

1 DEVELOPMENT AND CHARACTERIZATION OF UNMODIFIED KAOLINITE /  
2 EVOH NANOCOMPOSITES BY MELT COMPOUNDING

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26  
27 **Abstract**

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31 14 Nanocomposites of unmodified kaolinite (Kaol) / ethylene-vinyl alcohol copolymer  
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33 15 (EVOH) with different Kaol contents have been obtained by a two-step process: melt  
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35 16 blending in an internal mixer and film processing by co-extruding the obtained clay  
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37 17 polymer nanocomposites pellets in between two low-density polyethylene (LDPE)  
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39 18 layers. The addition of the clay mineral to the molten polymer has been carried out by  
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41 19 using a Kaol/EVOH masterbatch containing 15mass% Kaol. The so-obtained samples  
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43 20 have been analysed by means of WAXS, SEM, TEM, DMA and tensile tests. Finally,  
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45 21 barrier properties to water vapour and oxygen at two relative humidities have been  
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47 22 assessed. Morphological analysis has revealed high degree of dispersion and  
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49 23 distribution of the Kaol within the EVOH matrix. A considerable increase in the  
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51 24 mechanical and in the barrier properties has been found. The present work puts forward  
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53 25 the effectiveness of an unmodified kaolinite for obtaining ultra-high barrier clay mineral  
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55 26 / polymer nanocomposites.

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59 **1. Introduction**

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30 Ethylene-vinyl alcohol (EVOH) copolymers are a family of semi-crystalline random  
31 copolymers widely used in the food-packaging sector due to their outstanding gas  
32 barrier properties to oxygen and organic compounds (solvents and food aromas); as well  
33 as their considerable chemical resistance and high transparency(Lagaron et al., 2001).  
34 The major drawback of these materials is their moisture sensitivity that causes a  
35 significant decrease in their gas barrier properties at high relative humidities( Lagarón et  
36 al., 2001; Muramatsu et al., 2003; Cava et al., 2006; Kim et al., 2014). Therefore,  
37 EVOH is commonly used as a barrier intermediate layer in co-extruded multilayer  
38 structures, being hence protected by layers of hydrophobic materials such as  
39 polyolefins(Villalpando-Olmos et al., 1999). The presence of EVOH in the packaging  
40 structure is key to food quality and safety, because it reduces the ingress of oxygen and  
41 the loss of aroma components during extended packaging shelf-life(Martínez-Sanz et  
42 al., 2012).

44 It is well known that the addition of nanofillers to a pure polymer can lead to an  
45 increase in some relevant material properties, such as mechanical properties or thermal  
46 stability, without significant reductions in toughness and transparency(Alexandre and  
47 Dubois, 2000; Kotsilkova et al., 2001; Sinha Ray and Okamoto, 2003; Wan et al., 2003;  
48 Pavlidou and Papaspyrides, 2008). In the particular case of the EVOH copolymers, it  
49 has been widely reported that the addition of clay-based nanofillers is a convenient  
50 approach to increase the barrier properties mainly due to an increase in the tortuosity of  
51 the diffusion path(Gimenez et al., 2004; Lagarón et al., 2005; Arora and Padua, 2010;  
52 Ophir et al., 2010; Kim et al., 2014; Kim and Cha, 2014).

54 Among the clay polymer nanocomposites (CPN) the most widely studied clay mineral  
55 is montmorillonite (Mt) due to its large cation exchange capacity which facilitates the  
56 organomodification enhancing its dispersion in polymer matrices(Giannelis, 1996;  
57 Lambert and Bergaya, 2013). However, the kaolinite (Kaol) has been also a very  
58 suitable clay mineral for obtaining CPN (Chen and Evans, 2005; Arora and Padua,  
59 2010; Vahabi et al., 2012; Detellier and Letaief, 2013; Zulfiqar et al., 2015), despite the  
60 problem associated to its chemical structure which makes it difficult to organomodify  
61 permanently (Kenne and Detellier, 2016) . In previous works, Kaol CPN with different  
62 polymer matrix have been successfully obtained(Cabedo et al., 2004, 2006b, 2009;  
63 Villanueva et al., 2010; Fukushima et al., 2012). For the particular case of EVOH / Kaol

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CPN a decrease in oxygen permeability at 45°C from  $3.6 \cdot 10^{-5} \text{ (cm}^3 \text{ m)/(m}^2 \text{ day atm)}$  to less than  $10^{-5} \text{ (cm}^3 \text{ m)/(m}^2 \text{ day atm)}$  was achieved (Cabedo et al., 2004).

