

Polyurethane–Cement-Based Foams: Characterization and Potential Uses

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ABSTRACT: The production of a new lightweight composite material based on polyurethane and Portland cement was investigated. The composite was obtained by the mixture of polyurethane foam precursors with different amounts of cement and water. To allow cement hydration, samples were aged in water and characterized through scanning electron microscopy, X-ray diffraction, differential scanning calorimetry, and compressive testing. We studied the cement hydration reactions and the effect of the organic phase on hydration by determining the amount of chemically bonded water by calcination. The results showed that the amount of water affected the morphology and porosity of the foams and thereby affected the cement hydration reaction. Furthermore, the mechanical properties of the hybrid composite var-

ied in a wide range, depending on the cement and water contents and on whether the hydrated cement particles behaved as fillers or were allowed to interact to form stronger inorganic networks within the polymeric matrix forming the bubble walls. The polyurethane–cement composite foams showed an increase in the stiffness and the yield strength. In addition, the ductile behavior of the polymeric foams was preserved, even at high filler loadings, due to the chemical compatibility between the hydroxyl groups of the polyol and the cement. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 1–8, 2008

Key words: composites; mechanical properties; polyurethanes

INTRODUCTION

Polyurethane (PU) foams are among the most important and diffuse plastic materials in the construction industry and in the domestic device industry for their excellent characteristics as insulating materials (both thermal and acoustic insulation), impact properties, and more generally, specific properties (i.e., the property over density ratio). As structural materials, however, they have to possess some strength and stiffness.^{1,2} Filling the polymeric matrix with a rigid phase is a common method for achieving stiffening effects,^{3–9} but the density and the morphology of the foams are extensively affected by the filling reinforcement, which, in turn, changes the final foam properties and thereby makes this field complex and fascinating.

Reinforced PU foams have been prepared with several kinds of fillers, including glass fibers, silicon dioxide powder, polyacrylonitrile fibers, nylon fibers,² and aluminum powder.⁹ These studies pointed out the problem of adhesion between the polymeric matrix and the filler for mechanical application. In par-

ticular, at high filler contents (i.e., > 30 wt %), the overall behavior of the PU foam shifts from ductile to brittle as a consequence of the incomplete bonding of the filler to the polymeric matrix. Thus, although the filler may act to strengthen the foam, the individual particles can act as pre-existing flaws and allow for easier crack initiation and propagation. Pretreatments of fillers have been successfully performed to improve the adhesion,² although they increased material cost.

Conventional cement and concrete represent the most widely used construction materials. Despite their physical properties and relatively low cost, these materials have a number of limitations, including low flexural strength, low failure strain, susceptibility to frost damage, and low resistance to chemicals. One can overcome these problems by assembling composite materials in which an organic polymer has been added in conjunction with cement powder. These materials, known as *polymer-impregnated concrete* and *polymer cement concrete*, have been widely studied^{10–14} and actually offer the advantages of higher strength, improved durability, good resistance to corrosion, reduced water permeability, and greater resistance to damage from freeze–thaw cycles. Along with the macrodefect-free materials,^{15,16} the polymer-impregnated concrete and polymer cement concrete

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TABLE I
Portland Cement Chemical Composition

Chemical	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	Na ₂ O–K ₂ O	Others
% w/w	23	6	3.5	63	2.5	0.9	0.3	0.8

represent at the moment the most important attempt to produce composite materials involving the conventional cement.

Recently, an increase in lightweight concrete demand has been observed. In particular, new possible applications are emerging, including cave filling or thermal and sound insulation, which require a combination of low weight and appreciable mechanical properties. The production of lightweight concrete has been achieved in different ways: (1) the substitution of ordinary aggregates with lightweight natural or artificial aggregates characterized by high porosity and very low densities (e.g., expanded polymers such as polystyrene,¹⁷ scraps of tire rubber¹⁸ scraps of PU foams from cushioning goods,¹⁹ and expanded clay²⁰); (2) the insufflation of gas inside the mortar or the addition of specific additives (chemical blowing agents) able to promote the formation of a cellular structure during hardening of the cement²¹; and (3) the opportune tuning of aggregate dimensions to create pores among the granules.²² In these systems, like in the aforementioned PU-filled systems, segregation and adhesion between the two phases are a big concern, influencing processability and properties and, hence, limiting application fields.

