
The organic phase became ***'temporarily hydrophilic'*** *and* ***well-mixable*** *with the aqueous inorganic phase.*

⬇

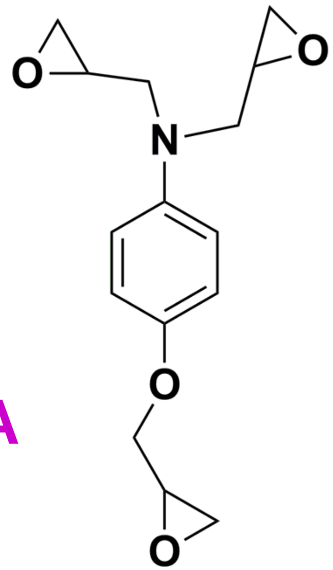
Possible formation of hydrogen bonds (class I hybrid)



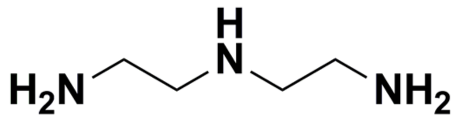
Resin 2



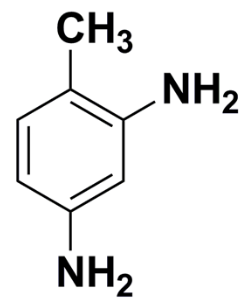
Epoxy organic resins 1 and 2



A



B



C

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

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

- a thermally stable polymer.

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.

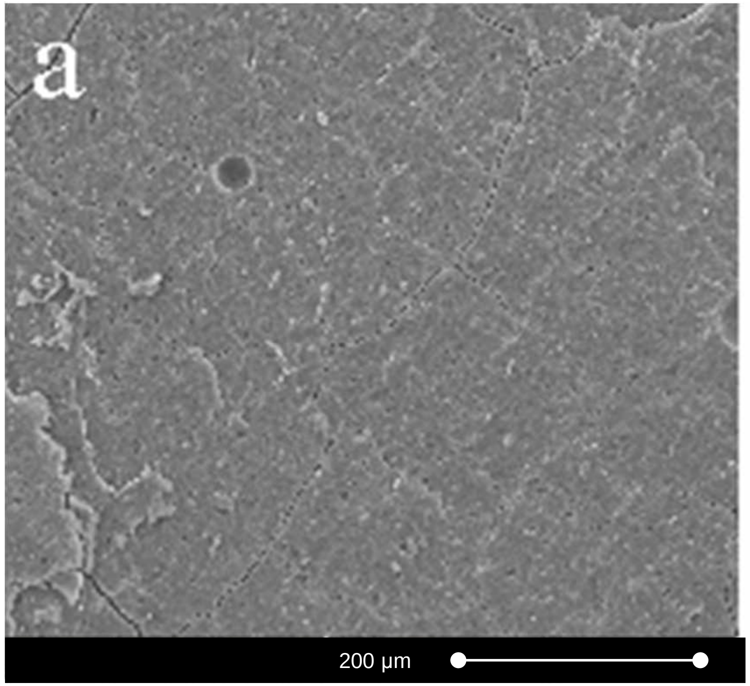
Homogeneous and stable in time dispersion of the organic microdomains into the inorganic phase, without addition of external additives.

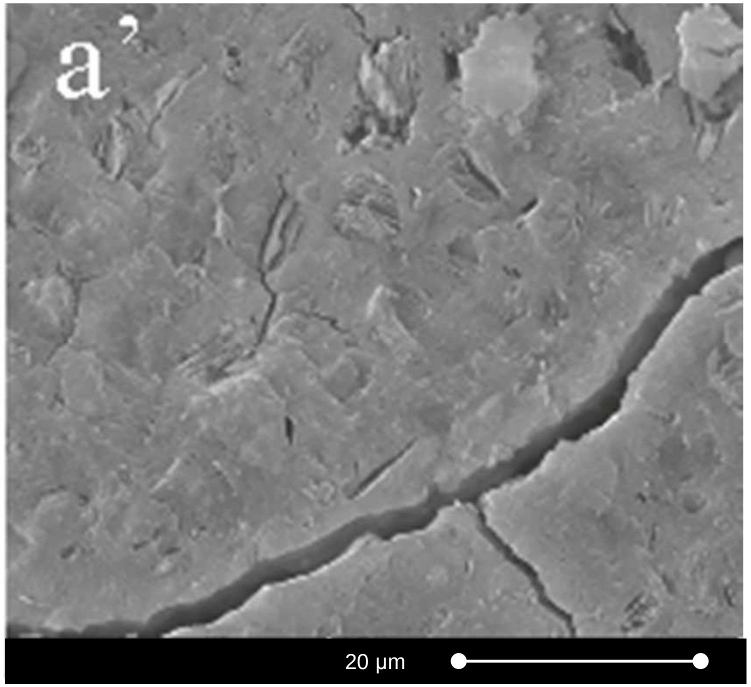
Hybrid I → MK-GEO:Resin 1 (80:20)

Hybrid II → MK-GEO:Resin 2 (80:20)