Kaol is a very common material in earth and is widely used as raw material in several industrial sectors. Kaolinite ( $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ ) is a 1:1 clay mineral that is composed of silicon oxide tetrahedral sheets bonded to aluminium oxide/hydroxide (gibbsite) octahedral sheet (Schoonheydt and Johnston, 2006). This particular structure leads to an asymmetric configuration that is responsible for the formation of hydrogen bonds between consecutive layers, thus leading to a large cohesive energy. As a consequence of these strong layer-to-layer interactions, intercalation of polymeric chains between the Kaol layers is not favoured. For this reason, it is necessary a previous chemical treatment to facilitate the intercalation and potential exfoliation of Kaol during the melt mixing (Yoshihiko et al., 1999; Gardolinski et al., 2000; Kenne and Detellier, 2016; Zhang et al., 2016). The chemical modification of the clay mineral surface, necessary for achieving a good degree of dispersion of the Kaol, can interact negatively with the polymer (Fornes et al., 2003; Bordes et al., 2009) or even migrate to the food (Xia et al., 2015). These are potential drawbacks for the use of Kaol in food packaging applications. In this work, however, a different approach is explored: an EVOH/Kaol masterbatch. This approach is very convenient since the clay mineral is incorporated to the polymer in a highly dispersed condition, hence being the shear forces applied during compounding enough to obtain a favourable morphology in a non-modified Kaol. Moreover, the masterbatch route can be implemented in conventional polymer compounding equipment in normal operating conditions without significant modification of the process.

This work aims at exploring the masterbatch route for obtaining unmodified Kaol / EVOH nanocomposites with improved performance for food packaging applications. The morphological characteristics, mechanical properties and oxygen and water barrier properties of the materials developed are also reported as a function of the Kaol content.

## 2. Experimental

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97 **2.1. Materials**

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99 The ethylene-vinyl alcohol copolymer (EVOH) used in this work was a commercial  
100 grade (Soarnol®), containing 32mol% ethylene, kindly supplied by The Nippon  
101 Synthetic Chemical Industry Co., Ltd. (NIPPON GOHSEI).

102

103 The clay mineral was a natural kaolinite supplied by Arciblansa (Alcora, Spain). The  
104 isopropanol (>99.7%) was purchased from Sigma Aldrich and used as received.

105

106 **2.2. Masterbatch preparation**

107

108 Unmodified Kaol/EVOH masterbatch was prepared according to Cabedo(Cabedo,  
109 2007). For so, EVOH pellets were dissolved in an isopropanol / water solution (50 / 50  
110 by volume) at 90°C under constant stirring. A Kaol dispersion was prepared in the same  
111 solvent composition at similar conditions. Once the polymer was fully dissolved the  
112 Kaol dispersion was added dropwise to the polymer solution and kept for 12 hour at  
113 90°C and constant stirring. The system is then precipitated by pouring it into a container  
114 of cold water, milled and dried under vacuum. The masterbatch composition was  
115 15weight% of Kaol.

116

117 **2.3. CPN processing**

118

119 The CPN were processed by melt blending in an internal mixer (Rheomix-Haake)  
120 during a mixing time of 5 minutes at a temperature of 210°C and rotor speed of 40 rpm.  
121 Prior to the blending step, both masterbatch and polymer were dehumidified at 100°C  
122 during an hour in a Piovan. The masterbatch was added to the mixer once the polymer  
123 was fully melted. The CPN resulting of the mixing was cooled with liquid nitrogen and  
124 grinded into powder in a rotating mill. CPN with three different Kaol contents were  
125 obtained: 2.5, 5 and 7weight% (further referred as EVOH/2.5Kaol, EVOH/5Kaol and  
126 EVOH/7Kaol respectively).

127

128 The CPN powder was transformed into samples with two different thicknesses: plates  
129 (0.8mm) and films (15µm). The plates were obtained by compression moulding at  
130 200°C and 4 manometric bars during 2 minutes and allowed to cool to room temperature

131 under pressure at a cooling rate of 20°C/min. The so-obtained plates were used for the  
132 morphological and DMA characterization. 20µm thick films of the 2.5% and 5% Kaol  
133 content samples were obtained by co-extrusion in between two 80µm thick layers of  
134 low-density polyethylene (LDPE) under identical conditions of a previous  
135 work(Cabedo, 2007). The co-extruded films were subsequently delaminated and the  
136 CPN layer used for the mechanical and barrier characterization.