The combined use of a polymeric foam and cement in a new hybrid-interpenetrated material, where the two different phases are continuously and intimately connected, can represent a methodology for optimizing these materials and at the same time producing lightweight materials of a new generation.

In this study, a new type of lightweight hybrid cement-based material was examined. The system was designed to meet both the needs of reinforcing the PU foams and of lightening cement based composites without sacrificing ductility. An improvement in the adhesion between the inorganic filler and the polymeric matrix was achieved via the chemical compatibility between the hydroxyl groups of the polyol (in our case, a polyether) and the cement, as largely demonstrated in the production of macrodefect-free materials.²³ Compatibility between organic and inorganic materials was obtained without any chemical pretreatment of the filler, and therefore, this route represents a cheap system for the modification of the mechanical properties of the PU foam, with interesting potential applications in the construction field.

EXPERIMENTAL

Materials

Portland cement (CEM type IIA-S class 42,5R) was supplied by Cementir S.p.A. (Spoleto, Italy). The chemical composition is reported in Table I. Polyether and toluene diisocyanate (TDI) were supplied by Bayer (Deltapur S.p.A., Bergamo, Italy) and were used as received. According to the producer's specifications, the polyether/TDI ratio was 1 : 1.2 to achieve an open-cell, flexible foam. Distilled water was used to control foaming.

Methods

We prepared the samples by first mixing the cement and water with the polyether. This mixture was stirred mechanically for 1 min, and then, under continuous stirring, TDI was added. The resulting mixture was mixed finally for 1 min. The water/cement weigh ratio varied between 0 and 0.083. The liquid/solid ratio varied between 15 and 0.67. Table II reports the compositions of the mixtures; the letters refer to the amount of water (A = 0% w/w water, B = 0.5% w/w water, and C = 5% w/w water), and the numbers refer to the cement content (0 = 0% w/w cement, 1 = 6.25% w/w cement, 2 = 12, 3 = 21% w/w cement, 4 = 40% w/w cement, and 6 = 60% w/w cement).

Mixtures were poured in molds (40 × 40 × 160 mm³) and cured at room temperature and 50% relative humidity for 24 h, according to the producer's

TABLE II
Compositions of the Tested Mixtures: Adopted Classification

Sample	Polyol (% w/w)	Diisocyanate (% w/w)	Water (% w/w)	Cement (% w/w)
A0	66.7	33.3	0	0
A1	62.5	31.2	0	6.2
A2	58.8	29.2	0	12
A3	52.6	26.3	0	21
A4	40.0	20.0	0	40
B0	66.3	33.2	0.5	0
B1	62.2	31.1	0.5	6.2
B2	58.3	29.2	0.5	12
B3	52.4	26.2	0.5	21
B4	39.9	19.9	0.5	40
B6	26.3	13.2	0.5	60
C0	63.3	31.6	5	0
C1	59.2	29.6	5	6.2
C4	36.7	18.3	5	40
C6	23.3	11.7	5	60

