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LETTER

Hydration-induced reinforcement of polyurethane–cement foams: solvent resistance and mechanical properties

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Hybrids are characterized by the combination of organic and inorganic phases interacting through primary and/or secondary bonds [1–3]. These materials can be described in terms of particulate and interconnected or co-continuous morphologies. Particulate hybrids are usually produced by embedding inorganic phases in the form of discrete units in a polymeric matrix. Co-continuous hybrids, conversely, are characterized by interconnected nanoscopic domains and are usually generated from a precursor formerly introduced within the organic matrix [2–6].

The co-continuous morphology is generally the aimed one, since it creates the conditions to achieve the most efficient mechanism for the transfer of external excitations through the two phases, thereby maximizing the contribution of both components (organic and inorganic) to the overall properties of the hybrid (synergistic effect) [6–9]. This is particularly desirable in the case of foams, where the low density contributes to functional properties, such as thermal and acoustic insulation, while the inorganic reinforcement increases the stiffness and strength and dimensional stability, as well as water vapor permeability, improving also fire resistance and the adhesion to inorganic binders [10–12].

Recently, we have developed [10, 11] a new interconnected hybrid material produced by a non-conventional approach, which does not involve the usual sol–gel reactions [2, 6, 7]. The new hybrid is a porous material, in which the solid phase is composed of polyurethane and hydrated Portland cement particles. In this novel approach, the hybrid is produced in two steps: (a) formation of a polyurethane–anhydrous cement composite foam (see Scheme 1, composite material) and (b) formation of the hybrid through the hydration reaction of the Portland cement particles to produce the amorphous inorganic phases such as hydrated calcium silicates and aluminates that are commonly observed in the hydration of ordinary cement mixtures (see Scheme 1, hybrid material). This newly formed inorganic hydrated phase has the classical needle-shape structure of ordinary cements. The formation of an interconnected inorganic network depends on the original amount and dispersion of anhydrous cement particles within the polyurethane foam, as well as on the extent of the hydration [10, 11]. This new approach can be referred to as “Hydration-Induced Reinforcement of Polymer–Cement” (HIRP-C) hybrid materials.

In view of the higher resistance to swelling of the inorganic phase when in contact with solvents, solvent sorption measurements have often been used to discern the presence of particulate or interconnected and co-continuous morphologies [13].

In this letter, we report the results of solvent swelling measurements to highlight the strong influence of the interconnected inorganic acicular structure type reinforcement within the walls of the cells of newly developed polyurethane/cement hybrid foam. In particular, we demonstrate that before the hydration step the cement particles are discretely dispersed in the polyurethane matrix, while, after the hydration step, a state of interconnected network is acquired, which provides a high resistance to solvent

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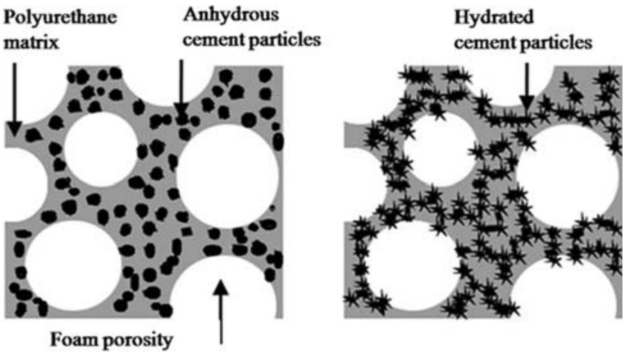

Scheme 1 Schematization of composite (Portland cement particles dispersed in polyurethane matrix) and hybrid structure (hydrated Portland cement continuous within polyurethane matrix)

swelling after hydration, as well as a large increase in modulus and strength (see Fig. 1, Table 2).

The polyurethane/cement foams were prepared by mixing initially the polyol with catalysts, surfactants, water, and anhydrous cement particles and then with methylene-diphenyl di-isocyanate [10, 11] (compositions, densities, and designations are shown in Table 1).