### 138 **2.3. Characterization techniques**

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140 WAXS (Wide Angle X-Ray Scattering) experiments were performed using a Bruker  
141 AXS D4 Endeavour instrument (Bruker Corporation, Karlsruhe, Germany) equipped  
142 with an automatic sample change system. Radial scans of intensity versus scattering  
143 angle ( $2\theta$ ) were recorded at room temperature in the range 2° to 30° ( $2\theta$ ). The step size  
144 was 0.02° ( $2\theta$ ) and the scanning rate was 8s/step. The X-ray source used was a filtered  
145 Cu  $K_{\alpha}$  radiation tube ( $\lambda = 1.54\text{\AA}$ ), at an operating voltage of 40kV and a filament  
146 current of 40mA. The sample holder allows rotating the sample in-plane, removing thus  
147 any in-plane orientation effect. Bragg's law was applied to calculate clay mineral basal  
148 spacing.

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150 The scanning electron microscopy (SEM) experiments were developed using a LEO  
151 440i (Leo Electron Microscopy, Cambridge, UK) equipped with a digital image  
152 acquisition system. Normal operating conditions were 20kV and 100pA for the  
153 secondary electron detector. The polymeric samples were cryofractured in liquid  
154 nitrogen and coated by sputtering with Au-Pd.

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156 Transmission electron microscopy (TEM) was performed using a JEOL 1010 (Jeol Ltd,  
157 Akishima, Japan) equipped with a digital Bioscan (Gatan) image acquisition system.  
158 TEM observations were performed on ultra-thin sections of cryoultramicrotomed CPN  
159 sheets.

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161 Dynamic-mechanical experiments were performed in a Perkin Elmer DMA 7e (Perkin  
162 Elmer, Waltham, USA) equipment in three-point bending mode. The temperature range  
163 registered was from -90°C to 150°C at a heating rate of 5°C/min, at 1Hz frequency and a

164 dynamic deformation of 0.15%.

165

166 Tensile testing up to failure was carried out at room temperature on an Instron 4469  
167 H1907 Universal Tester (Instron Norwood, USA). A fixed crosshead rate of 10 mm/min  
168 was utilized in all cases and the results were taken as the average of five tests. Dumb-  
169 bell shaped specimens according to ASTM D638 were used. Experiments of the co-  
170 extruded films were conducted both in the machine direction (MD) and in the transverse  
171 direction (TD).

172

173 The oxygen transmission rate through vacuum dried co-extruded film specimens was  
174 measured at room temperature under two relative humidity conditions (0% R.H: and  
175 80%R.H.) using an Oxtran 2/21(Modern Control Inc., MN, USA, MOCON) instrument.  
176 The carrier gas was nitrogen while the ambient gas was oxygen with 99.9% purity. The  
177 surface analysed was in all cases 50cm<sup>2</sup>.

178

179 Direct permeability to water vapour was measured from the slope of the weight loss–  
180 time curves at 24°C and 40% RH. The films were sandwiched between the aluminium  
181 top (open O-ring) and bottom (deposit for the permeant) parts of a specifically designed  
182 permeability cell with screws. A Viton rubber O-ring was placed between the film and  
183 the bottom part of the cell to enhance sealability. Then the bottom part of the cell was  
184 filled with water and the pinhole secured with a rubber O-ring and a screw. Finally, the  
185 cell was placed in an environment with controlled moisture of 40% RH and the water  
186 weight loss through a film area of 0.001m<sup>2</sup> was monitored and plotted as a function of  
187 time. Cells with aluminium films (with a thickness of ca. 10 µm) were used as control  
188 samples to estimate water loss through the sealing. The permeability sensibility of the  
189 permeation cells was determined to be better than 0.01·10<sup>-13</sup> kg·m/s·m<sup>2</sup>·Pa based on the  
190 weight loss measurements of the aluminium cells. Cells clamping polymer films but  
191 with no solvent were used as blank samples to monitor water uptake. Water vapour  
192 permeation rates were estimated from the steady-state permeation slopes. The tests were  
193 done in triplicate and average values and standard errors are provided.

194

### 195 **3. Results and discussion.**

196

197 **3.1. Morphological analysis of kaolinite and kaolinite / EVOH nanocomposites.**

198  
199 SEM micrograph of the natural Kaol in its natural state is presented in Figure 1a.  
200 Imperfect stacking of the clay mineral platelets is detected, thus being the predominant  
201 microstructure a fine distribution of small sized Kaol aggregates with broken platelets  
202 and an uneven size distribution. WAXS pattern of the unmodified Kaol is plotted in  
203 Figure 1b. Since it is a natural clay without any kind of purification, other minor phases  
204 can be detected together with the Kaol; among them the more relevant are quartz and  
205 illite.