SEM micrographs

Geopolymer

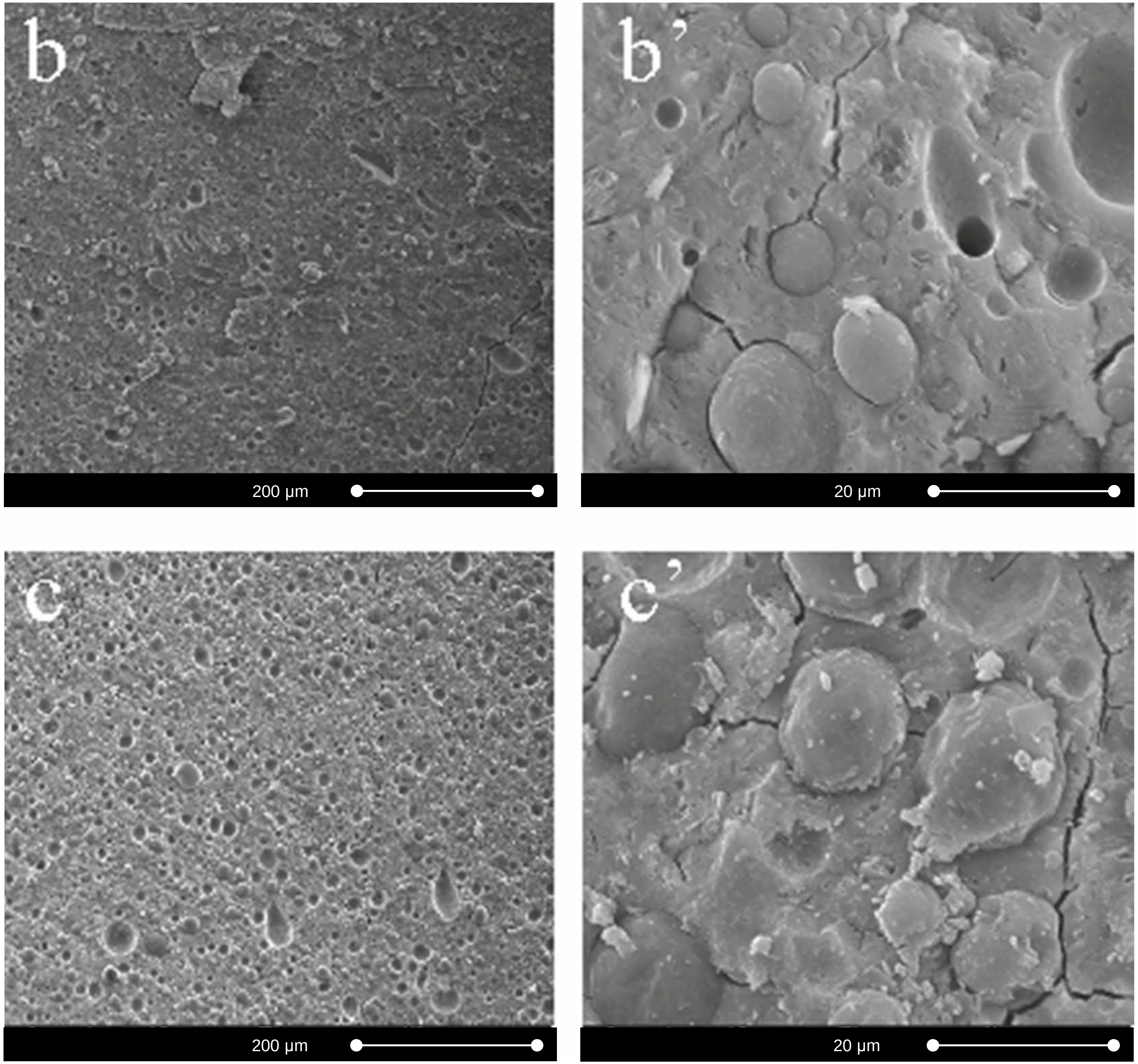


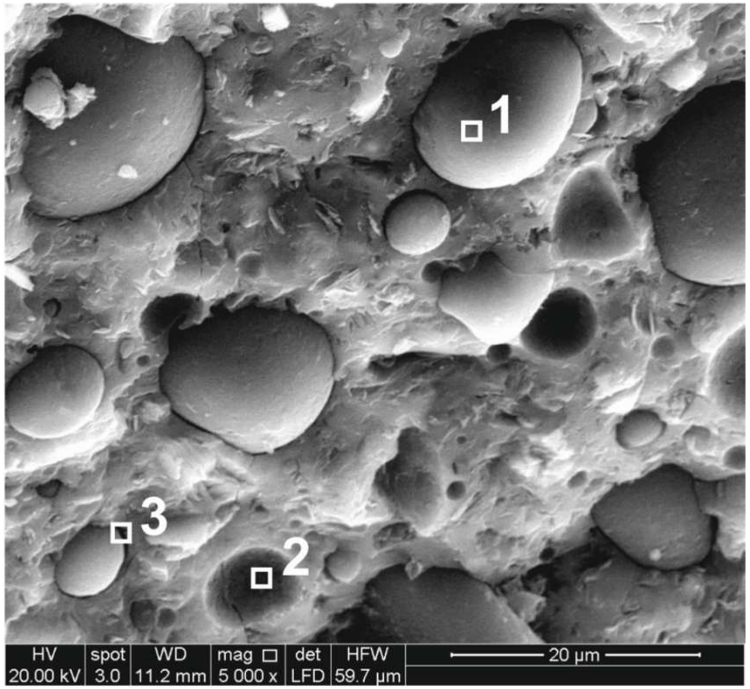


SEM micrographs

Hybrid I

Hybrid II



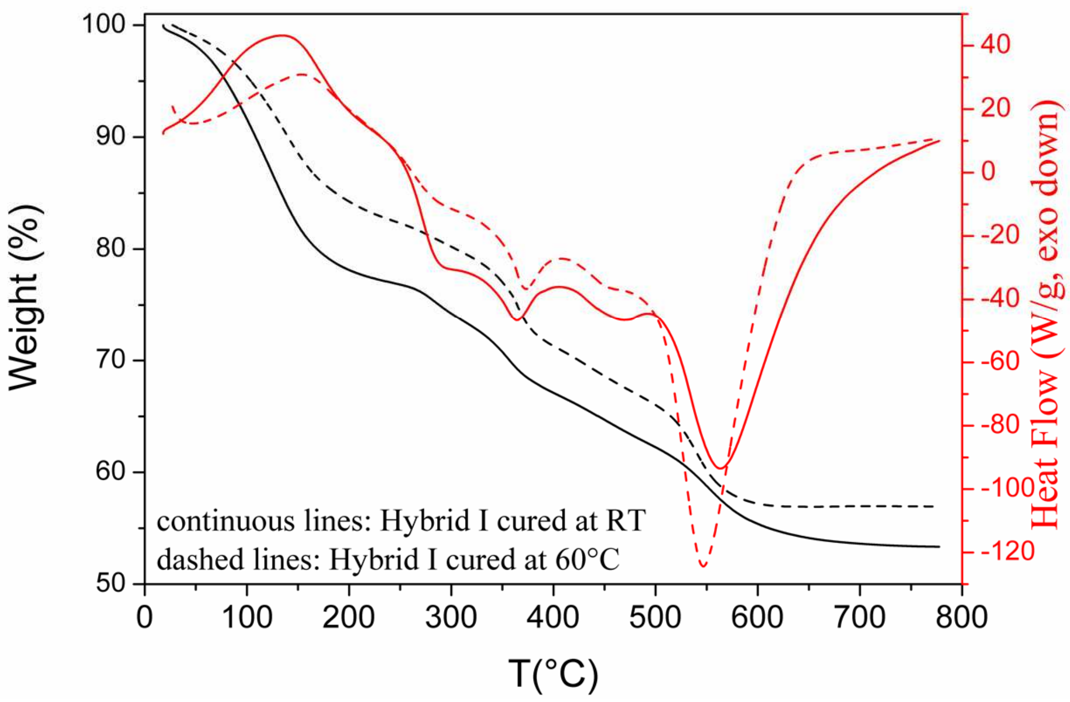


SEM micrographs (amplification 5×10^3) of the hybrid II cured at room temperature.

Spectrum	In stats.	C	O	Na	Al	Si	Total
Spectrum 1	Yes	65.54	29.15	1.49	1.48	2.35	100.00
Spectrum 2	Yes	25.14	42.93	6.11	8.68	17.13	100.00
Spectrum 3	Yes	20.73	49.67	6.64	8.09	14.87	100.00

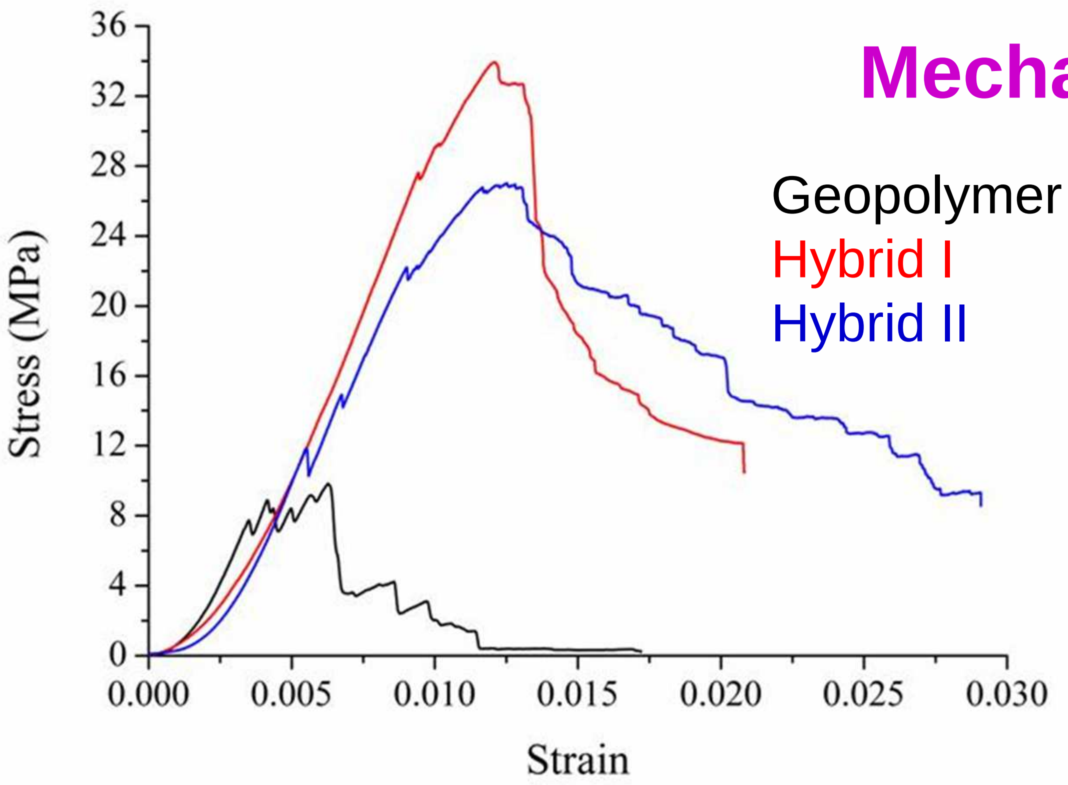
Chemical characterization obtained by energy-dispersive X-ray spectroscopy (EDS) in the regions indicated by white rectangles. All results are in weight %.

Thermal properties



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

Mechanical properties



- **Higher compressive strenght** than neat geopolymer
- **Reduction of the brittle behavior** (a sort of "pseudo-plasticity")

	Compressive Strength (MPa)	$\sigma_{0.015}$ (MPa)	$\sigma_{0.018}$ (MPa)
Geopolymer	8.2	0.0	0.0
Hybrid I	28.2	21.4	15.4
Hybrid II	29.0	20.6	16.9

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.

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)

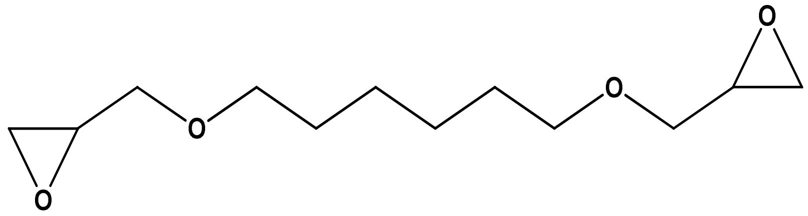
selected on the basis of:
- chemical-physical properties
- chemical composition (similar to that of previously described synthetic ones, designed in order to obtain a good incorporation in the geopolymeric matrix).

