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Additional Information

Effect of the filler on the nanomechanical properties of polypropylene in contact with paraffinic phase change material

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Abstract

As the changes on the mechanical properties with depth of indentation provide valuable information that may be suitable for design purpose, nanoindentation is an adequate technique for investigating the nanomechanical changes in the surface and in the inner polymers, also when they are used as macroencapsulated container materials and exposed to an organic fluid, such as paraffin wax (saturated hydrocarbons), used as a phase change materials (PCM), for a long time. This material can be used for Thermal Energy Storage (TES) in buildings applications for passive systems or heating and cooling usages. Four different samples of the thermoplastic polyolefin polypropylene (PP) were evaluated: PP, filled polypropylene with 60 % Mg(OH)₂ (PP-60Mg), PP-60Mg with PCM (RT-25), and PP-60Mg with PCM (RT-45). It was studied the thermal stability by Thermogravimetric analysis of these samples, and also it was evaluated the Hardness, Elastic modulus and Loss modulus for the unfilled PP and PP-60Mg in contact with two different PCM at different temperatures (30 °C, 45 °C and 60 °C for RT-25 and 45 °C for RT-42) for 32 days. It was concluded that the mechanical properties Hardness (H), Elastic modulus (E) and Loss modulus (E_{loss}) for PP-60Mg increase compared PP ones. Nevertheless, these properties decrease significantly when the PP and the PP-60Mg are in contact with PCM, because it acts as a plasticizer, weakening the polymer. Besides, for higher temperatures in service for a PCM and the higher PCM's melting point, the lowest mechanical properties were observed.

36

37 *Keywords:* Polypropylene; Nanoindentation; Phase Change Material; Mechanical properties;
38 Loubet method.

39 **1. Introduction**

40 Phase Change Materials (PCM) have the principal advantage of high capacity energy storage in
41 form of latent heat [1,2,3,4]. When a solid PCM is heated up and reaches its melting point, it
42 goes through a phase change, from solid to liquid absorbing heat, known as melting enthalpy
43 while the temperature remains constant. Equally, when the phase change process is reversed,
44 that is from liquid to solid, the stored latent heat is released, again at a nearly constant
45 temperature [5]. Materials studied for this application are salt hydrates, paraffin waxes, fatty
46 acids, and eutectics of organic and non-organic compounds [6]. Paraffin waxes are one of the
47 organic PCM most employed [7,8] due to their latent heat, thermal energy storage (TES)
48 capacity, abundance, low cost, large number of applications, and because their stability after
49 several charging/discharging cycles [9]. Paraffin waxes with a melting point between 30 °C and
50 90 °C have chains with the number of carbons atoms in the range between 18 and 50. The
51 longer the chain of the paraffin waxes, the higher the melting point [10]. Depending on the
52 service temperature, it will be chosen one PCM or another, so the temperature of the system is
53 really important when the PCM has to be selected [11].

54 PCM can be used in passive systems such as floors [12] and walls, or in active systems like in
55 domestic applications as heating [13] and hot water [14,15]. Otherwise, they must be
56 encapsulated or contained to avoid leakage when phase change occurs. This encapsulation may
57 be in the microscale [16], leading to microencapsulated PCM (MPCM), or in the macroscale
58 where the use of common thermoplastics as container materials in commercial applications [17]
59 is extensively reported in research. Polypropylene (PP) has been tested as good container for
60 PCM in microscale [18,19]. Nevertheless, long exposure to organic substances may be
61 responsible of the premature mechanical failure of such containers [20]. ESC mechanism is a
62 physical interaction connecting highly localised plasticisation via stress enhanced fluid
63 absorption, which does not carry molecular degradation of the plastic nor chemical variations.
64 The absorption of organic PCM (such as paraffin waxes) plasticises the polymer and also
65 reduces its yield strength. This reduction is directly associated with the concentration of
66 absorbed fluid [1]. For this reason, and for increasing the resistance, stiffness, rigidity, and
67 durability of the polymeric container, it was decided to evaluate filled PP and compare it with
68 PP homopolymer. PP with PCM is widely used as a macroencapsulated systems for heating and
69 cooling applications and passive systems, to store energy in buildings. Moreover, PP was

70 chosen due to this polyolefin has good properties and can resist higher temperatures (ranged
71 between [ref]) than other polymers. Using inorganic filler in a polymeric matrix increases the
72 stiffness, the mechanical resistance, reduces the degradation effect avoiding the premature
73 mechanical failure, and improves properties against fire, which is relevant in this study because
74 the paraffin waxes used as PCM are flammable materials. A filler that is commonly used for PP
75 is $Mg(OH)_2$ [21,22] because of its flame retardant property [23], which also improves the
76 mechanical response [24,25,26]. Therefore, the filler used in this work has been $Mg(OH)_2$.