206  
207 WAXS patterns of the powder masterbatch and the three CPN samples obtained by  
208 compression moulding direct from the CPN powder are presented in Figure 2. A  
209 reflection at  $12.4^\circ(2\theta)$  in all patterns that can be associated to the basal reflection (001)  
210 of the Kaol, having thus a basal spacing of 0.72nm. This peak is visible in masterbatch  
211 and all CPN patterns, revealing the presence of Kaol in an aggregate state. Nevertheless,  
212 the low relative intensity of the basal reflection together with its high degree of  
213 imperfection would indicate either bad stacking of the clay or small size of the  
214 aggregates, or both. This is particularly noticeable for the masterbatch sample, although  
215 the Kaol content is much higher. Comparing the three CPN patterns, the intensity of the  
216 basal reflection of the clay mineral is higher in the EVOH/7Kaol diffractogram than in  
217 the lower content samples. This may indicate higher degree of aggregation in the former  
218 with respect to the other two, in which this reflection shows almost the same intensity,  
219 despite the difference in composition. Attending to this behaviour, it can be inferred that  
220 better morphology has been achieved in the EVOH/2.5Kaol and EVOH/5Kaol samples  
221 when compared to the EVOH/7Kaol sample. However, microscopy analysis is required  
222 to figure out the actual state of dispersion of the Kaol within the polymer matrix in these  
223 samples.

224  
225 The reflection labelled EVOH in Figure 2 is ascribed in the scientific literature(Cerrada  
226 et al., 1998; J. M. Lagarón et al., 2001) to the (100) reflection of the ethylene-vinyl  
227 copolymer. In the pattern of the masterbatch this reflection is barely visible, which  
228 together with the low perfection of the other reflections associated to the EVOH, could  
229 be interpreted as a low crystallinity or a highly imperfect degree of cristallinity. On the  
230 other hand, the reflection appearing at  $8.6^\circ(2\theta)$  corresponds to the (002) plane of an

231 illite, which is a very common natural impurity of kaolinitic clays. This impurity,  
232 having also a laminar structure, seems to collapse to its natural position during the CPN  
233 processing, since it is visible in all three CPN and not in masterbatch pattern.

234

235 SEM micrograph of the masterbatch powder at 5000X is shown in Figure 3. It is  
236 possible to detect the presence of small aggregates well integrated within the EVOH  
237 matrix. This reveals a good interaction between the unmodified Kaol surface and the  
238 polymer. SEM micrographs of the fractured surface of the EVOH/5Kaol and  
239 EVOH/7Kaol samples are presented in Figure 4. At a first glance, no major aggregates  
240 can be noticed, therefore, it can be said that in both cases the morphology of the CPN is  
241 highly favourable, i.e. high degree of dispersion of the Kaol platelets within the EVOH  
242 matrix. However, the presence of small aggregates (pointed in the micrograph with  
243 white arrows) can be noticed, which, in all cases, have a considerably high aspect ratio  
244 (length/thickness) and its thickness is in the nanometre range. The presence of these  
245 nanometric aggregates is higher in the sample containing 7% Kaol loading. This trend is  
246 also observed by means of TEM analysis (see Figure 5). In both cases, the Kaol is  
247 homogeneously dispersed throughout the analysed surface, revealing a high level of  
248 interaction between the clay mineral surface and the polymer matrix. The presence of  
249 nanometric aggregates can be detected in both samples, although is considerably higher  
250 in the EVOH/7Kaol, according to SEM results. These small sized aggregates,  
251 particularly in the EVOH/5Kaol, are small aggregated structures containing a low  
252 number of clay platelets stacked to each other at the natural distance. However, since  
253 the aspect ratio of these entities is very high and the thickness is below 100nm, the  
254 effect may not affect negatively to the final properties of the CPN.

255

256 Morphological analysis indicates that clay loadings beyond 5% lead to the aggregation  
257 of the Kaol under these particular processing conditions, therefore it can be inferred that  
258 the limit in the amount of Kaol that EVOH matrix can hold without collapsing is, in this  
259 system, around 5weight%. Small Kaol aggregates are detected in all the samples studied  
260 by means of WAXS and microscopic techniques, revealing the presence of a fraction of  
261 the clay mineral that cannot be fully exfoliated; however, attending to the high degree of  
262 delamination and the nanometer size of the residual Kaol aggregates, it can be said that  
263 favourable morphology is achieved, particularly in the EVOH/2.5Kaol and  
264 EVOH/5Kaol samples.



