

Mechanical Properties of Composite Mortars Using Fluorogypsum and PVC Particles

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Received 16 January 2014; revised 17 February 2014; accepted 28 February 2014

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Abstract

The present work describes the viability of a mortar binder based on two industrial by-products: poly(vinyl chloride) (PVC) particles from scrap and anhydrite (CaSO_4) from fluorogypsum. Mortar composites were made incorporating different amounts of PVC particles and cured at constant room temperature during various periods of time. From X-ray diffraction, it was possible to follow the hydration process and to estimate the effect of the PVC particles on anhydrite transformation to gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$). Compressive strength from uniaxial testing was measured from stress-strain curves carried out at room temperature. According to these results, the hydration rates of the composites depend on the concentration of PVC particles and there is an enhancement in their compressive strength as particle content increases, reaching values of 36 MPa after 28 days.

Keywords

Compressive Strength; Recycled PVC; Hydraulic Binder; Alternative Building Materials; Gypsum-Composite

1. Introduction

Poly(vinyl chloride) PVC is one of the most commonly used thermoplastic materials in respect to the worldwide polymer consumption. At global level, demand for PVC exceeds 35 million tonnes per year, and it is rated second only after polyethylene as volume leader in the plastics industry [1]. Currently, PVC can be processed into a wide variety of short-life products, such as packaging materials used in food, cleansing materials, textile, beverage packaging bottles, and medical devices, and also long-life building material products such as pipes, window frames, cable insulation, floors coverings, roofing sheets, etc. [2]. In recent years, the question of the

disposal of PVC waste has gained increasing importance in the public discussion, resulting from the rapid growth of the PVC wastes. Despite the advantages of recycling, unfortunately only a small part of PVC waste is now recycled in the world [3] [4].

Gypsum has been used as a construction material since ancient times. The modern building industry can utilize not only natural gypsum, as commonly done in the past, but also other forms of gypsum that appear as waste secondary raw material from various sources, such as phosphogypsum and fluorgypsum [5] [6], red gypsum [7] and flue-gas desulfurization gypsum [8]. The current application of gypsum in construction is relatively limited, despite the low price of raw material and the general recognition of recycled gypsum as an environmental-friendly material. Besides, there is an increasing interest in alternative binders for sustainable building construction [9]. The most often use of gypsum in buildings is still in the form of interior plasters and plasterboards, however, the potential for gypsum applications could be much wider. Another prospective way is the development of lightweight gypsum which can be produced either as foamed-gypsum paste where the pore structure is formed by chemical additives [10] or using light aggregates of polyamides [11], rubber [12] polystyrene and polypropylene fibers [13]. Besides, the preparation of gypsum-based materials for thermal isolation and latent heat storage is a major research goal for this material [14].

Industrial activity creates a huge quantity of by-products as fluorgypsum, one kind of anhydrite (CaSO_4) by-product from the production of hydrofluoric acid. Its annually discharged magnitude is as high as 100,000 tons for a middle-scale plant. Though some of the fluorgypsum is used in the cement industry as a set regulator of Portland cement, its main part is still placed in disposal areas. There are reports concerning fluorgypsum mortars made by mixing other by-products as fly-ash [15], Portland cement [16], slag [5] and silica fume [17], but to the best of the authors' knowledge, no previous research has been conducted on the effects of using PVC particles on fluorgypsum.

The present work investigates the effects of incorporating particles from recycled PVC scrap as a partial reinforcement for anhydrite on the properties of these composite mortars. This preliminary study emphasizes the effect induced by PVC particles in gypsum hydration and the enhancement in compressive strength as particle content reaches an optimal value, opening the prospective of lightweight gypsum composite. Hence, this work presents the preliminary results about the influence of PVC particles on anhydrite and their combined properties for alternative composite binders.

2. Experimental Procedure

The materials used were domestic fluorgypsum (Mexichem Fluor, Matamoros, México), PVC particles (scrap obtained from milling of PVC pipes), K_2SO_4 (Fluka 98%) as additive to promote anhydrite hydration and industrial grade slaked lime $\text{Ca}(\text{OH})_2$ as neutralizing agent.