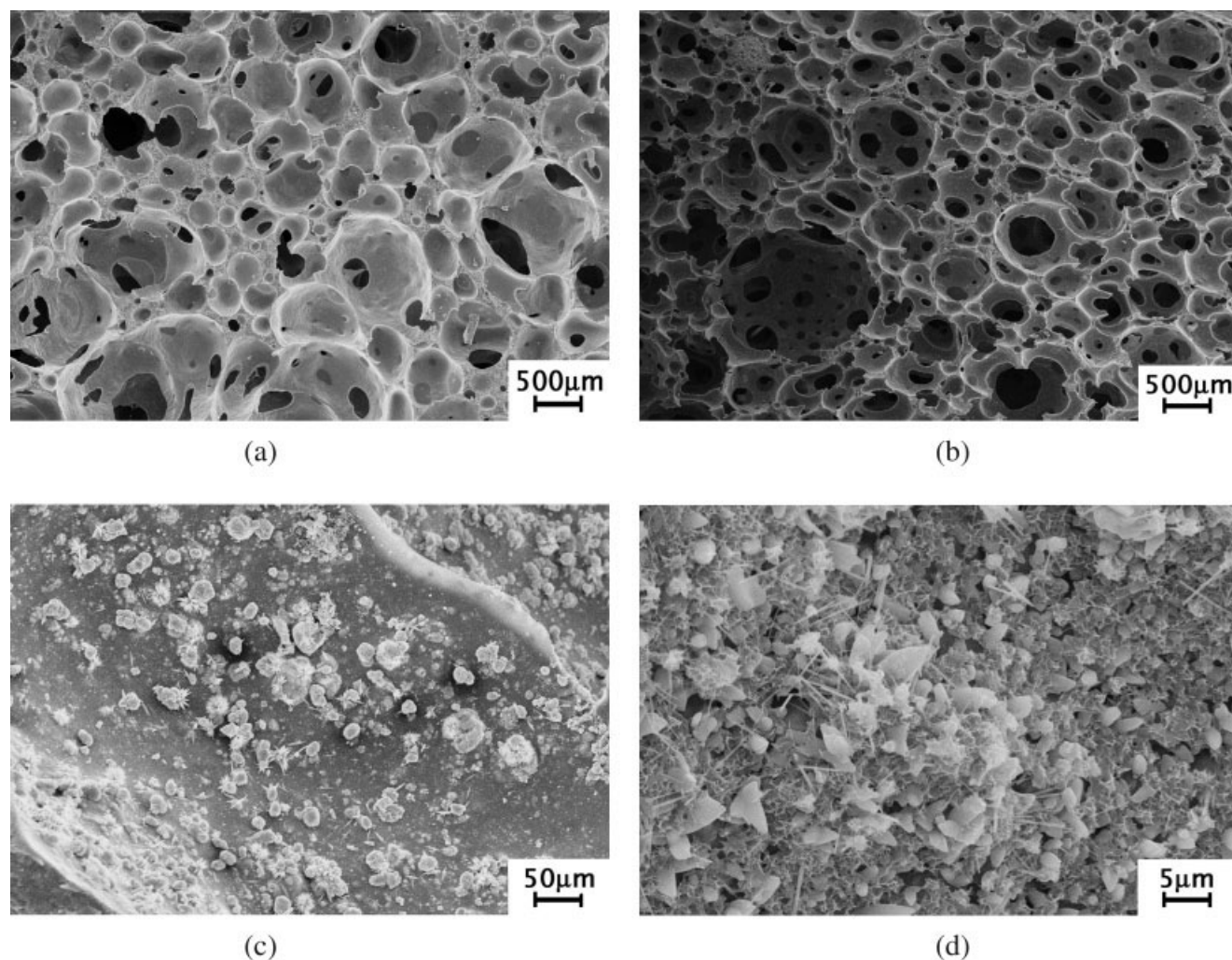


Figure 1 SEM micrographs for selected systems before and after the hydration reaction: (a) A4, unhydrated (35 \times); (b) C4, unhydrated (50 \times); (c) A4, hydrated (500 \times); and (d) C4, hydrated (5000 \times).

specifications. Subsequently, samples were removed from the molds and aged in water according to UNI EN 196-1 : 1996, for 7, 14, and 28 days. Subsequent analyses were performed on both hydrated and unhydrated samples. We stopped hydration by crushing samples in a mortar and flushing the powder with acetone and ethyl ether twice. Milled and crushed samples were used for the analyses.

Differential scanning calorimetry (DSC) analysis was carried out on a DSC2920 (TA Instruments, New Castle, DE). The samples were heated from 20 to 250 $^{\circ}$ C at 10 $^{\circ}$ C/min under a nitrogen atmosphere.

Wide-angle X-ray diffraction analysis was performed at room temperature with a Philips X-ray generator and a Philips diffractometer (Eindhoven, The Netherlands), type PW1710. The X-ray beam was nickel-filtered Cu K α radiation with a wavelength of 1.54 \AA operated at a generator voltage of 40 kV and a current of 20 mA. The diffraction intensity data were collected automatically at a scanning rate of 0.6 $^{\circ}$ /min with 0.01 $^{\circ}$ /s steps.