Epojet®

EpojetLV®

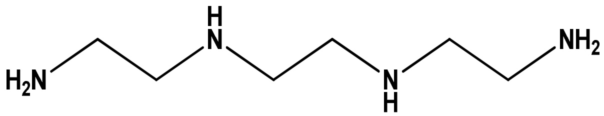
Epojet®

Component A:

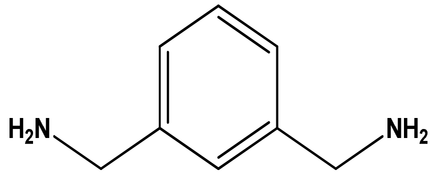


diglycidyl ether hexanediol

Component B:



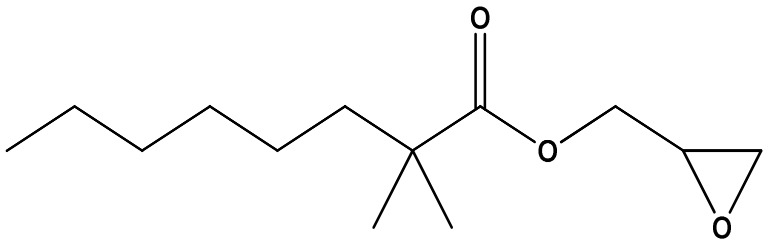
3,6-diazaoctane-1,8 diamine



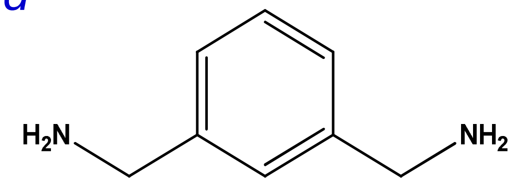
m-xililen-diamine

EpojetLV®

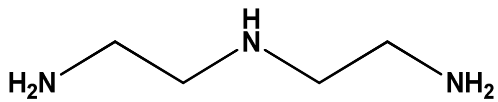
Component A: *glycidylester of neodecanoic acid*



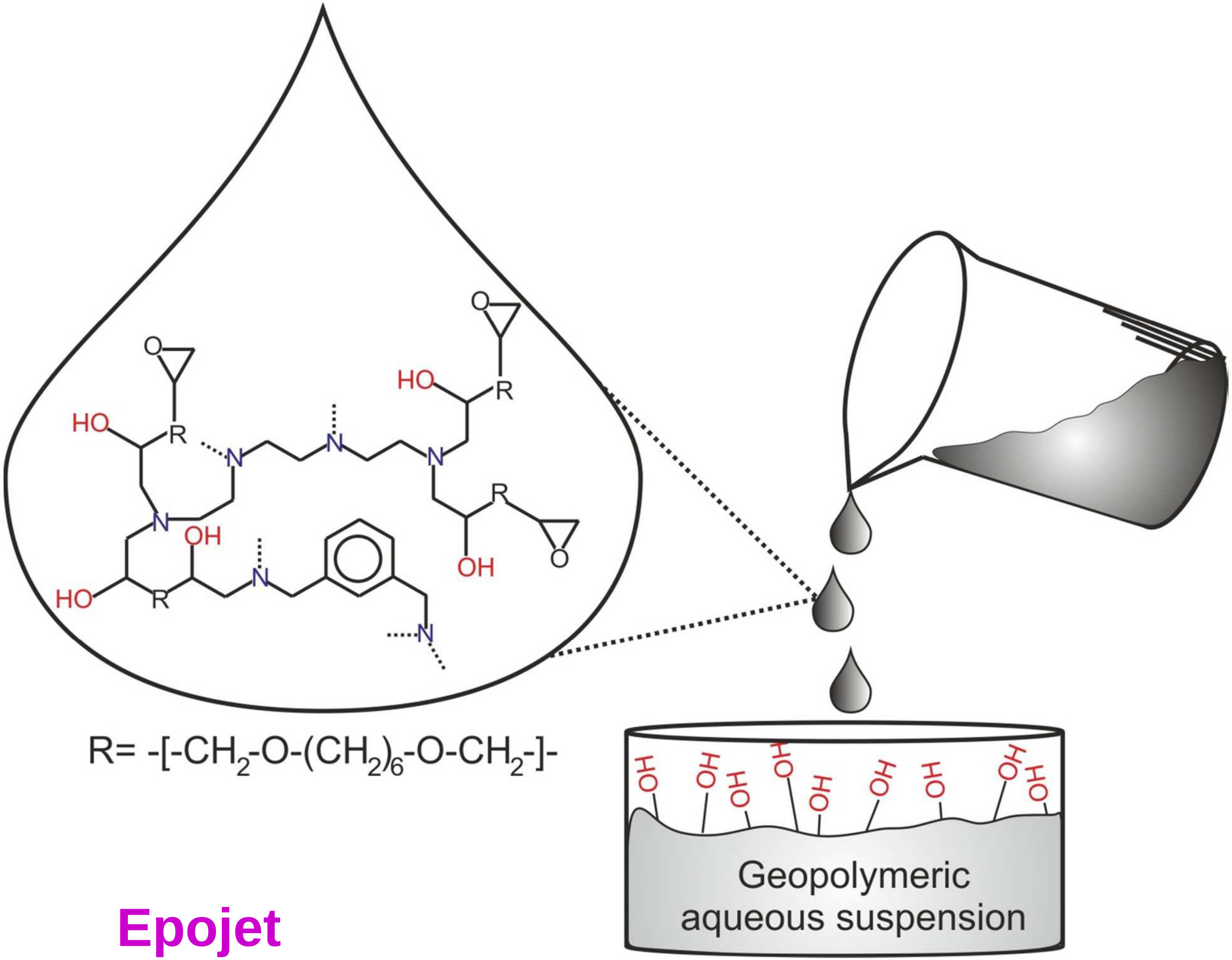
Component B:



m-xililen-diamine



3-azapentane-1,5 diamine



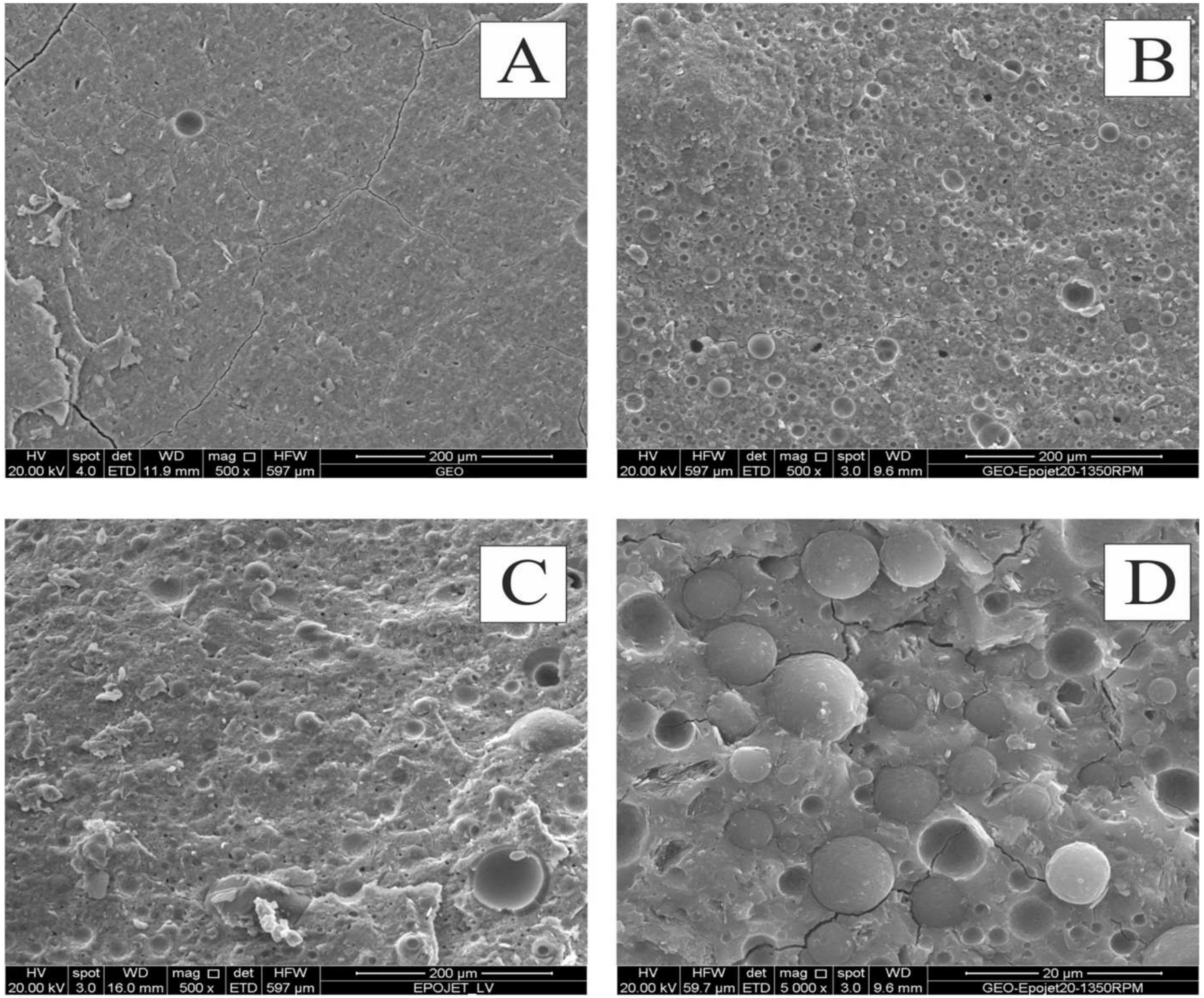
HO
R
O
N
N
N
OH
HO
R
N
HO
R
O
R
O
OH
N
R= -[-CH2-O-(CH2)6-O-CH2-]-
HO
Geopolymeric
aqueous suspension

Epojet

Geo-Epojet5 (geopolymer:resin 95:5 w/w)

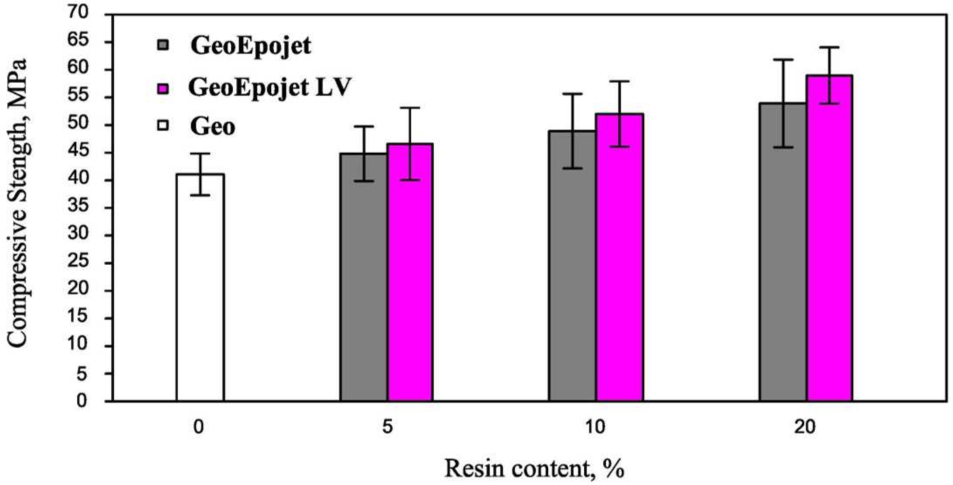
Geo-Epojet20 (geopolymer:resin 80:20 w/w)