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266 **3.2. Mechanical and dynamic-mechanical properties of Kaolinite / EVOH**  
267 **nanocomposites.**

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269 DMA curves of the pure EVOH and the Kaol/EVOH nanocomposites are plotted in  
270 Figure 6. EVOH copolymers present three different relaxations in the temperature range  
271 analysed: the most relevant ( $\alpha$ -relaxation) is ascribed to the mechanical relaxation due  
272 to the glass transition. The  $\alpha'$ -relaxation is generally attributed to chain movement in the  
273 crystal boundaries and imperfect crystals and the  $\beta$ -relaxation is assigned to  
274 collaborative chain movements in shorter fragments than the  $\alpha$ -relaxation (Cabedo et al.,  
275 2006a).

276

277 Storage modulus ( $E'$ ) of all CPN is higher than that of the pure EVOH throughout the  
278 full temperature range studied (Figure 6a). At temperatures below the  $\alpha$ -relaxation, Kaol  
279 platelets have a *reinforcing* effect, increasing the value of the storage modulus ( $E'$ ) and  
280 decreasing the loss modulus ( $E''$ ). This effect increases proportionally with the Kaol  
281 content of the sample. The difference in the DMA behaviour between the EVOH and  
282 the CPN is more evident at temperatures above  $T_{\alpha}$ , however the dependence with the  
283 Kaol loading is not clear. Attending to the temperatures at which relaxations take place,  
284 the addition of the Kaol results in an increase in all three cases ( $\alpha$ ,  $\alpha'$ ,  $\beta$ ). In the case of  
285 the  $\alpha$ -relaxation, the maximum of the peak in the  $\tan\delta$  curve of the CPN (see Figure 6b)  
286 is shifted over 15°C towards higher temperatures with respect to the pure EVOH.  
287 Loadings above 2.5% do not seem to enhance significantly this behaviour. From the  
288 DMA results, Kaol platelets seem to act as a reinforcing agent by increasing the elastic  
289 response of the matrix both at temperatures below and above the glass transition. The  
290 increase in the temperatures at which the relaxations take place could be explained by  
291 the fact that phyllosilicate platelets hinder chain mobility being thus necessary higher  
292 energies for relaxations to take place.

293

294 Table I gathers the results of the tensile tests conducted on films obtained from the co-  
295 extruded structures, both the pure EVOH and the CPN. The experiments were carried  
296 out in the machine direction (MD) as well as in the transversal direction (TD). Figure 7  
297 plots the stress-strain curves of the samples analysed. According to the data, mechanical  
298 properties of EVOH copolymers are very dependent upon the direction of testing, hence

299 presenting more rigid and less ductile behaviour in MD than in TD. This behaviour can  
300 be attributed to the orientation of both the crystals and the polymer chains in the  
301 amorphous fraction in MD.

302  
303 The addition of Kaol results in an increase of the elastic modulus (E), both in MD and  
304 TD, due to the reinforcing effect of clay mineral platelets. This effect is found to be  
305 more severe at higher Kaol loadings. Specifically, addition of 2.5% of Kaol increases  
306 the elastic modulus (E) value in 25% in MD and in 10% in TD; whereas a 5% Kaol  
307 loading results in an increase of the E of 80% in MD and 60% in TD. The increase in  
308 the elastic modulus is not correlated to an increase in the yield stress ( $\sigma_y$ ), which  
309 remains almost unaffected in the EVOH/2.5Kaol sample, while is increased in MD in  
310 the EVOH/5Kaol sample. The considerable difference found between MD and TD when  
311 the clay was incorporated can be explained by a more severe orientation of the Kaol  
312 platelets and nanometric aggregates in the MD than in the TD. On the other hand, the  
313 addition of Kaol decreases the strain at break ( $\epsilon_R$ ).

314

### 315 **3.3. Barrier properties of Kaolinite / EVOH nanocomposites.**

316

317 Water weight loss permeation experiments for neat EVOH and the Kaol/EVOH  
318 nanocomposites are presented in Figure 8. The slope of the straight line is considerably  
319 lower in the case of the CPN than that of the pure copolymer. This fact reveals a clear  
320 enhancement on the water barrier with the addition of the Kaol. The calculated  
321 adsorption and diffusion coefficient of the three samples analysed are gathered in Table  
322 II. The addition of a 2.5% of Kaol to the pure matrix results in a decrease in water  
323 vapour permeability of 23%, whilst for the EVOH/5Kaol sample, the drop is above  
324 46%. Together with the reduction in the water permeation rate, a decrease in the water  
325 diffusion coefficient has been found for the samples containing Kaol; specifically, this  
326 drop has been found to be of 20% in the case of the EVOH/2.5Kaol and of ca. 50% in  
327 the EVOH/5Kaol.