The nonevaporable content of chemically bonded water ($\text{H}_2\text{O}_{\text{cb}}$), defined as the mass loss per gram of original cement, was measured between the temperatures 105 and 1000 $^{\circ}$ C, according to ASTM Bulletin 158 (1949). From the $\text{H}_2\text{O}_{\text{cb}}$, we estimated the degree of hydration by assuming a value equal to 40% for the nonevaporable water of a fully hydrated sample.

Compressive tests were carried out on an Instron testing machine (model 4204) (Norwood, MA) with a 5-kN load cell. A 40 \times 40 \times 160 mm 3 mold was chosen for the production of the samples to perform the mechanical testing according to UNI-EN 196-1. This procedure was not applicable to our samples because they did not fracture under flexural load. To mechanically test these materials, therefore, we performed compressive testing according to ASTM D 638.

The density was calculated as the ratio between the foam weight (as measured with an analytical balance) and volume (as measured by a high-resolution caliper).

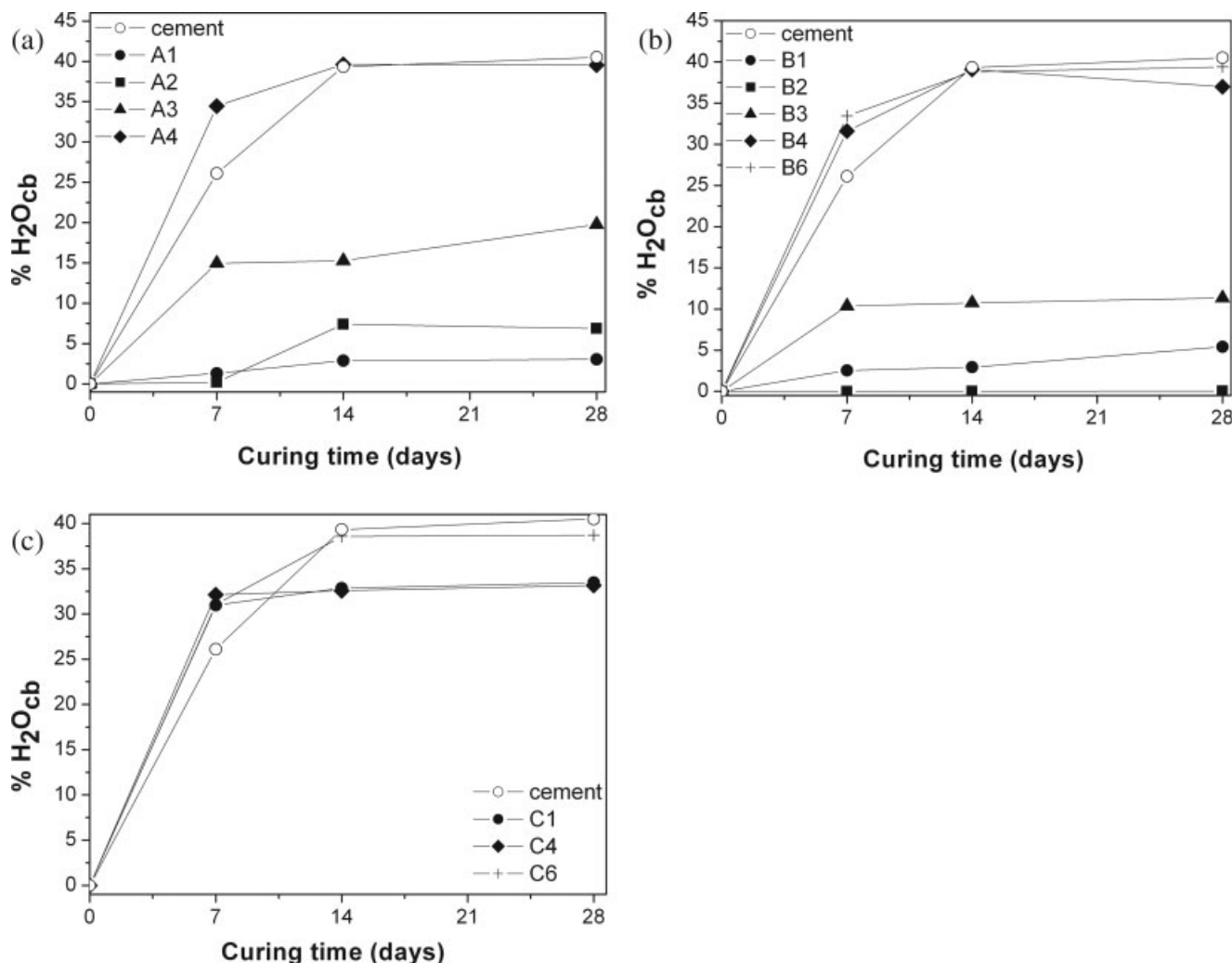


Figure 2 Progression of the hydration reaction for neat cement and tested foams (see Table II for the foam compositions and classification): (a) system A, (b) system B, and (c) system C.

For microstructural analysis, the foamed samples were analyzed by scanning electron microscopy (SEM). The samples were first sectioned and then coated with gold with a sputter coater (Emscope SC500, Ashford, UK). The morphology of the fracture surface was studied with a Leica model S440 instrument (Leica Microsystems GmbH, Wetzlar, Germany) operating at 20 kV.