The resulting mixture was poured in 10 × 10 × 3 cm^3 molds and allowed to expand and cure for 8 h at room temperature and humidity conditions. Subsequently, cylindrical specimens ($d = 9.6$ mm, $h = 10$ mm) were drilled out from the foamed slab. The specimens were finally subjected to the hydration process by immersion in water at 60 °C for 72 h. The hybrid foams were found to have an amount of chemically bonded water (H_2O_{cb}) in the region of 20 wt%, corresponding to the hydration of cement of about 60% [14], which was measured according to the ASTM Bulletin 158 [15].

Swelling experiments were carried out by dipping the pre-weighed samples in acetone. The samples were kept submerged for different periods of time (from 0.5 to 72 h) and then weighed, after the removal of the excess of acetone with a filter paper. The diameter of the specimens, d, was also measured before and after swelling using a precision caliper.

The degree of swelling was recorded as the increase in the diameter and the weight gain of the samples after immersion. Both measurements were normalized to take into account the original cement content and density of the foam.

The percentage increase in diameter due to swelling, D_w, was calculated as:

$$D_w = 100(d - d_0)/d_0\, v^{1/3}, \quad (1)$$

where the d_0 is the initial diameter of the sample and v is the volumetric fraction of the polyurethane phase, equal to 1 in the case of the neat polyurethane and to 0.55 for the polyurethane–cement systems. Measurements were performed on 10 specimens for each system and the results are reported as average values.

The degree of swelling, S_w, [16] was calculated as the relative weight change of the sample (weight liquid adsorbed/weight dry sample), normalized to account for the different polyurethane content of the different materials:

$$S_w = (w - w_0)/(1 - f_{cem})w_0, \quad (2)$$

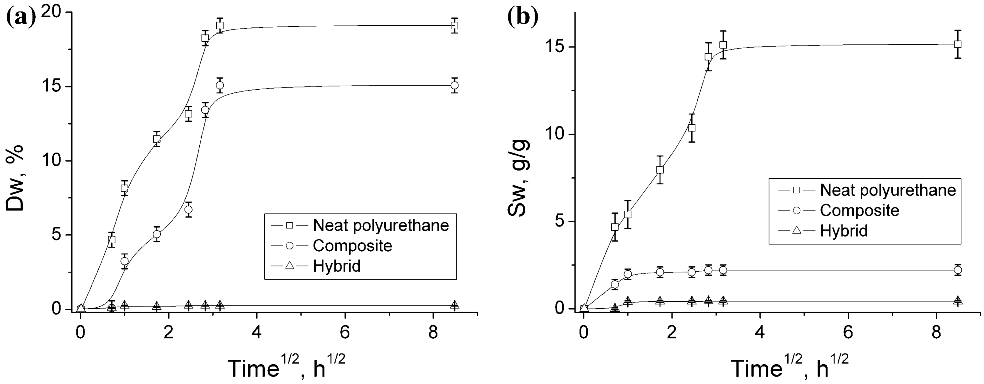

Fig. 1 **a** Diameter swelling for neat polyurethane, composite, and hybrid specimens. **b** Swelling degree for neat polyurethane, composite, and hybrid specimens

Table 1 Compositions and adopted classification of analyzed systems

Samples	Cement weight fraction, f_{cem}	Density, ρ (kg/m^3)	Label
Polyurethane	0	170 ± 10	Neat polyurethane
Un-hydrated polyurethane–Portland cement	0.60	350 ± 5	Composite
Hydrated polyurethane–Portland cement	0.60	370 ± 5	Hybrid

where w is the weight of the sample after swelling, w_0 is the weight of the dry sample and f_{cem} is the weight fraction of the cement.

The detailed results of the swelling experiments in acetone (D_{w} and S_{w}) are reported in Fig. 1. From these curves it is possible to determine the significantly different behavior of the systems (i.e., neat polyurethane, composite, and hybrid material). In particular, the diameter of the samples at the end of the swelling experiments (Fig. 1a) for both the neat polyurethane and the composite is 15–20% higher than the initial diameter, while for the hybrid it is only 0.3% higher. The results indicate that the presence of non-absorbing interconnected inorganic acicular structure produces an efficient obstacle to the swelling of the organic phase, thereby restraining volumetric changes. These amount to a reduction of equilibrium weight gain (S_{w}) of the hybrid by a factor of 34 with respect to the neat polyurethane and a four fold reduction relative to the particulate composite (un-hydrated) foam (Fig. 1b).