2.1. Instrumental Techniques

X-ray diffraction (XRD) experiments were performed employing a diffractometer using Cu K_α ($\lambda = 0.154056$ nm) radiation and nickel monochromator over the range 2θ from 10° to 60° , with a scanning speed of $0.01^\circ/\text{min}$ and an integration time of 2 seconds. Compressive strength from uniaxial testing was measured from stress-strain curves carried out at room temperature using a universal testing machine with capacity of 20 kN under displacement control and a crosshead speed of 0.50 mm/min. Micrographs of the composites were taken using a scanning electron microscope (SEM) under an accelerating voltage of 20 kV and chemical microanalysis was performed using an energy dispersive spectrometer (EDS) attached to the SEM. To assess the particle size distribution of the granular materials, SEM and sieve analysis were carried out using a mechanical shaker with a column of wire mesh screens.

2.2. Materials Characterization and Composites Preparation

All raw materials were dried and milled before mixing to avoid particle agglomeration. Fluorgypsum and slaked lime were grinded using a ball mill, meanwhile PVC particles were obtained by crushing pipes and then powdered using a pulverizer. Afterwards, samples were prepared by blending the proper amounts of each powder. Chemical analysis using atomic absorption spectrometry together with phase identification by X-ray diffraction were employed to obtain the chemical composition shown in **Table 1** for the inorganic raw materials.

The results of particle analysis of the raw materials and their corresponding particle size distribution are

shown in **Figure 1**. From these results it is found that PVC powder is conformed of coarse particles, having a mean particle diameter of 235 μm , whereas in the case of fluorgypsum, the mean particle size is quite small, approximately of 1.85 μm . SEM micrographs obtained from the powdered samples are presented in **Figure 2**, showing particle morphology for each case and the mean particle size.

XRD analysis was carried out in all raw materials to discern the mineralogical phases. **Figure 3** shows the XRD patterns, indicating that fluorgypsum was conformed basically of anhydrite (CaSO_4) with a minor amount of fluorspar (CaF_2). PVC particles showed the presence of CaCO_3 usually added as a filler and broad peaks associated to the poly(vinyl chloride) non-crystalline structure.

Because fluorgypsum is generated from the reaction between sulfuric acid (H_2SO_4) and calcium fluoride (CaF_2) to obtain hydrofluoric acid (HF), there is always a small amount of sulfuric acid (H_2SO_4) remaining adsorbed at the surface of the CaSO_4 particles, therefore a neutralizing treatment is required for the safe reprocessing of this product. **Figure 4** represents the relationship between the pH of fluorgypsum slurry and the slake lime added. From the neutralization curve, it was observed that the as received fluorgypsum leads to a pH of 3, nevertheless, a neutral pH of 7 is easily achieved when 0.26 wt% of $\text{Ca}(\text{OH})_2$ was added.

Table 1. Chemical composition of raw materials.

wt%	Fluorgypsum	Slaked lime
SiO_2	0.53	3.50
Al_2O_3	0.06	-
CaO	40.03	89.20
Na_2O	0.04	0.62
MgO	0.09	2.13
$\text{Al}(\text{OH})_3$	-	3.12
Fe_2O_3	0.16	0.83
K_2O	0.03	0.60
CaF_2	1.45	-
SO_3	57.61	-

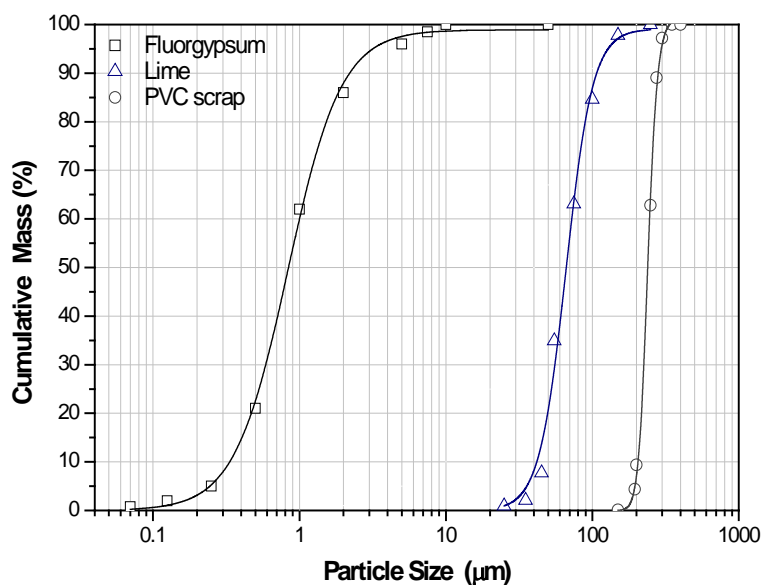


Figure 1. Particle size distribution curves of the powdered raw materials. The mean particle sizes were: fluorgypsum 1.85 μm , slaked lime 75 μm and PVC particles 235 μm .