Fluidity

The fluidity of the mixtures with the polyether (with and without water) and the cement was quite good for almost all of the tested compositions except systems with 60% cement (quite difficult to mix). After the addition of the TDI, the fluidity immediately increased, which allowed for optimal mixing, and then decreased progressively for the occurrence of the polymerization reaction.

RESULTS AND DISCUSSION

Morphological characterization

SEM micrographs for systems A4 and C4 (see Table II for classification) before aging in water are reported in Figure 1(a,b). The morphology of partially open cells characteristic of flexible PU foams was observed. When the amount of water increased, foams with smaller cells (and with lower densities) were obtained. At the same time, the open-cell content increased considerably. This morphological change was responsible for a reduction in the thickness of the cell walls/struts and, in turn, as will be discussed later, for the increase in the number of the cement particles which were partially exposed directly to water during hydration. Figure 1(c,d) reports the micrographs of the internal surface of the bubbles for samples A4 and C4 aged for 28 days in water. Worth noting was the presence of the typical

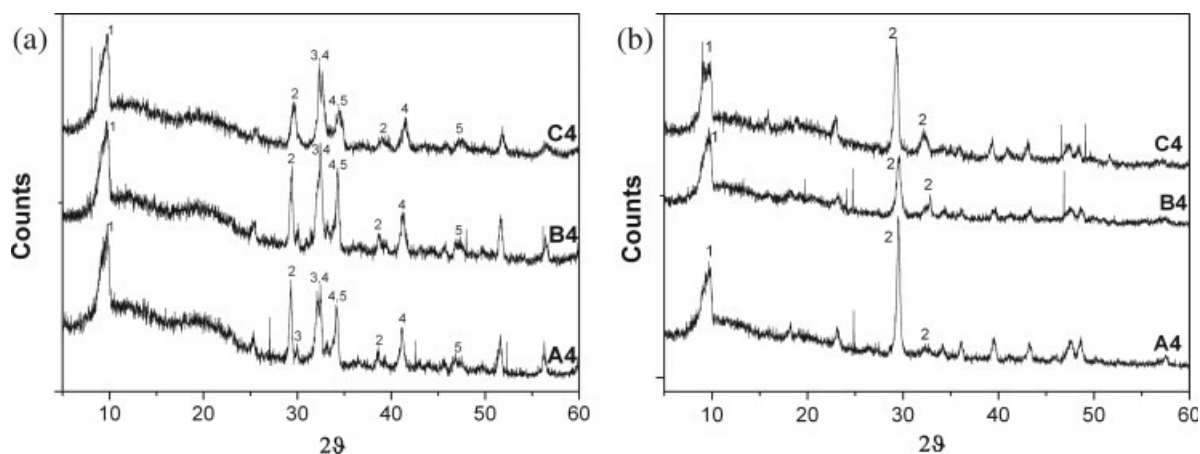


Figure 3 X-ray diffraction patterns for selected samples (a) before and (b) after hydration. The peaks are attributed as follows: (1) pure PU, (2) CaCO_3 , (3) C3S, (4) C2S, and (5) Ca(OH)_2 .

needle morphology of the calcium silicate hydrate at higher magnitudes.