328

329 The oxygen barrier properties of the co-extruded samples were evaluated under dry  
330 conditions and under high relative humidity conditions (80%). Table III gathers the  
331 results obtained. The addition of Kaol to the EVOH matrix results in a considerable  
332 enhancement in the barrier properties to oxygen; e.g. under dry conditions, oxygen

333 permeability decreases 48% for the EVOH/2.5Kaol sample and up to 59% for the  
334 EVOH/5Kaol one. According to this, in high relative humidity conditions, the barrier to  
335 oxygen is improved by a 36% and 47% with a 2.5% and 5% Kaol loading respectively.

336  
337 The improvement in the water and oxygen barrier properties it is due to an increase in  
338 the tortuosity of the diffusion path of the permeant throughout the polymeric film. This  
339 effect is more sever when all the clay mineral platelets and small sized aggregates are  
340 oriented perpendicularly to the diffusion direction, which is the case of the co-extruded  
341 films. The good interaction observed between the unmodified Kaol and the polymer  
342 matrix can also affect positively to this improvement.

343

#### 344 **4. Conclusions**

345

346 From the results, it can be said that obtaining unmodified Kaol/EVOH nanocomposites  
347 by melt compounding is possible when the addition of the clay mineral is done by  
348 means of an appropriate Kaol/EVOH masterbatch; having these CPN enhanced  
349 properties for their application as high barrier material. From the morphological  
350 analysis it can be concluded that favourable morphology is achieved by blending in an  
351 internal mixer. However, full exfoliation has not been reached, as derived from the  
352 detection in all samples of nanometer-ranged aggregates. The presence of these  
353 structures is more common in the samples containing 7mass% Kaol loading.

354

355 DMA and tensile tests reveal a reinforcing effect of the Kaol platelets in the studied  
356 CPN, being higher their rigidity as well as the temperatures at which the matrix  
357 relaxations take place. Regarding the barrier properties, the presence of the nanofillers  
358 resulted in great enhancement to both water and oxygen. Hence, for the sample  
359 containing 5% of Kaol, the diffusion coefficient to water vapour was found to be  
360 reduced in 50%, while the oxygen permeability decreased up to 59% under dry  
361 conditions and 47% under high relative humidity conditions.

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#### 363 **Acknowledgements**

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503 **Figure Captions:**

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3 505 **Figure 1:** SEM micrograph (a) and WAXS pattern (b) of the Kaol.

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5 506 **Figure 2:** WAXS patterns of the masterbatch and the Kaol/EVOH nanocomposites.

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7 507 **Figure 3:** SEM micrographs of masterbatch powder. The white arrows indicate the  
8 presence of small clay aggregates.

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10 509 **Figure 4:** SEM micrographs of criofractured surface of the EVOH/5Kaol (a) and  
11 EVOH/7Kaol (b) samples. The white arrows indicate the presence of small clay  
12 aggregates.

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14 511  
15 512 **Figure 5:** TEM micrographs of Kaol/EVOH nanocomposites: a) EVOH/5Kaol and b)  
16 EVOH/7Kaol.

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19 514 **Figure 6:** DMA curves of the pure EVOH and the Kaol/EVOH nanocomposites: a)  
20 Storage modulus ( $E'$ ) and loss modulus ( $E''$ ) vs. temperature, b)  $\tan\delta$  vs. temperature.

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22 515  
23 516 **Figure 7:** Stress-strain curves of the co-extruded EVOH and Kaol/EVOH  
24 nanocomposites in machine direction (MD) and in the transverse direction (TD).

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27 518 **Figure 8:** Direct permeability to water vapour of pure co-extruded EVOH and co-  
28 extruded EVOH CPN.

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522 **Table Headings:**  
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4 524 **Table I:** Tensile tests results of the pure EVOH and the Kaol/EVOH nanocomposites  
5 525 obtained by co-extrusion.  
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7 526 **Table II:** Permeability (P), solubility (S) and diffusion (D) to water vapour of the co-  
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9 527 extruded samples.  
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11 528 **Table III:** Oxygen permeability and reduction with respect to the EVOH of the co-  
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13 529 extruded samples under dry conditions and at 80% R.H.  
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## Highlights (for review)

- Nanocomposites of unmodified kaolinite / EVOH have been obtained by melt blending
- Kaolinite/EVOH nanocomposites exhibited improved mechanical and thermal performance
- The water diffusion coefficient in the nanocomposites decreased by 50%
- Oxygen barrier of the nanocomposites (dry and high humidity) was increased by 50%

1 **Table I:** Cabedo et al.