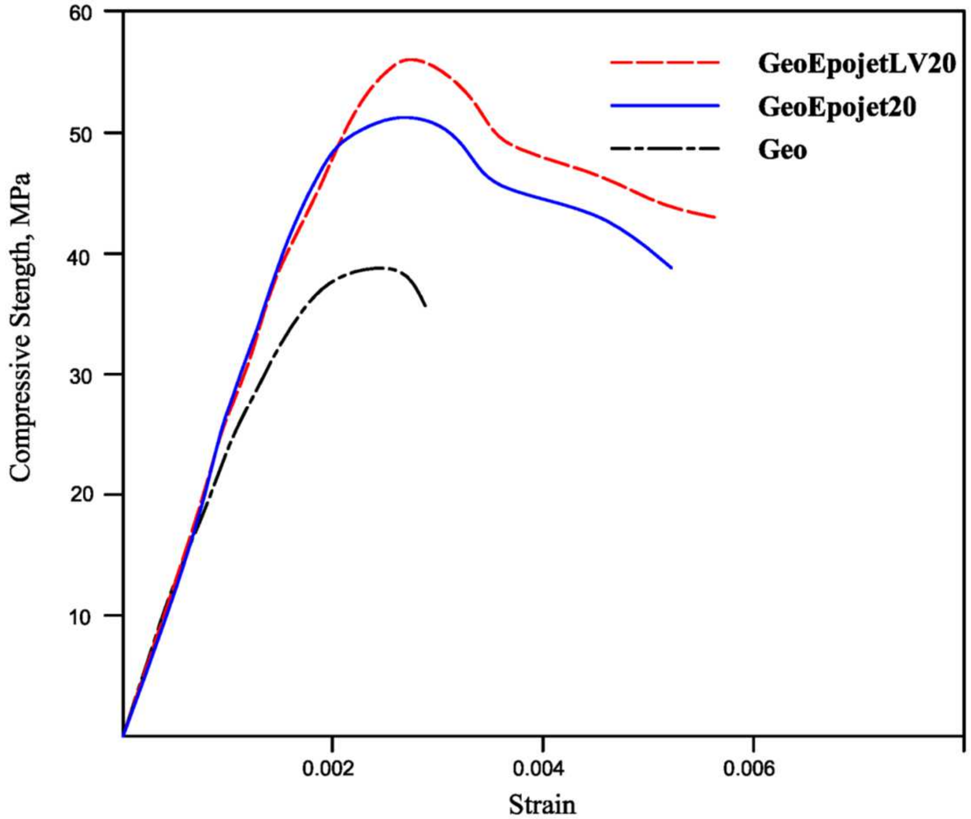
SEM micrographs



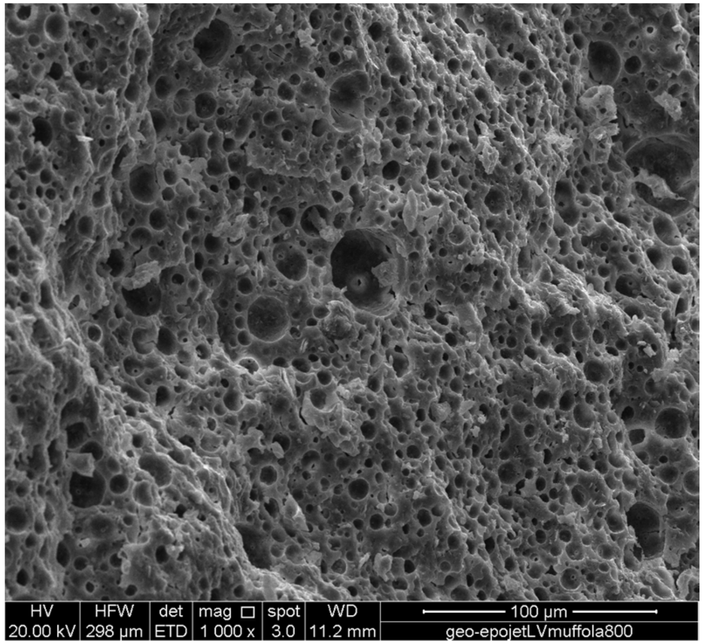
a) neat geopolymer;
b) and d) GeoEpojet20
c) GeoEpojetLV20