The hydration products of the cement allowed for the constitution of an inorganic network, depending on the reciprocal distance between the single cement particle and on the cement concentration in the bubble walls. This network was not observed for sample A4. Conversely, the inorganic network was clearly observable for sample C4, where a noticeable reduction in the bubble wall thickness minimized the distance among the cement particles and favored the creation of a network during the hydration reactions.

Chemical bonded water ($\text{H}_2\text{O}_{\text{cb}}$)

Figure 2 reports the results of the $\text{H}_2\text{O}_{\text{cb}}$ measurements tests. The $\text{H}_2\text{O}_{\text{cb}}$ values were normalized with respect to the effective amount of cement in the composite materials. This parameter was very effective in showing the effects of the composition on the hydration reactions of the cement. The results for the neat cement are also shown for comparison. All systems showed that $\text{H}_2\text{O}_{\text{cb}}$ changed quickly due to the rapid hydration of cement particles.²⁴ After 14 days, almost all curves reached a plateau. As expected, the decrease in the amount of cement led to an inhibition of the hydration reactions. For example, after 28 days of hydration, when the amount of cement was reduced from 40 to 6.25 wt %, the $\text{H}_2\text{O}_{\text{cb}}$ for system A decreased from 38 to 2.5%, whereas for system B, it decreased from 36 to 2%. Samples A4, B4, and C4 showed plateau $\text{H}_2\text{O}_{\text{cb}}$ values similar to that of pure cement. In the hybrid systems A and B, therefore, the 40% cement content seemed to represent a threshold value for complete hydration. The C systems showed different behavior: C1 (with a cement content of 6.5%

w/w) showed a plateau value of $\text{H}_2\text{O}_{\text{cb}}$ equal to 33.5%, which was comparable to those of foams at higher (40 and 60%) cement content.

One can discuss this behavior by considering both the effect of the water added during mixing on the morphology of the foams and the possible gathering of the cement particles in the bubble walls. When a small amount of cement was mixed with the PU precursors, a thin skin of hydrophobic PU covered the cement particles. In this case, they did not come into contact with water and were not allowed to hydrate. Conversely, when the amount of cement in the hybrid material increased, cement particles gathered in the thickness of the bubble walls, forming a continuous path, accessible to water. As already observed, the amount of initial water content affected the cell morphology and density. In this context, therefore, water played an important role in the hydration mechanism by affecting the gathering

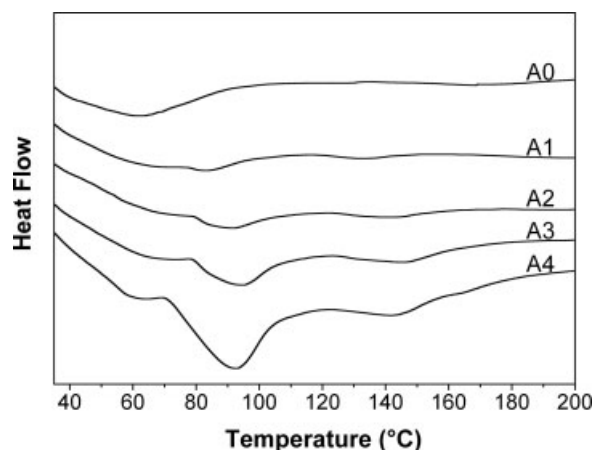


Figure 4 DSC of sample A after hydration.

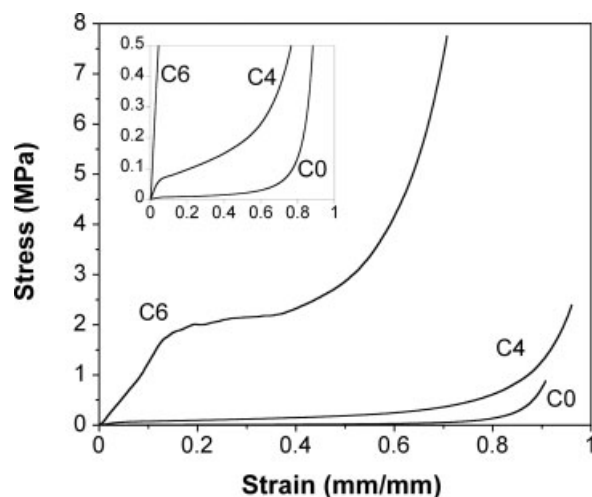


Figure 5 Average stress–strain curves for selected foams (a magnification at lower stresses is shown in the inset).

of the cement particles and, hence, controlling hydration (cf. systems C4 with A4 and B4).