<b>Direction</b>	<b>Sample</b>	<b>E (GPa)</b>	<b><math>\sigma_y</math> (MPa)</b>	<b><math>\sigma_R</math> (MPa)</b>	<b><math>\epsilon_R</math> (%)</b>
	<i>EVOH</i>	2.4±0.2	78±4	66±5	13±1
<i>MD</i>	<i>EVOH/2.5Kao</i>	3.0±0.2	78±4	70±4	12±4
	<i>EVOH/5Kao</i>	4.3±0.4	95±8	86±8	10±1
	<i>EVOH</i>	2.2±0.2	75±1	59±3	35±4
<i>TD</i>	<i>EVOH/2.5Kao</i>	2.4±0.5	68±4	58±3	15±2
	<i>EVOH/5Kao</i>	3.5±0.3	75±4	62±1	23±10

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1 **Table II:** Cabedo et al.

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	<b>P (kg·m/s·m<sup>2</sup>·Pa)</b>	<b>S (kg/m<sup>3</sup>Pa)</b>	<b>D(m<sup>2</sup>/s)</b>
<i>EVOH</i>	$1.94 \cdot 10^{-16}$	0.048	$4.04 \cdot 10^{-15}$
<i>EVOH/2.5Kao</i>	$1.49 \cdot 10^{-16}$	0.046	$3.24 \cdot 10^{-15}$
<i>EVOH/5Kao</i>	$1.05 \cdot 10^{-16}$	0.051	$2.06 \cdot 10^{-15}$

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1 **Table III:** Cabedo et al.

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	$P_{O_2} (m^3 m/m^2 sPa)$			
	<b>24°C y 0%R.H.</b>		<b>24°C y 80%R.H.</b>	
<i>EVOH</i>	$2.9 \cdot 10^{-21}$	----	$4.5 \cdot 10^{-21}$	----
<i>EVOH/2.5Kao</i>	$1.5 \cdot 10^{-21}$	48%	$2.9 \cdot 10^{-21}$	36%
<i>EVOH/5Kao</i>	$1.2 \cdot 10^{-21}$	59%	$2.4 \cdot 10^{-21}$	47%