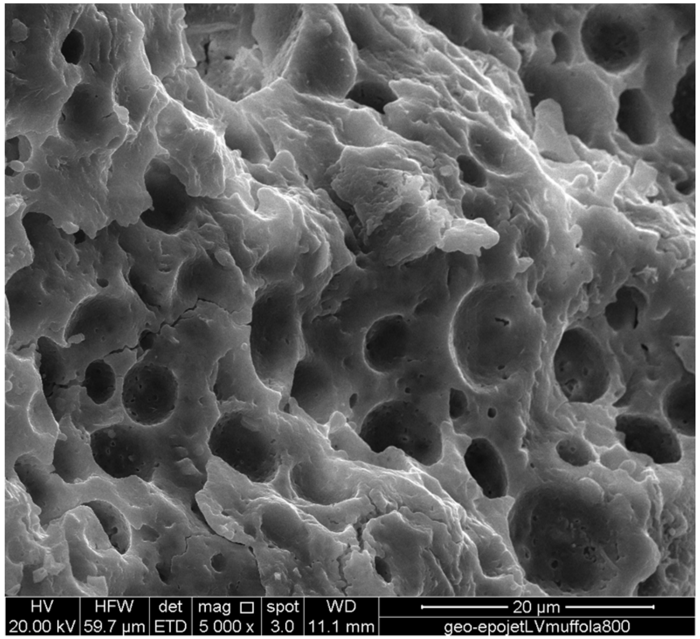
Compressive strength





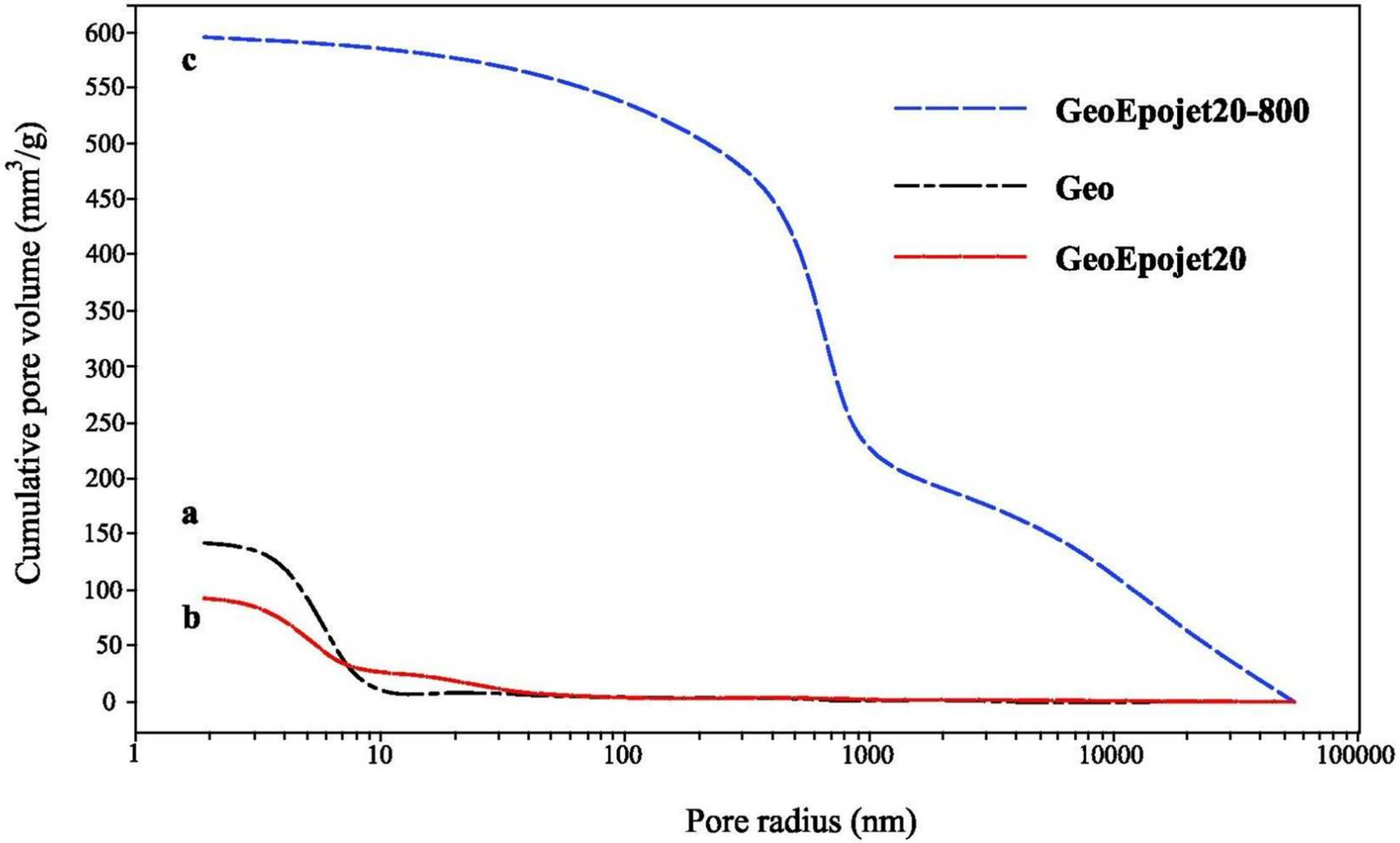
SEM micrographs of heat treated samples





GeoEpojet20 kept for 24 h at 800°C in air

Hg intrusion porosimetry

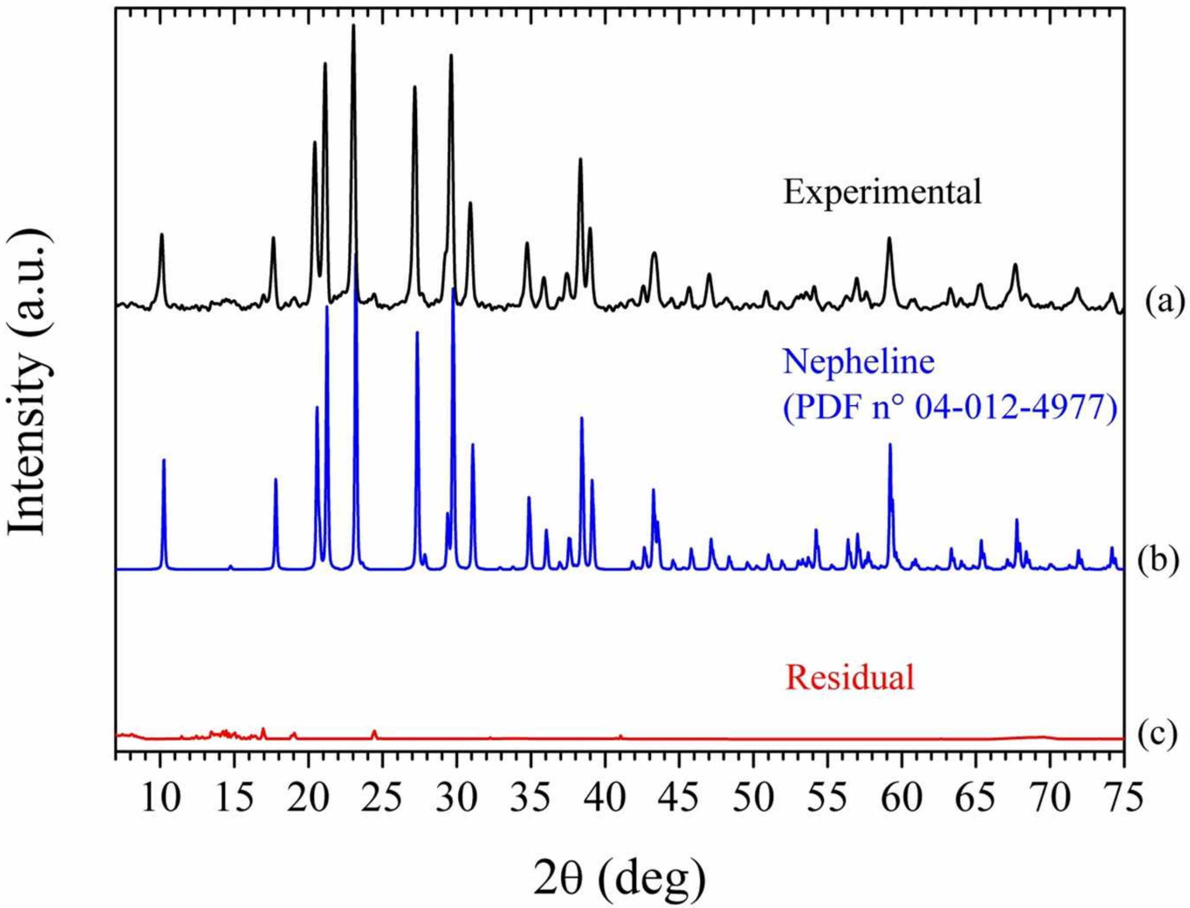


Cumulative pore volume *vs* pore radius