77 The nanoindentation technique was used to measure the nanomechanical properties of selected
78 materials containing PCM. Nanoindentation technique is perhaps the most commonly applied
79 means of testing the mechanical properties of materials at micrometric and nanometric scale.
80 The ability to measure the microscopic regions responses is a key to understand the mechanical
81 behaviour of technological material systems [27].

82 The probe in nanoindentation technique is forced into the surface at a programmed rate and to a
83 selected maximum force or depth. By means of special transducers the load and penetration
84 depth are registered during the experiment. The area of contact between indenter and sample is
85 then estimated using the known geometry of the indenter. For a Berkovich indenter, which is
86 used in this work, the relationship between the projected area A of indentation and the
87 indentation depth h beneath the contact is $A = 24.5 h^2$. Consequently, Hardness (H) and Elastic
88 modulus (E) can be calculated by the stiffness obtained by the known equations reported
89 elsewhere [27] without the necessity to observe the indentation marks. This procedure has the
90 advantage that very low loads can be used avoiding the material damage and makes possible to
91 analyze thin films and small volume of material.

92 There are a great number of studies using the nanoindentation technique in polymers showing
93 that is a simple but effective mechanical testing method. Nanoindentation has been successfully
94 used to study the hardness and elastic properties of several polymers and nanocomposites. To
95 give some examples of these studies on several polymers under different experimental
96 strategies, Lee *et al.* [28], studied the H and E of a single cellulose fiber and PP matrix in a
97 cellulose fiber-reinforced PP composite using the continuous stiffness measurement technique.
98 Besides, Fang *et al.* [29] studied the nanomechanical characteristics of polycarbonate polymer
99 films under different applied loads, hold times, and loading rates. Moreover, Hu *et al.* [30] used
100 it to investigate mechanical properties of Nylon 11 (PA11) and its nanocomposites with
101 different clay loading.

102 Nanoindentation has been successfully compared with other techniques normally used to study
103 the mechanical properties of polymers such as the atomic force microscopy (AFM) and the

104 Dynamic Mechanical Analysis (DMA) instruments; Griepentrog *et al.* [31] compared the
105 nanoindentation technique and the Atomic Force Microscopy (AFM) methodology for the
106 determination of mechanical properties of poly(methyl methacrylate) (PMMA) and
107 polycarbonate (PC) polymers. Besides, Ah-Young *et al.* [32] studied AFM through both the
108 force-indentation and area-depth curves for different polymers, concluding that the two methods
109 give almost identical results with self-consistency. In a previous work, J. Giró-Paloma *et al.*
110 [27] published a comparison study between mechanical data extracted from nanoindentation
111 measurements and from classical dynamic mechanical analysis of several amorphous and
112 crystalline polymers. In that study, we demonstrated that the elastic modulus obtained by
113 nanoindentation can be well correlated with that obtained by DMA.

114 In this study were used two different types of paraffin waxes provided by Rubitherm® with
115 different melting temperatures (T_m): RT-25 ($T_m= 25\text{ °C}$) and RT-42 ($T_m= 41\text{ °C}$). These paraffin
116 waxes were melted in separate vessels and two different polymeric materials were submerged in
117 each paraffin sample for 32 days. Polypropylene (PP) was chosen as case study as it has been
118 evaluated as container material of PCM [1] and a filled PP sample with a filler content of 60 %
119 Mg(OH)_2 (PP-60Mg) was also evaluated to compare the effect of the filler in the decrease of
120 mechanical properties after long exposure to an organic fluid.

