RESEARCH LETTER

Recycled high-density polyethylene/gypsum composites: evaluation of the microscopic, thermal, flammability, and mechanical properties

F.J.H.T.V. Ramos* and L.C. Mendes

Instituto de Macromoléculas Professora Eloísa Mano (IMA), Centro de Tecnologia, Universidade Federal do Rio de Janeiro-UFRJ, Rio de Janeiro, Brazil

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Sustainable composites comprising scraps of high-density polyethylene (HDPE) and gypsum waste in proportions HDPE/gypsum 100/0, 50/50, 40/60, and 30/70 wt% were prepared. The morphology of the injected specimens was core-shell. Thermal, flammability, water absorption, and compression resistance were also evaluated. Progressively, the presence of gypsum increased the HDPE crystallinity and $T_{\text{onset}}$. Concerning the flammability, the composite 30/70 exhibited the burning rate three times lower than HDPE, indicating that the gypsum played a role as a flame retardant. The HDPE acted as waterproofing for gypsum. The compression resistance of the composites was similar to HDPE.

Keywords: HDPE; gypsum; composite; sustainability

Introduction

Natural gypsum is essentially composed by dihydrate calcium sulfate (CaSO$_4$$ \cdot $2H$_2$O) in which the crystal can be arranged in different forms. Throughout the centuries, gypsum has been used as plaster due to its excellent performance, attractive appearance, and easy application and has become the most popular building material for indoor finishing (1). Generally speaking, gypsum is a fragile material. Its reinforcement process includes its impregnation with water soluble or emulsion polymers leading to lower values of shrinkage and better load transfer. According to Gomina and co-workers, these improvements can be attributed to the adsorption of the polymer onto the gypsum crystals which enhance the impermeability through the control of rate of dehydration of the gypsum (2, 3). Rubio-Avalos et al. (4) prepared plaster with SBR latex (5–20 wt%) in order to investigate the microstructure and flexural properties. They observed a thin film among the gypsum crystals increasing its flexural behavior. Composites of plaster and polyester aqueous solution (1–5 wt%) were developed resulting in material with low porosity and yield strength (5). The effect of admixtures on the rheological behavior of natural and commercial plasters was reported by John and co-workers (6). The authors stated that the mixing procedures have affected the plasters’ setting behavior in opposing ways. A study discussing the properties of cotton stalk fiber/gypsum composite with different admixtures was reported (7). After being treated with acrylic emulsion, the fibers can form deformable flexible interface which improves some properties of the composites remarkably.

The cost reduction and optimization of the industrialization of some products are reasons for searching new materials. Eligible as environmental friendliness material, the glass fiber reinforced gypsum (GFRG) walls were investigated by Wu and co-workers concerning its structural behavior (8, 9). Compressive strength of gypsum and gypsum–polymer composites in protein-free simulated body fluids (SBF) was studied by Greish and his group (10).

Recently, due to the appeal of sustainability, the searching for eco-friendly materials has been encouraged considering wastes from industrial processes – synthetic gypsum such as phosphogypsum, citrogypsum, borogypsum, flue gas desulfurization (FDG gypsum) (11–13) and many others – and those provided from urban solid wastes – plastics and cellulosics. Plastics presented distinguished properties such as low density, ductility, rigidity, easy processability, recyclability as well as atoxicity, then their reuse must be stimulated (14). Gypsum and azodicarbonamide (AZC) were tested as foaming agents for recycled polyethylene. The gypsum presented the worst
performance (15). Microstructure and mechanical properties of a composite material made of natural and recycled gypsum reinforced with cellulose fibers from discarded Kraft cement bag were investigated by Carvalho et al. (16). In an article addressed to the study of bending strength and fracture toughness mode, wood fiber gypsum panels composed of recycled paper fibers embedded in a gypsum matrix were studied (17). Melt-blending composites, starting from gypsum as a by-product of lactic acid fermentation and polylactide (PLA), have been produced by Dubois et al. (18). It was reported that the modulus increased and the impact strength was maintained owing to the good adhesion between PLA and gypsum. Kowalska and Wielgoszw (19) described the use of the phosphogypsum as filler for polyolefin compositions showing a considerable improvement of the modulus and flexural strength.

The work intends to reinsert two waste materials – HDPE and gypsum – in the productive process thinking on sustainability in order to develop an eco-friendly material. Composites of HDPE/gypsum were prepared in different proportions. Microscopic, thermal, flammability, and mechanical evaluation were performed. Mutual benefits were achieved.