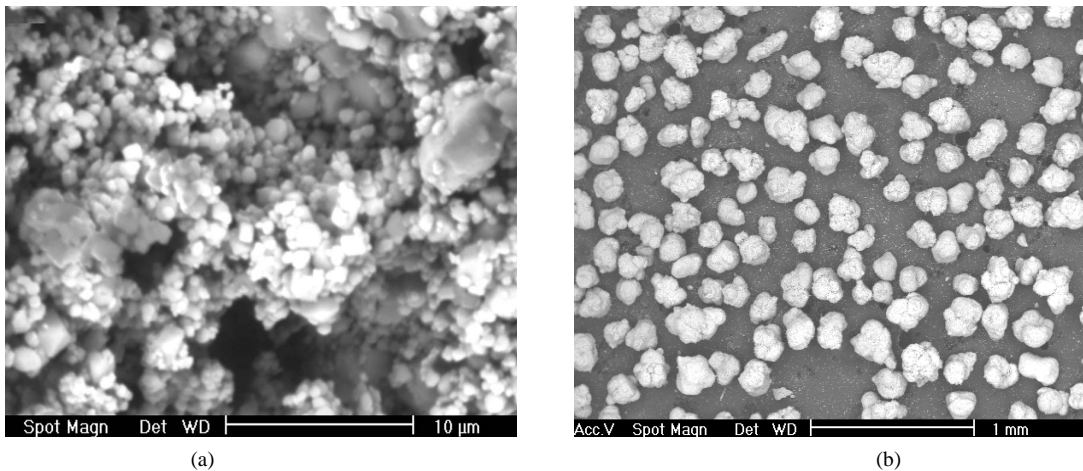


Figure 2. Scanning electron photographs of: fluorgypsum powder (a) and PVC particles (b).

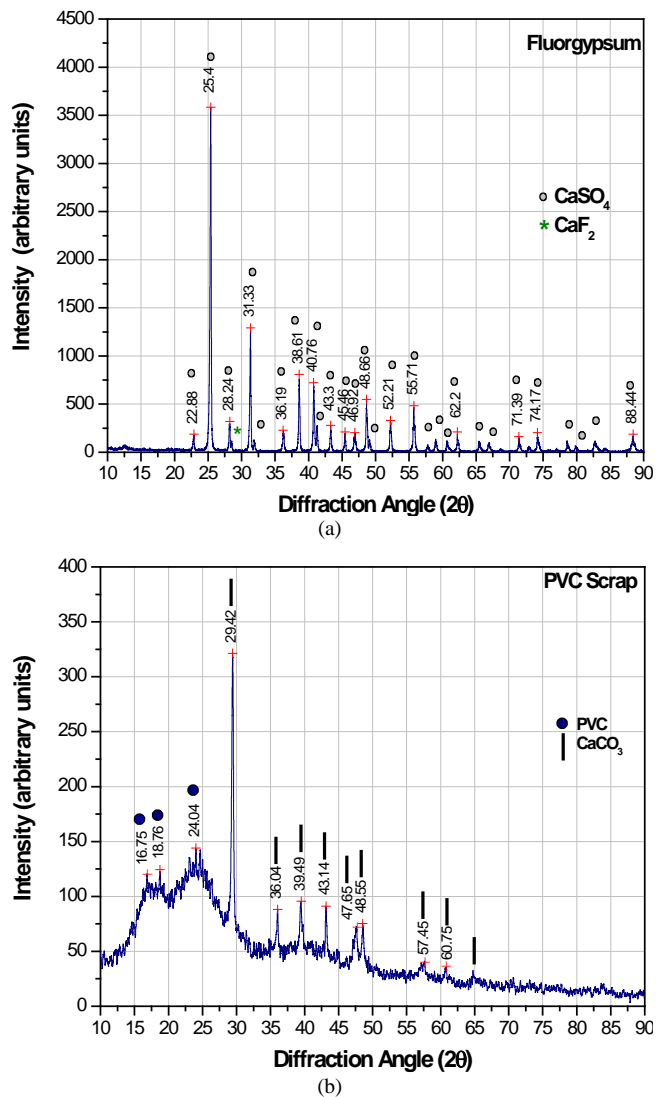


Figure 3. X-ray diffraction patterns of raw materials: (a) Fluorogypsum; (b) PVC particles.