Characterization with X-ray diffraction

The X-ray diffraction patterns of selected samples, before and after hydration, are reported in Figure 3(a,b). Diffraction peaks characteristic of pure PU and the $2\text{CaO}\cdot\text{SiO}_2$ (C2S) and $3\text{CaO}\cdot\text{SiO}_2$ (C3S) composites, together with the diffraction peak of CaCO_3 , are highlighted in the figures. After hydration, the diffraction peaks relative to C2S and C3S disappeared, and the amorphous halo of calcium silicate hydrate appeared. Furthermore, the diffraction peak of CaCO_3 increased due to the carbonation reaction of the calcium hydroxide. These modifications [cf. Fig. 3(a,b)] were justified with the classical chemistry involved in the hydration reactions of the cement.²⁴

Characterization with DSC

DSC curves for selected samples are reported in Figure 4. All of the samples showed an endothermic peak at about 70°C . This transition was attributed to the PU phase and represented an annealing peak of

the PU, as also reported by Karkanis and Partridge.²⁵ In the thermographs of samples A1, A2, A3, and A4, an endothermic effect was observed around 90°C , which was attributed to the removal of the bonded water from the calcium silicate hydrate produced in the cement hydration. This peak increased with cement amount. Samples A3 and A4 showed another endothermic peak, around 140°C , caused by ettringite dehydration; this peak was less evident, obviously, for samples with a lower amount of cement.²⁴ The same experimental evidence was observed for specimens B and C (data not reported).

Mechanical properties

Compressive testing evidenced the dramatic effect of the filler on the elastic and plastic properties of the reinforced foams. Figure 5 reports the stress–strain curves for selected foams and shows the stiffening effect of the cement particles. The curves show the typical behavior of elastomeric foams characterized by an initial linear portion, related to the elastic deformation of cells; a macroscopic yield with an almost horizontal plateau; and a densification part, identified by a progressive increase of the curve. This behavior has been observed in both open- and closed-cell structures.^{26,27} These structures do not fracture under compressive deformation, even at higher filler content, and provide good adhesion between the filler and the polymeric matrix, which is achieved via the hydroxyl groups' compatibility. The mean values of the mechanical compressive properties are reported in Table III. In addition to the stiffening effect of the cement particles with increasing cement concentration, a great increase in the mechanical properties (e.g., in the elastic modulus) with increasing water content (cf. A4 and B4 with C4) was observed. This phenomenon was attributed to the formation of a stronger inorganic network of the hydrated cement particles (C4) with respect to the systems in which the cement particles just behaved as individual fillers (A4 and B4), as also evidenced previously.

The values of the elastic moduli of the foams are also reported, as a function of foam densities, in

TABLE III
Results of Compressive Tests on Selected Foam Compositions

Foam	Young's modulus (MPa)	Strain at yield (mm/mm)	Yield stress (MPa)	Stress at 25% strain (MPa)	Stress at 40% strain (MPa)	Stress at 50% strain (MPa)	Stress at 60% strain (MPa)
C0	0.11	0.10	0.01	0.012	0.015	0.019	0.032
C4	1.58	0.089	0.086	0.104	0.135	0.179	0.41
C6	16.49	0.153	2.05	2.0936	2.3192	2.8316	5.182
A4	0.47	0.094	0.036	0.048	0.065	0.085	0.177
B4	0.36	0.108	0.031	0.047	0.087	0.094	0.19