### Experimental

The lactidegypsum – density of 2.32 g cm$^{-3}$ and moisture content of 21.6 wt% – was kindly supplied by Purac Sínteses Indústria e Comércio Ltda., Brazil.

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**Table 1.** TG/DTG properties of the injected specimens.

| Sample  | $T_{\text{onset}}$ $(^\circ\text{C})^a$ | $T_{\text{end}}$ $(^\circ\text{C})^b$ | $T_{\text{max}}$ $(^\circ\text{C})^c$ | Residue (%) |
|---------|----------------------------------|----------------------------------|----------------------------------|-------------|
| HDPE    | 442                              | 480                              | 474                              | 2           |
| Gypsum  | 126                              | 196                              | 160                              | 80          |
| 50/50   | 442                              | 448                              | 477                              | 36          |
| 40/60   | 447                              | 490                              | 478                              | 36          |
| 30/70   | 461                              | 500                              | 479                              | 55          |

*aOnset degradation temperature.

*bEnd degradation temperature.

*cMaximum degradation temperature.

**Table 2.** Calorimetric properties of the injected specimens.

| Sample | HDPE | Gypsum$^e$ | 50/50 | 40/60 | 30/70 |
|--------|------|------------|-------|-------|-------|
| $T_m$ $(^\circ\text{C})^a$ | 128 | 155/194 | 127 | 128 | 128 |
| $X_{\mathrm{c}}$ (%)$^a$ | 53 | – | 78 | 65 | 90 |
| $T_c$ $(^\circ\text{C})^b$ | 118 | – | 118 | 118 | 118 |
| $T_m$ $(^\circ\text{C})^b$ | 130 | – | 129 | 130 | 129 |
| $X_{\mathrm{c}}$ (%)$^b$ | 59 | – | 80 | 70 | 100 |

*a1° scan.

*b3° scan.

$^{155/194 \, ^\circ\text{C}}$ – temperatures of gypsum transformations: dehydrate to hemihydrate and hemihydrates to dehydrate, respectively.

Figure 1. Optical micrograph of the wet (a) and dry (b) gypsum.

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Scraps of high-density polyethylene (HDPE) from bottle wastes previously washed, dried, and cut were provided by Cooperativa de Catadores de Materiais Recicláveis de Itatiba, Brazil. Its melt flow rate (ASTM D 1238) (20) and density (ASTM D 792) (21) were determined experimentally – melt flow ratio (MFR) = 3.02 g/10 min$^{-1}$ and $d = 0.953 \text{ g cm}^{-3}$, respectively. The synthetic gypsum was used as received. The HDPE waste was cryogenically treated with liquid nitrogen in order to reduce its size particles attaining dimension of 40 mesh (0.42 mm). The proportions of HDPE/gypsum were 100/0, 50/50, 40/60, and 30/70 wt%. In reference to the composite preparation, the two components were mixed manually in a mortar. Rectangular injected specimens were molded in a Ray Ran injection machine with the following molding conditions: $T$ (temperature) = 230$^\circ$C, $P$ (pressure) = 1 MPa, MT (mold temperature) = 80$^\circ$C and IT (injection time) = 15 s. Circular-compressed specimens were molded in a Carver heat press according to these conditions: $T$ (temperature) = 230$^\circ$C, $P$ (pressure) = 4.4 MPa and CT (compression time) = 10 min.

Calorimetric analysis was carried out in a TA differential scanning calorimeter (TA Q1000) using ASTM D 3418 as a guidance. The sample was heated from 0 to 250$^\circ$C at a heating rate of 10$^\circ$C/min (first scan), under nitrogen atmosphere for 2 min and then cooled down to 0$^\circ$C, at 200$^\circ$C min$^{-1}$ (second scan). A second heating (third scan) was carried out in the same protocol as the first one. The cold crystallization temperature ($T_{cc}$), melting temperature ($T_m$), and enthalpy of fusion ($\Delta H_m$) were determined from the curves. The HDPE degree of crystallinity ($X_c$) was calculated from the ratio of the HDPE enthalpy of fusion ($\Delta H_m$) in the composite and the enthalpy of

Figure 2. (a and b) SEM photomicrographs of the structure core-shell of the injected HDPE/gypsum (50/50 and 40/60) composites, (c) external layer 30/70 composite, and (d) embedding of gypsum plaques, respectively.
fusion 100% crystalline HDPE (290 J/g) (22). For the calculation, it was considered the enthalpy of fusion in the second heating cycle and the values were corrected according to the amount of the HDPE in the composite.