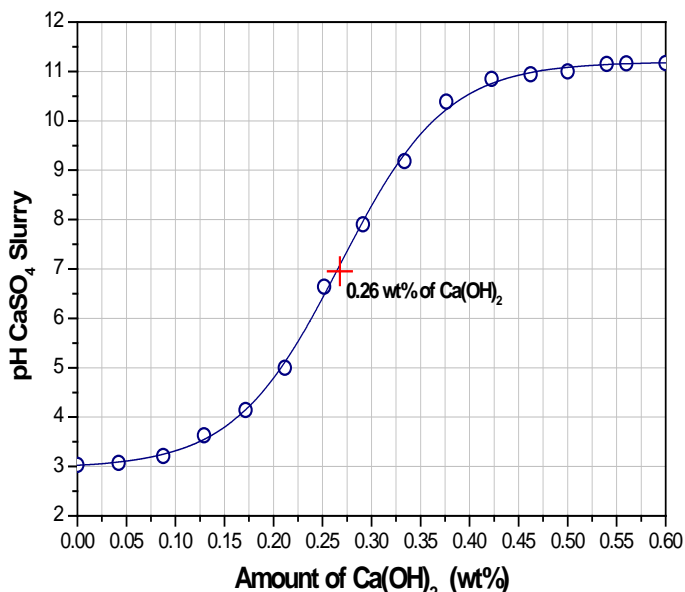


Figure 4. Variation of the pH versus the amount of Ca(OH)₂ added to a slurry made of 50 g fluorgypsum and 17.5 g H₂O (water/fluorgypsum = 0.35) at room temperature.

When water is added to anhydrite (CaSO₄), the hydration reaction must take place leading to gypsum (CaSO₄·2H₂O) according to reaction [18]:



Unfortunately this process occurs very slowly leading to a solid with low strength development. However, when certain activators are added to the anhydrite, the hydration and strength are enhanced considerably.

From a large number of chemical activators, mainly metal sulfates, probably the most effective activator is potassium sulfate K₂SO₄ [19]-[21]. **Figure 5** shows the evolution of the compressive strength of fluorgypsum once neutralized with 0.30 wt% Ca(OH)₂ and catalyzed with different concentrations of K₂SO₄. In all samples, the same 0.35 water/fluorgypsum ratio was kept constant and curing was carried out at a temperature of 25°C. It was observed that formulations with K₂SO₄ gain strength quite rapidly, producing a compressive strength of over 10 MPa after several days, where samples without activator fail to display any appreciable strength as indicated in **Figure 5**. From these results, therefore all composites were prepared using a water/fluorgypsum ratio of 0.35 wt% and 1.5 wt% of K₂SO₄.

Uniaxial compressive strength testing of the fluorgypsum-PVC composites after 3, 7, 15 and 28 days was performed on cylindrical samples with height and diameter of 4 and 2 cm respectively.

3. Results and Discussion

The hydration effect induced by PVC particles on the evolution of reaction (1) was examined from the XRD patterns of the composites at different times, indicating that the main crystalline compounds found in the cured composites were CaSO₄ (anhydrite) and CaSO₄·2H₂O (gypsum) and no evidence was detected of CaSO₄·1/2H₂O (bassanite) after 3 days.

Figure 6 corresponds to XRD patterns obtained after curing composites for 3 days. The main peak of CaSO₄ (anhydrite) corresponding to the (100) crystallographic planes appears at a 2θ angle of 25.43°. The two main peaks of CaSO₄·2H₂O (gypsum) corresponding to the (020) and (021) planes appear at 11.58° and 20.72° respectively. It can be observed that intensity of these peaks changes as the PVC particles content does. From **Figure 6**, following the peak intensity ratio between (100)_{anh}/(020)_{gyp}, it was observed that (100) intensity of CaSO₄ decrease and the (020) intensity of CaSO₄·2H₂O increase as the PVC increase, indicating that reaction 1 was proceeding faster until a limiting value of approximately 20 wt% of PVC was reached. Consequently, experimental evidence indicates that PVC has some catalytic effect on the hydration reaction, but it has a deleterious