Figure 6. The mechanical behavior of foams was modeled by the following equation, as proposed by Gibson and Ashby:²⁷

$$\frac{E^*}{E^s} = \left(\frac{\rho^*}{\rho^s}\right)^n \quad (1)$$

where E is the Young's modulus, ρ is the density, the superscript s indicates a property of the solid cell wall material, and the superscripted asterisk refers to a property of the foams itself. Gibson and Ashby showed that the Young's modulus of foams varies quadratically ($n = 2$) with the density if cell walls are much thinner than cell edges and the deformation is governed by edge bending. In our case, the exponent n was equal to 2.8. To clarify the high value for n , it should be emphasized that, in our case, the stiffening effect was obtained via the increase in the filler content and not via a porosity reduction (also responsible for the densification). In our case, therefore, the increased dependence of the moduli on the density was expected.

Figure 7 reports the stress at 40 and 60% deformation during compression of the hybrid foams and shows a wide range of mechanical behavior of the cellular structure, from 0.03 to 16.5 MPa. Power-law dependence, with an exponent equal to 2, was observed.²⁷

Local regulations (UNI 7548) on the use of lightweight concrete define materials having a density of less than 0.8 g/cm³ and a uniaxial compression stress in the range 7–70 kg/cm² as lightweight non-structural concrete composites. Selected PU-cement foams, therefore, proved to be suitable for use in the construction field as an interesting alternative for insulating or shock-absorbing panels.

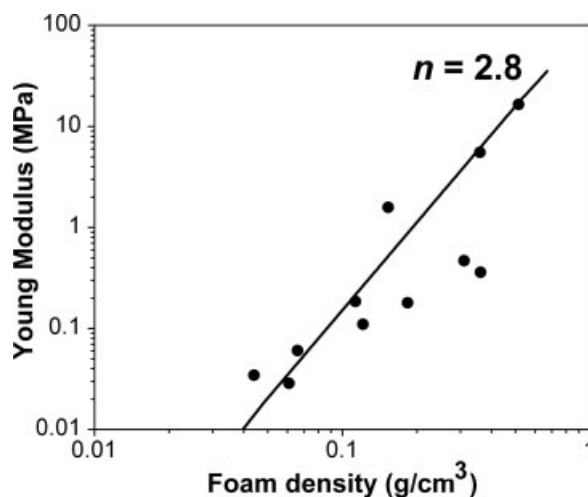


Figure 6 Results of the compressive testing of the PU/cement hybrid materials: Young's moduli and eq. (1) fitting results.

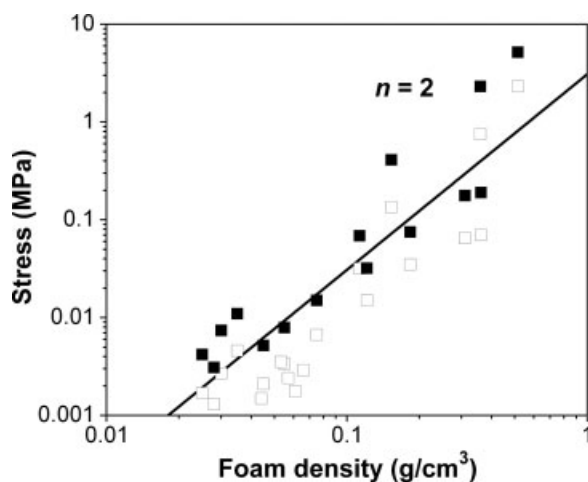


Figure 7 Results of the compressive tests of the PU/cement hybrid materials: the stress corresponding to (□) 40 and (■) 60% deformation and the power-law fit of the data.

CONCLUSIONS

In this study, the feasibility of producing hybrid PU/cement foams was investigated. The achieved characteristics of the composites were

1. Final foam densities between 30 and 90 kg/m³.
2. Compressive strengths, at 25% deformation, in the range 0.025–2 MPa, with the highest compressive strength of 2 MPa for the composite with a density equal to 90 kg/m³.
3. The formation of a network of calcium silicate hydrate within the PU foam for selected composition and blowing agent content.

In particular, the hydration of the cement powder and the resulting formation of the network led to a significant increase in the mechanical properties with respect to foams with unnetworked cement particles. PU-cement hybrid foams proved to be suitable for use in the construction field as lightweight nonstructural concrete composites for their interesting specific compressive properties.

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