The thermogravimetry (TG) and its derivative (DTG) were performed using TA Q500 equipment. Two slices were taken from different regions of the molded composite. No special preparation was performed on the composite in order to carry out the TG analysis. The test was conducted from 30 to 700°C, at 10°C min⁻¹, under nitrogen atmosphere. The $T_{\text{onset}}$ and $T_{\text{end}}$ were then determined. The experiments were performed twice. The margin of error was 2°C.

Optical microscopy (OM) of the dry and wet gypsum crystals was performed with an Olympus stereo microscope: model SZH10, with a Nikkon Coolpix 5.400 digital camera attached.

Scanning electron microscopy (SEM) was carried out in a Fei Company microscope model Quanta 200, and the specimens were coated with 300 nm gold particles (Au) using a JFC 1500 (JEOL Ltd.). The photographs were taken from the cryogenic fracture of the transversal section in order to evaluate the morphology.

Flammability was assessed in order to notice the effect of lactidegypsum on HDPE. The essay was performed according to the ASTM D 635 (23). Rectangular specimens with a dimension of 127×10×3 mm were tested and the time and rate of burning were expressed taking into consideration the average of seven specimens.

Water absorption was conducted according to the ASTM D 570 (24). Cylinder with 490 mm of height and 230 mm of diameter were tested and results were expressed considering the average of five specimens.

Figure 3. (a–d) SEM photomicrograph (core region) of the injected HDPE/gypsum composites with coarse gypsum is fixed and agglomerated in the HDPE matrix (50/50, 40/60, and 30/70), respectively.
Compression properties were performed according to the ASTM D 695 (25). Cylinder of 490 mm height and 230 mm diameter specimens were processed in a compression machine. The results were taken considering the average of seven specimens.

Results and discussion

Thermal evaluation

The differential scanning calorimetry (DSC) results for injected specimens are provided in Table 1. During the first scan of the gypsum, two endothermic peaks appeared with maxima at 155 and 194°C. This can be attributed to two gypsum-endothermic transformations. The former was related to the change of dihydrate to hemihydrate and the latter to anhydrite gypsum, which is in accordance with Greco et al. (15).

The HDPE crystallization and melting temperatures, \(T_c\) and \(T_m\) respectively, seem to be unaffected by gypsum. On the contrary, the HDPE degree of crystallization \(X_c\) increased progressively as the gypsum enriched the composite, attaining a value almost over 70% in the composite. Commonly, after melting, the bulk molten of a semicrystalline polymer can be recrystallized under cooling. It takes place under homogeneous nucleation and the amount of the crystalline portion has the same order of magnitude as the initial material. Concerning the composites, a phenomenon called transcrysallization may occur when a discontinuous phase, e.g. a fiber, is presented. It is a special case of crystallization where heterogeneous nucleation is feasible along a fiber surface and the resulting crystal growth is restricted to the lateral direction, so that a columnar layer develops around the embedded fiber. This nucleation of the transcrysallized region on the reinforcing fiber is thought to be

Figure 4. SEM photomicrograph (core region and ellipsoidal heterogeneous cells) of the injected HDPE/gypsum (a and b) 50/50, (c) 40/60, and (d) 30/70 composites.
central to the improvement of some composite properties. The transcry stallization is a function of nucleating activity of the fiber surface and crystallization kinetics of the resin matrix (26). We believe that in the case of HDPE/gypsum composites, the discontinuous phase – crystal of gypsum – is playing the same role as the fiber in polymer–fiber composites. The additional amount of crystals could be attributed to the gypsum predisposition in fitting as germ for HDPE crystallization through the transcry stallization.

The TG/DTG data are listed in Table 2. The gypsum curve showed a step of degradation between 126 and 196°C which was attributed to the transformation from dihydrate to dehydrate gypsum. HDPE also degraded in a single step. With respect to the $T_{onset}$, we agree that up to 60 wt% of gypsum the change was not remarkable but with 70 wt% there was an increase of 19°C which could be considered significant. The result could be interpreted as an improvement in thermal stability. $T_{max}$ seems to be unaffected by gypsum. Regarding the $T_{end}$, except for the composition with 50 wt% of gypsum, it is possible to notice a tendency to increase it. For composition with 70 wt% of gypsum, there was an increment of 20°C. The amount of residue after burning is in accordance with the gypsum content, but for the composite 40/60 the value was lower which could be attributed to uneven distribution of the components.