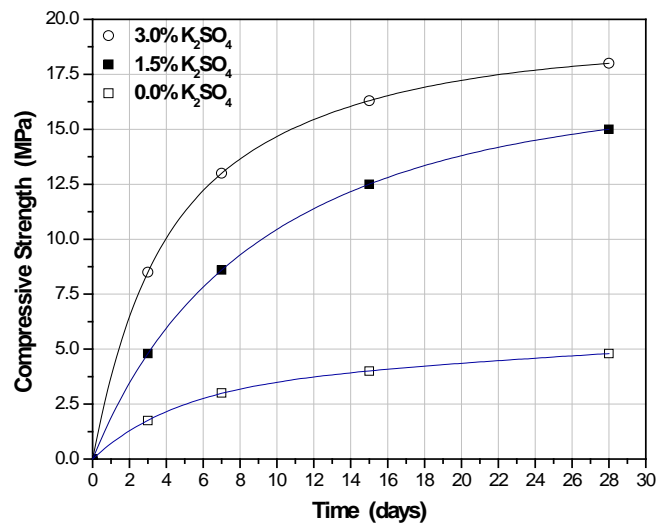
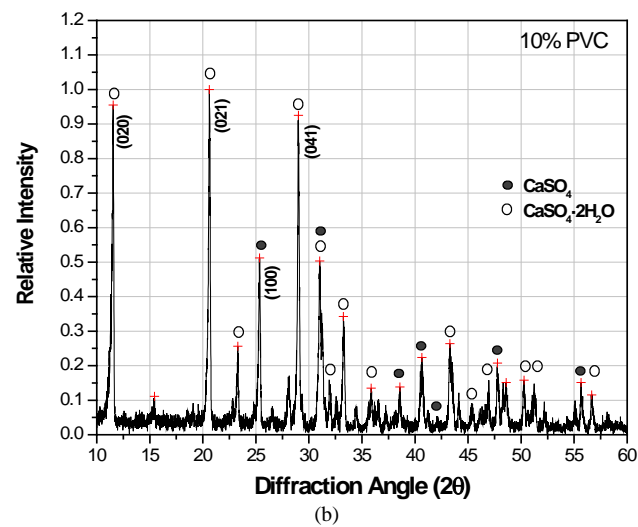
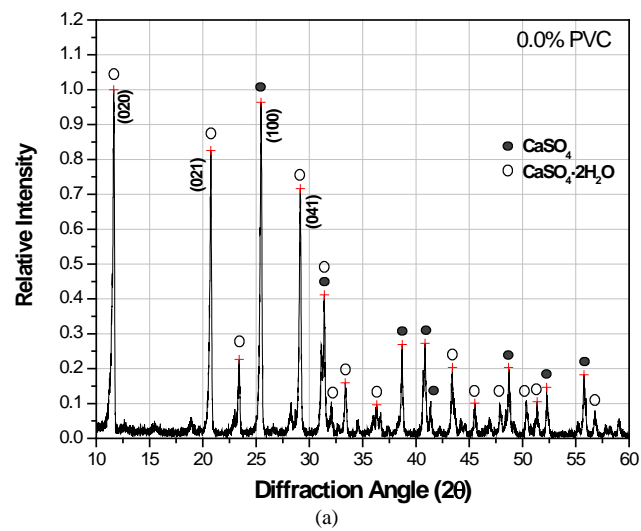


Figure 5. Compressive strength of anhydrite with 0.3 wt% $\text{Ca}(\text{OH})_2$ and using different amounts of K_2SO_4 catalyst. All samples made using water/fluorgypsum of 0.35 and cured at 25°C.