121

122 **2. Experimental Procedure**

123 **2.1. Materials**

124 **2.2.** Polypropylene from Repsol YPF (PP) and PP mixed with the flame retardant Mg(OH)_2
125 (PP-60Mg) from Magnifin, were submerged during 32 days in two different melted
126 PCM, paraffin waxes from Rubitherm (RT-25 and RT-42), at different temperatures
127 (RT-25 at 30 °C, 45 °C and 60 °C, and RT-42 at 45 °C). The melting temperatures for
128 both paraffin waxes are around 25 °C and 41 °C for RT-25 and RT-42, respectively.

129 **Procedure**

130 **2.3. Characterization**

131 **2.3.1. Thermogravimetric analysis (TGA)**

132 Thermogravimetric analysis (TGA) was used to study the thermal stability of the materials
133 [33]. Thermal stability of the samples under study was evaluated with a TA Instruments,

134 Simultaneous SDT Q600 under 100 ml·min⁻¹ N₂ atmosphere. The procedure of the TGA
135 analysis was a scanning rate of 10 °C·min⁻¹ in the temperature range between 30 °C and 700 °C.

136 **2.3.2. Nanoindentation technique**

137 It was performed nanoindentation assays to evaluate the mechanical response in an indentation
138 analysis with the purpose to calculate Hardness (*H*), Elastic modulus (*E*), and Loss modulus
139 (*E_{Loss}*) on the microscopic length scale and to estimate the changes produced by the contact with
140 the organic fluid. Nanoindentation measurements were performed on samples with PP and PP-
141 60Mg at room temperature before and after being immersed during 32 days in two different
142 types of PCM (RT-25 and RT-42) at the experimented temperatures.

143 A Nanoindenter G-200 (Agilent Technologies) was employed using a diamond three-sided
144 Berkovich indenter geometry. This was calibrated with a silica standard specimen with a known
145 Young's modulus. The stiffness was acquired under the continuous stiffness measurement
146 (CSM) at an oscillating frequency of 75 Hz and at 10 nm harmonic amplitude. The implemented
147 TestWorks software was used to control and record all experiments and the Origin 8.0Pro
148 version (OriginLab Corp. Massachusetts, USA), was used to treat and graph the obtained data.

149 An array of 100 nanoindentation imprints was performed at 600 mN maximum load and each
150 nanoindentation imprint was separated a constant distance of 500 μm. Several considerations
151 were carefully observed. Due to the viscoelastic characteristic behavior of these materials, the
152 typical hold segments in the unload curve were avoided by setting the hold time segment to
153 zero. In order to calculate the thermal drift without constant load segments, a double P-h curve
154 was executed for each test. Thermal drift is then considered well corrected by overlapping both
155 unloading curves.

156

157 **3. Results and discussion**

158 *3.1 Thermogravimetric analysis*

159 The thermal oxidative degradation of PP-60Mg was complete at temperatures up to 450 °C, with
160 28 % of residue remaining, as it is shown in Figure 1, revealing two decomposition steps. The
161 first step corresponds to Mg(OH)₂ decomposition around 250 °C and the second step is
162 attributed to the thermo oxidative decomposition of polypropylene matrix which is in
163 accordance with literature [34].

164

165

Figure 1.

166

167 The thermal degradation of the PP-60Mg after being submerged in PCM RT-25 during 32 days
168 shows three decomposition steps, as it is shown in Figure 2. Thermal analysis of polymer
169 immersed in organic PCM, such as paraffin wax, show a PCM absorption by the plastic in
170 agreement to the observations made by Castellón *et al.* [1]. The first degradation is because of
171 $Mg(OH)_2$ decomposition being 17 %. Then, the degradation of the PCM, around 24 % of the
172 sample takes place between 250 °C and 325 °C. Finally, the third step PP degradation finishes
173 around 450 °C [35]. The 33 % of residue corresponds to the MgO.

174

175

Figure 2.

176

177 *3.2 Nanoindentation technique*

178 *3.2.1 Mechanical properties of filled PP and unfilled PP*

179 The filler effect on mechanical properties can be observed in Figure 3. As expected, the sample
180 of PP-60Mg presents higher H , E , and E_{Loss} than PP ones, due to the reinforcement effect of
181 filler.

182

183

Figure 3.