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

Thanks to Parthenope Research Group

Prof.Ing. Raffaele Cioffi

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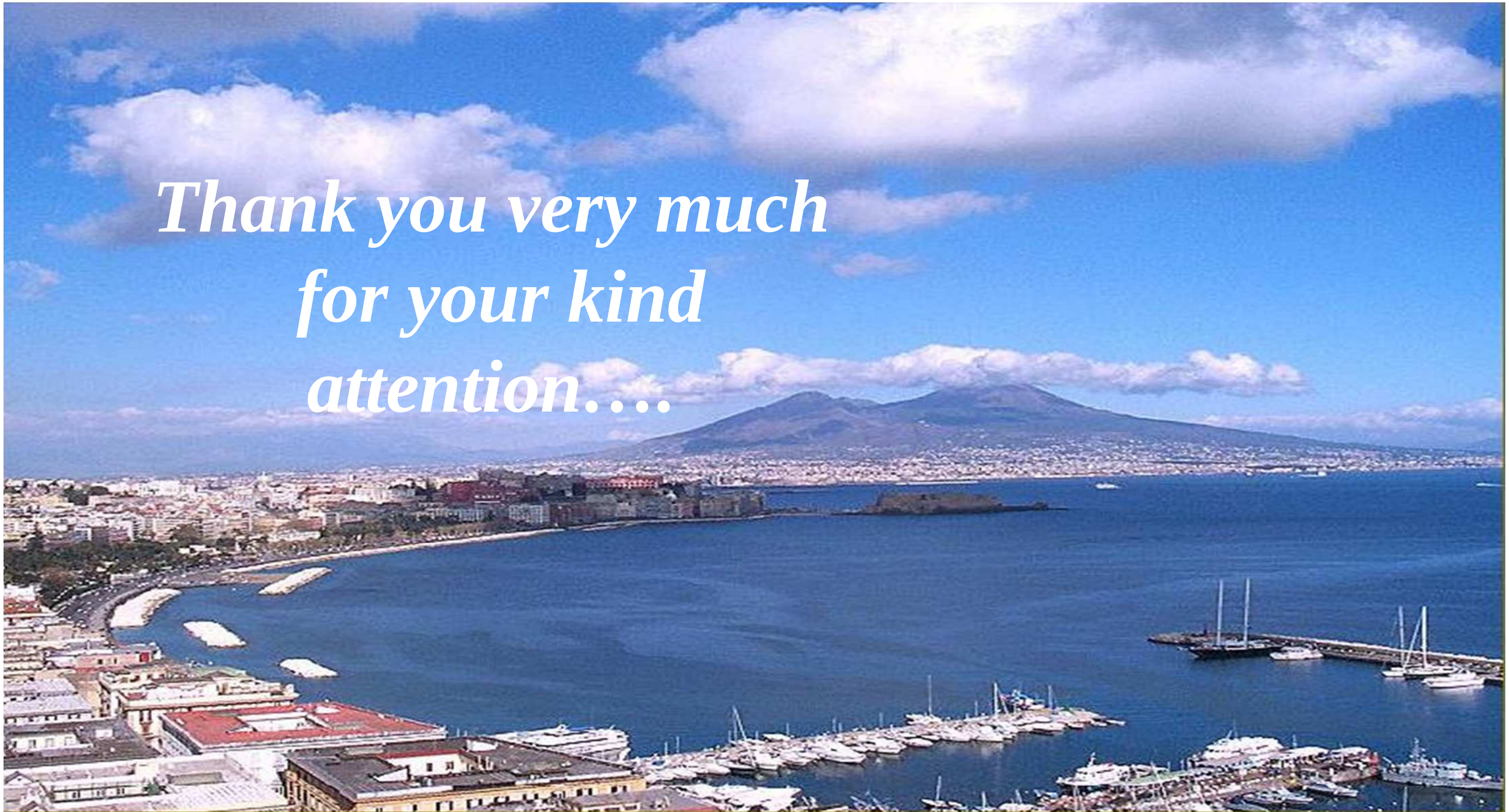

Thank you very much for your kind attention….

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