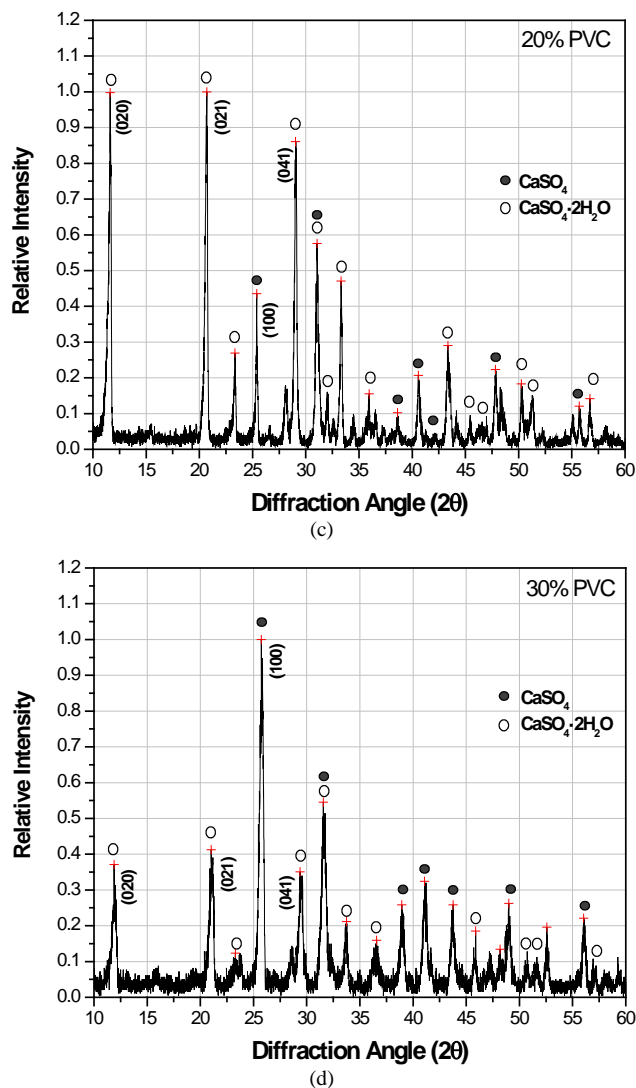


Figure 6. XRD patterns of fluorogypsum after 3 days with different concentrations of PVC particles. (a) 0.0 wt%; (b) 10 wt%; (c) 20 wt%; (d) 30 wt%.

effect on hydration if added in excess as shown in **Figure 6(d)**, where the amount of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ was the lowest value at 30 wt% of PVC particles. Therefore, there is probably some kind of chemical interaction between calcium sulfate and PVC particles.

From x-ray diffraction patterns obtained at different curing times varying the concentration of PVC particles as those shown in **Figure 6**, it was possible to estimate the amount of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) formed during the hydration process. Quantitative analysis by diffraction is based on the fact that the intensity of the diffraction pattern of a particular phase in a mixture of phases depends on the concentration of that phase in the mixture. The relationship between intensity and concentration is not generally linear, because diffracted intensity depends on the absorption coefficient of the mixture. Nevertheless, the concentration can be approximately calculated by means of a set of standard specimens and constructing a calibration curve [22]. **Figure 7** represents the relationship between gypsum produced with different PVC additions at different times. According to these results, PVC particles increase the amount of $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ produced during the hydration process of CaSO_4 . Nevertheless, adding PVC particles above 20 wt% seems to retard the kinetics of anhydrite hydration. In general, PVC pipes formulation incorporate together with the polymer other compounds like calcium carbonate (CaCO_3), titanium oxide (TiO_2), calcium stearate ($\text{Ca}(\text{C}_{17}\text{H}_{35}\text{COO})_2$) and small amounts of other additives used as stabilizers to

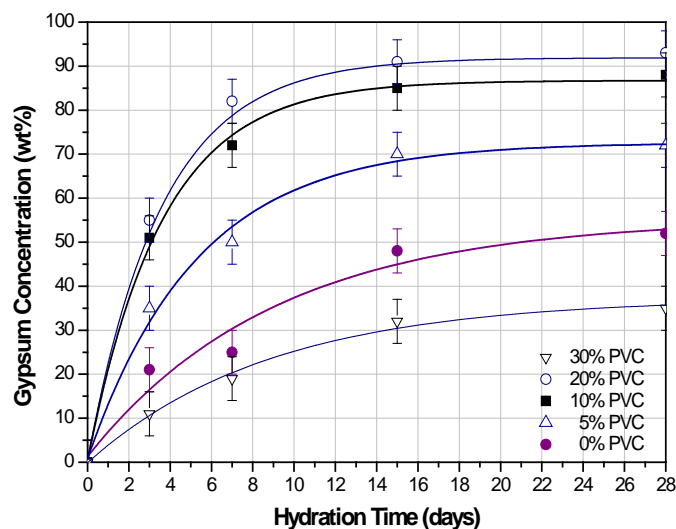


Figure 7. Experimental relationship between $\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$ (gypsum) formation and curing time in fluorgypsum composites formulated with different concentration of PVC particles.

improve the performance of the final product [23]. Probably at high concentrations one of these chemical compounds could be interacting with the CaSO_4 leading to the retarding effect observed in fluorgypsum hydration.