184

185 *3.2.2 Filled PP and unfilled PP in contact with an organic fluid (PCM)*

186 A prolonged contact of PP with PCM softens the material. The results for PP samples that have
187 been in contact and without contact with RT-25 during 32 days at different temperatures (30 °C,
188 45 °C and 60 °C) are shown in Figure 4. It is seen that the plasticizer effect of the paraffin
189 increases with the temperature. Also, it is observed a strong correlation between the temperature
190 and the drop of mechanical properties when the temperature increases. For this reason, after 32
191 days at 60 °C, the E , H and E_{loss} decrease significantly, whereas the mechanical properties after

192 these 32 days in contact with the paraffin at 35 °C and 45 °C do not differ significantly between
193 them and are slightly lower than those for the reference sample.

194

195 Figure 4.

196

197 Notably, when it is used the same paraffin (RT-25) in contact with the filled PP, all the studied
198 mechanical properties decreases in the same way as the temperature increase after 32 days of
199 exposure as it can be observed in Figure 5, because the PCM softens the material that is in
200 contact with.

201

202 Figure 5.

203

204 If the properties of Figure 4 and Figure 5 are compared, it can be concluded that although the
205 Hardness, Elastic Modulus and Loss Modulus values for the PP-60Mg are higher than the
206 unfilled PP, both samples follows the same tendency, which presents lower values for the
207 samples with PCM, and values even lower at higher temperatures because the PCM is have a
208 tendency to infiltrate and soften some plastics [36].

209 When a paraffin of a higher melting point as RT-42 is used, no significant differences were
210 observed in the measured elastic modulus for unfilled PP respect to RT-25, showing both
211 samples a modulus reduction around 35 %, as in Figure 6a can be seen. For the filled PP sample
212 the reduction of this parameter is almost the 60 % of the initial value (Figure 6b). Another effect
213 is observed between samples immersed in different paraffin waxes, at penetrations lower than
214 2000 nm, the low value of elastic modulus may be attributed to the residual coat of paraffin on
215 the surface that diminishes while the tip penetrates in the sample.

216

217 Figure 6.

218

219 There are some differences in the H and E_{loss} mechanical properties between PP unfilled
220 samples in contact with RT-25 and RT-42 PCM at 45 °C, as Figure 7 shows. The curves are not
221 identical for both cases, for depths superior than 3000 nm there is stabilization, but for the first
222 2000 nm the graphs are different. This may be attributed to the external thin coating of PCM.

223

224

Figure 7.

225

226 However, the same study is done in Figure 8 with the filled PP, and the results change
227 absolutely. The reason is because the PCM cannot be soaking up in this sample as much as
228 unfilled PP. Even so, all the three studied properties decreases again when the polymer (filled or
229 unfilled) is in contact with the paraffin wax.

230

231

Figure 8.

232

233 Table 1 summarizes the results of E , H and E_{loss} for a maximum penetration depth of 5000 nm
234 and a strain rate of 0.2 s^{-1} for both samples. This value was chosen following the study of Giro-
235 Paloma *et al.* [27], where they studied different strain rates to assure that this parameter is not
236 sensitive to the mechanical properties.

237 These results cannot be compared with another technique such as DMTA (Dynamic Mechanical
238 Thermal Analysis), because there are not reported results at 70 Hz of frequency.

239

240

Table 1.

241

242 **4. Conclusions**

243 Nanoindentation technique is an adequate tool to evaluate nanomechanical properties for
244 polymers. The usage of the fire retardant inorganic filler $\text{Mg}(\text{OH})_2$, in a polypropylene (PP)
245 matrix as a macroencapsulated container in TES applications, changes significantly some
246 mechanical properties. Hardness (H), Elastic modulus (E) and Loss modulus (E_{loss}) increase
247 compared with the same sample without the filler. To store thermal energy in a building in a

248 passive system or heating and cooling usage, PP-60Mg compound has to be in contact with a
249 PCM, i.e. paraffin wax. In this case, the properties decrease significantly because the organic
250 fluid acts as a plasticizer, softening the polymer. Moreover, for a given PCM as contact fluid,
251 the lowest mechanical properties were observed for the higher temperature in service. Also, the
252 higher PCM's melting point, the lower mechanical properties. It is highlighted to take into
253 account the temperature service of the PCM and of the final application of the system. Finally, it
254 can be concluded that the polymer degradation in contact with the fire retardant and the PCM
255 occurs only on the surface.

256

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263

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