**Morphologic observation**

Figure 1 shows the optical photomicrographs of the wet and dry gypsum. The wet one was opaque and presented formless agglomeration like plaster. In the absence of water, transparent, bright, well-formed needles and prismatic crystals can be seen.
Figure 2a–d shows the SEM photomicrographs of the injected specimens of the 50/50, 40/60, and 30/70 composites, respectively. The upper and lower regions represent external layers like a shell while the middle one it is similar to a porous core. The shell is made up of small domains – plaques of gypsum were encapsulated by HDPE. These domains were embedded into the HDPE matrix. Figure 3a–d shows the magnification

Figure 6. SEM photomicrograph adhesion crystals in the HDPE matrix (a, c, and e) of the composites and (b, d, and f) gypsum crystallized in different forms and cellular structure, 50/50, 40/60, and 30/70, respectively.
of the core region in that coarse gypsum is fixed and agglomerated in the HDPE matrix and they also co-exist intimately in the composites. Possibly, these factors were developed due to the injection processing and pressure of the moisture evaporating in the interior of damp gypsum. Additionally, cellular structure within the core was noticed as magnified in Figure 4a–d. There are quasi-ellipsoidal and heterogeneous cells in shape and size, indicating that closed cells were developed during the processing due to the release of the water from the gypsum. Figure 5a–d shows the photomicrographs of the injected specimen of composites in which they exhibited levels of stretching in some regions of HDPE chains. The amount of filler can affect the polymer characteristics. Naudy et al. (27) reported a study of static- and shear-induced crystallization carried out on glass fiber-reinforced poly(m-xylene adipamide) with various fiber contents. They highlighted that the shear effect is largely influenced by the fiber content, because the shear really undergone by the matrix between the fibers is locally higher than the nominal shear. Regarding the injected specimens, added to the machine pressure, there is the load of the gypsum crystals over HDPE chains compressed among them. This phenomenon may have favored some level of elongation of the HDPE chains which was kept after the cooling step (28).

For all compressed specimens, the matrix was HDPE and dispersed phase was constituted by gypsum encapsulated for HDPE (Figure 6a, c, and e). There is good adhesion between matrix and dispersed phase. Figure 6b, d, and f shows the presence of cellular structure as it was achieved in the injected specimens. It was also observed that the gypsum crystallized in different forms – as prismatic and anisotropic needles – as function of its percentage in the composite.

Flammability analysis

With respect to flammability, Figures 7 and 8 show the time and rate of burning as function of the gypsum content, respectively. For the composite 30/70, the time for attaining the specimen mark was at least twice higher than that for the neat HDPE. For the same composition, the burning rate was three times lower than 100/0 one. The results indicated that the gypsum may be playing a role as a flame retardant for HDPE.

Water absorption analysis

Table 3 shows the values of water absorption of the materials. Considering the high hygroscopicity of the gypsum, the values of the water absorption in the

| HDPE/gypsum composite | Weight average (g) | Increase (g/cm³) | Water absorption (%) |
|-----------------------|--------------------|------------------|----------------------|
| 100/0                 | Initial 1.93       | 24-h immersion 1.98 | After 6 days - dried environment 1.94 | Increase 0.01 ± 0.016 | Water absorption 0.5 |
| 50/50                 | Initial 2.86       | 24-h immersion 3.49 | After 6 days - dried environment 2.88 | Increase 0.02 ± 0.032 | Water absorption 0.7 |
| 40/60                 | Initial 2.52       | 24-h immersion 2.93 | After 6 days - dried environment 2.58 | Increase 0.06 ± 0.069 | Water absorption 2.3 |
Composites were similar to the HDPE, indicating that the polyolefin played a role as gypsum waterproofing.

**Compression property**

The modulus and compression resistance of the materials are presented in Table 4. For the composites, both properties are very close to the neat HDPE. There is a mutual benefit between the components on the mechanical properties of the composites. On the one hand, the neat gypsum has poor mechanical properties, but in the composites with some HDPE content the compression resistance attained appreciable values. On the other hand, the presence of gypsum improved the dimensional stability of HDPE until 60% of gypsum which is shown in Figure 9.

**Conclusion**

Composites of HDPE/gypsum were investigated in order to reduce the environmental impact and consumption of virgin plastics and to foment the use of waste gypsum. Morphological observations showed that distinct morphologies were obtained according to the molding process. The HDPE crystallinity degree enhanced gradually with the gypsum content. The gypsum content improved the HDPE thermal stability and flammability. HDPE acted as waterproofing of gypsum. There is a mutual benefit of the components on the composites’ compression properties. The HDPE provided the mechanical resistance to gypsum while the filler increased the dimensional stability of the polyolefin.

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