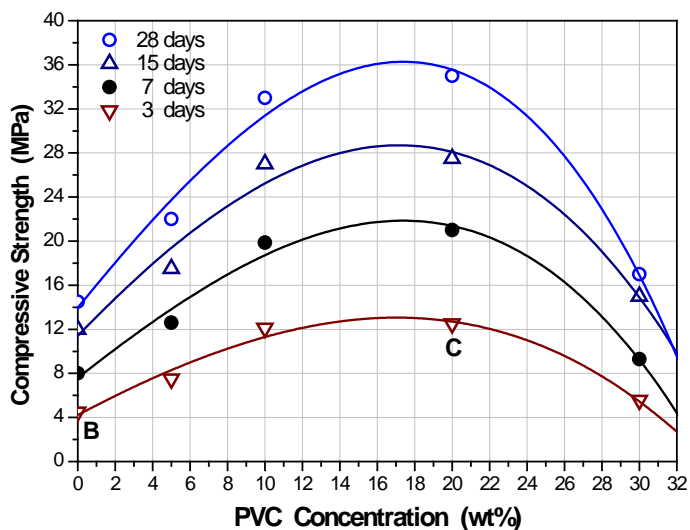
The average compressive strength values reported on **Figure 8(a)** were obtained from 5 samples made of each composition and tested in exactly the same conditions. SEM images from flat surfaces of fluorgypsum and 20 wt% PVC/fluorgypsum after 3 days are also shown in **Figure 8**. In all cases and according to these results, the highest compressive strength could be located at a PVC content between 10 wt% to 20 wt%. From the strength development process, one can see that the final strength of the fluorgypsum-PVC composites probably is related to the catalytic effect on density of gypsum crystals, suggested by the SEM pictures at high magnification shown in **Figures 8(b)** and **(c)**. According to these images, PVC particles probably promote the density of gypsum needles, increasing in some extent crystal bonding in the solid.

Gypsum does not behave like a compact solid due to its high void fraction. The change of mechanical strength in solids as a function of porosity has been estimated by the several exponential-type relationships [24]-[26], always porosity leading to lower strength values. Concerning gypsum plaster solids, the attained experimental compressive value experimentally reported fluctuates between approximately 15 to 20 MPa with porosity content of 2% to 45% [27]. Besides, experimental results have found that the addition of only 1% of deflocculating additives to calcium sulfate casts can lead to compressive strengths higher than 34 MPa [28]. From the SEM images shown in **Figure 8**, the porosity of the fluorgypsum composites can be estimated to be between 20% to 25%. From the compressive value of 36 MPa reached in the fluorgypsum-PVC composites here produced, because they present the same porosity as those reported elsewhere, the enhanced compressive value obtained suggests that PVC particles are reinforcing the gypsum matrix. Rigid PVC compounds generally used to produce pipes, present a yield strength that fluctuates between 40 to 60 MPa [23]. Then, the observed compressive increase could be assigned to the reinforcement of the matrix by the presence of PVC particles, together with the catalytic effect of the PVC scrap that modifies the density of the gypsum crystals and the number of bonds between them.