It is worth of note that, for both the composite and the hybrid materials, the amount of absorbed acetone at equilibrium is substantially lower than the theoretical amount achieved if the porosity of the foams would be filled with the organic solvent. This confirms the existence of a closed cell structure identified in Fig. 2 and the absence of pores channels within the walls of the cells.

The results of uni-axial compression tests, performed according to ASTM D1621 [17], using a CMT 4304 SANS, Testing Machine, are reported in Table 2. These indicate that the reinforcing efficiency of the inorganic phase depend upon the final morphology and relies, in particular, on the existence of an interconnected inorganic phase. In this respect, it is important to note the difference between the data for the particulate composite foam and the corresponding hybrid foam obtained after hydration. Although the two foams have the same density, porosity, and cement content, the hybrid foam exhibited a 100% higher modulus than the composite. An increase of 30% is also observed with respect to the failure stress as a result of the hydration treatment.

The cellular structure of the composite and hybrid materials (observed by using a Scanning Electron Microscopy, SEM, Leica mod. S440, Germany) are shown in Fig. 2 for samples taken before hydration (Fig. 2a) and after hydration (Fig. 2b–d). These show that, while the hydration step does not affect the cellular structure of the foam, substantial changes take place within the inorganic phase (Fig. 2c, d) [18]. Figure 2c reveals that, in the early stages, the hydrated component consist of foils and flakes originating from the anhydrous cement particles. The final stages of the hydration reactions cause the building up of an inorganic phase in the shape of acicular outgrowths (see Fig. 2d) within the polyurethane matrix.

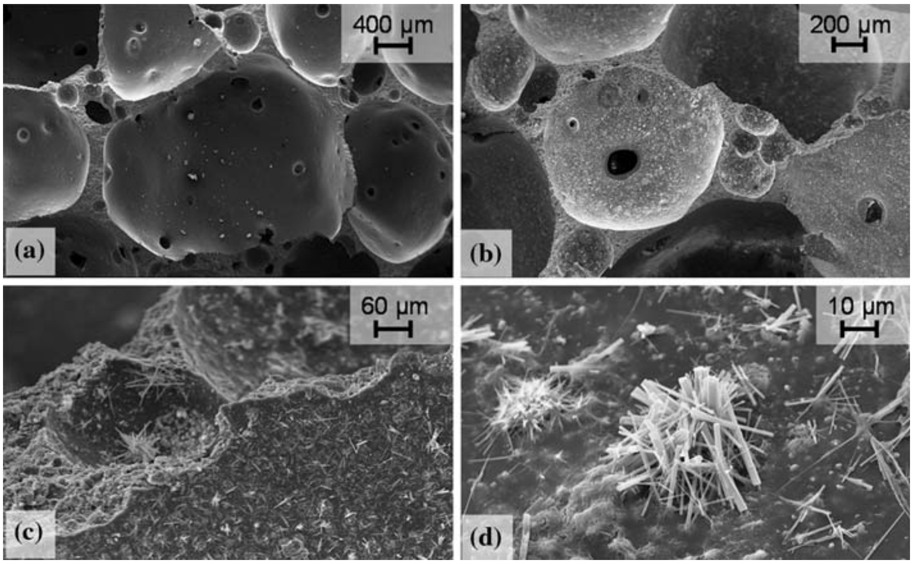

Fig. 2 **a** Micrograph of composite (magnification: 54×); **b** micrograph of hybrid (magnification 70×); **c** micrograph of hybrid (magnification: 500×); **d** acicular outgrowths from cement particles present in the hybrid (magnification: 2,500×)

Table 2 Mechanical results of neat polyurethane, composite and hybrid

Samples	Porosity, φ	Young modulus, E (MPa)	Failure stress, σ (MPa)
Neat polyurethane	0.91 ± 0.01	2 ± 0.2	0.1 ± 0.01
Composite	0.76 ± 0.01	90 ± 10	3.4 ± 0.15
Hybrid	0.76 ± 0.01	190 ± 15	4.3 ± 0.12

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