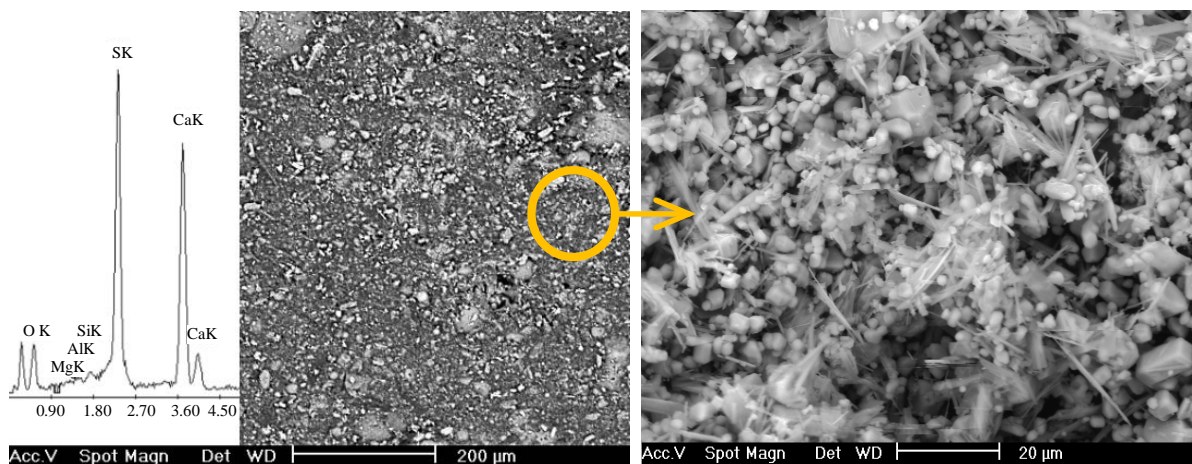
Nevertheless, more experimental work has to be carried out in this direction to study and completely appreciate the effect of PVC particle size, porosity and void size distribution on the final mechanical behavior of fluorgypsum-PVC composites. Because almost all hydraulic binders use small amounts of Portland cement and water-soluble polymers to even further improve mechanical properties and stability, therefore, there is a promising perspective to produce environmental friendly gypsum composites with compressive strengths well above the 36 MPa reported in the present work.

4. Conclusions

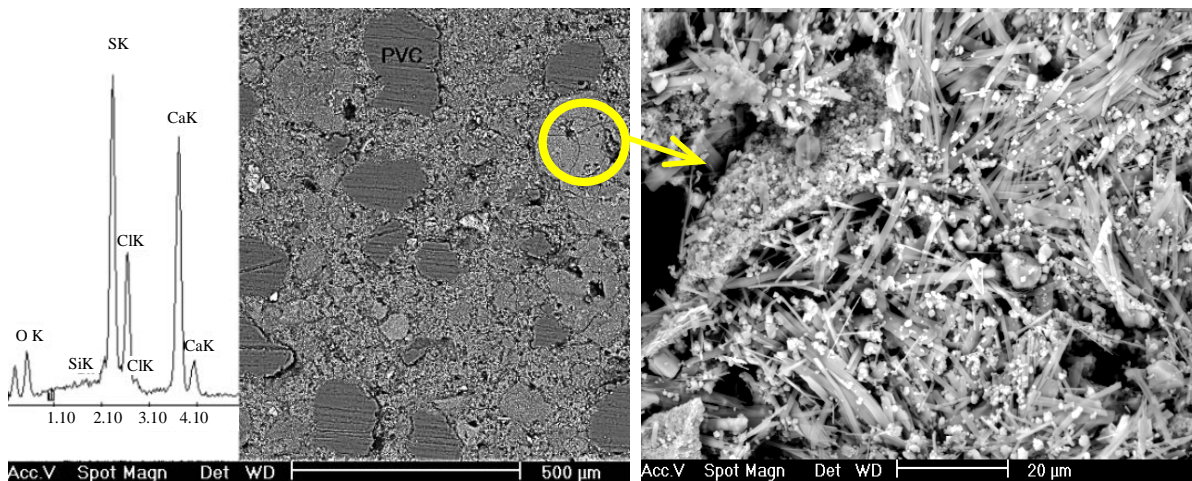
The dependence of the hydration process and the compressive strength for fluorgypsum-PVC particles composites



(a)



(b)



(c)

Figure 8. (a) Compressive strength of fluorgypsum/PVC composites after different curing times; (b) Microstructure and chemical analysis at low (left) and high magnification (right) of sample labeled with B on graph a; (c) Microstructure and chemical analysis at low (left) and high magnification (right) of sample labeled with C on graph a.

were analyzed experimentally in this preliminary work. The following conclusions can be drawn:

- PVC particles enhance the hydration process of anhydrite (CaSO_4) so the composite sets rapidly attaining a compressive strength of 8 MPa after 1 day.
- The strength of the material increases continuously reaching 36 MPa after 28 days probably due to the combined effect of PVC particles as reinforcement and catalyst.
- Adding more than 20 wt% of PVC particles have a deleterious effect on anhydrite hydration, retarding the formation of gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$).
- There is the possibility of reusing PVC scrap and fluorgypsum to produce a low cost composite binder that could be employed in block making and floor leveling.

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