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Figure 1  
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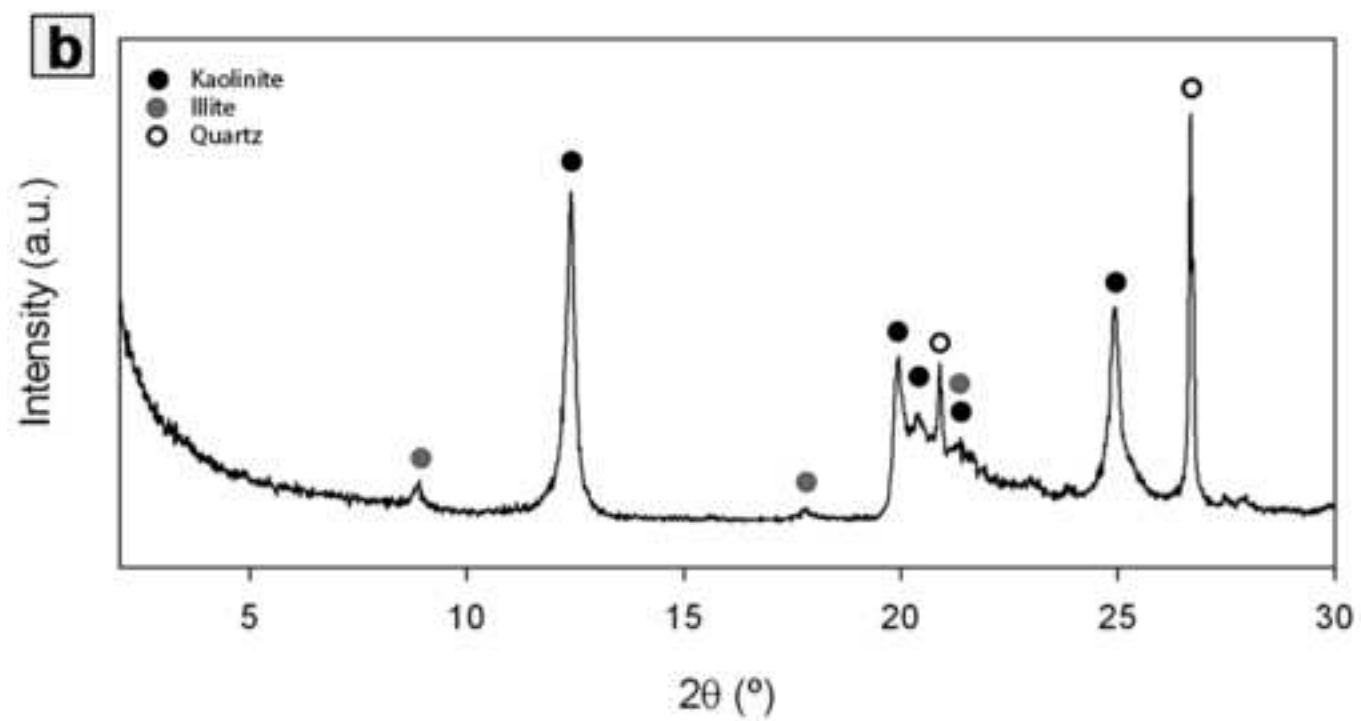
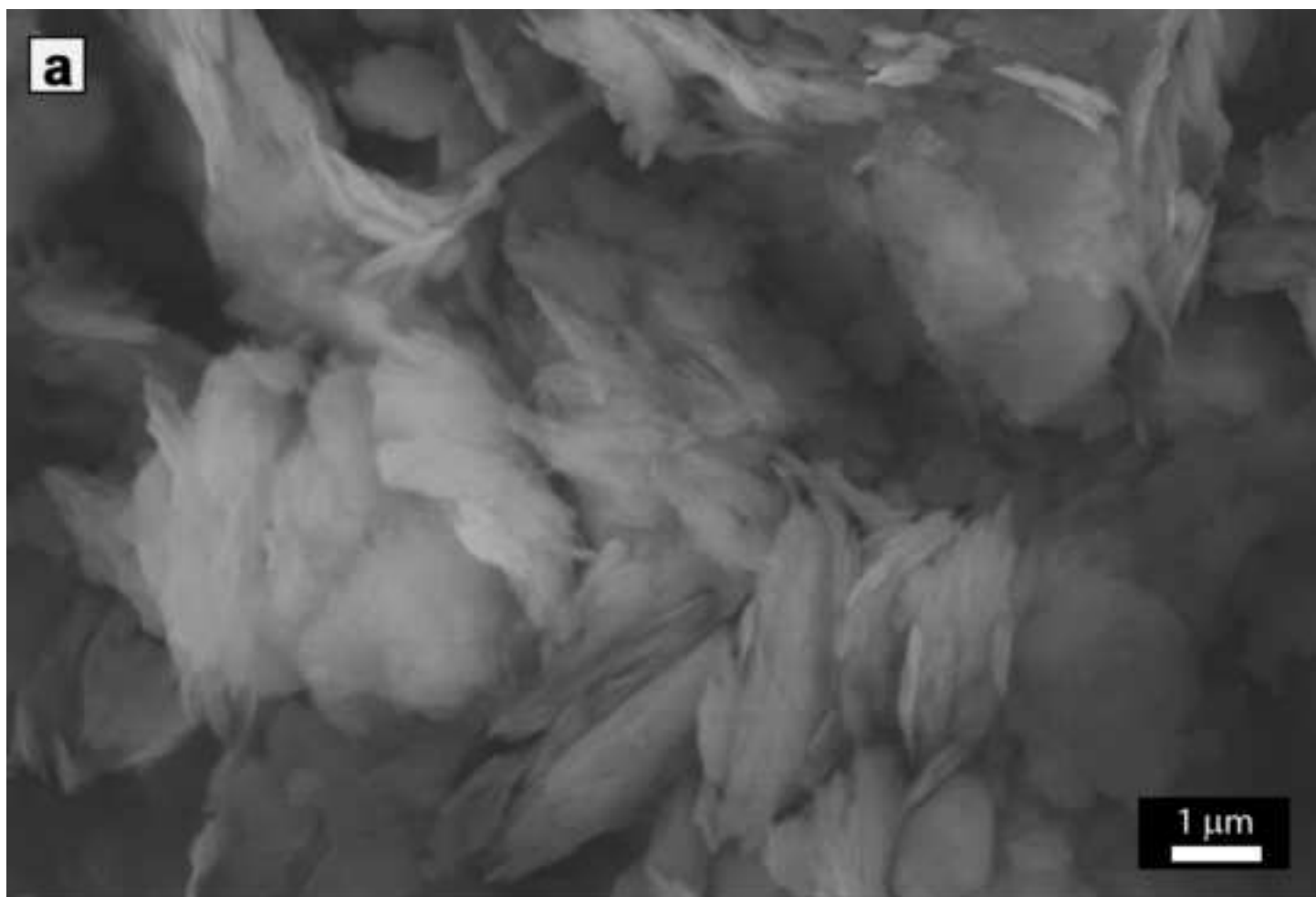


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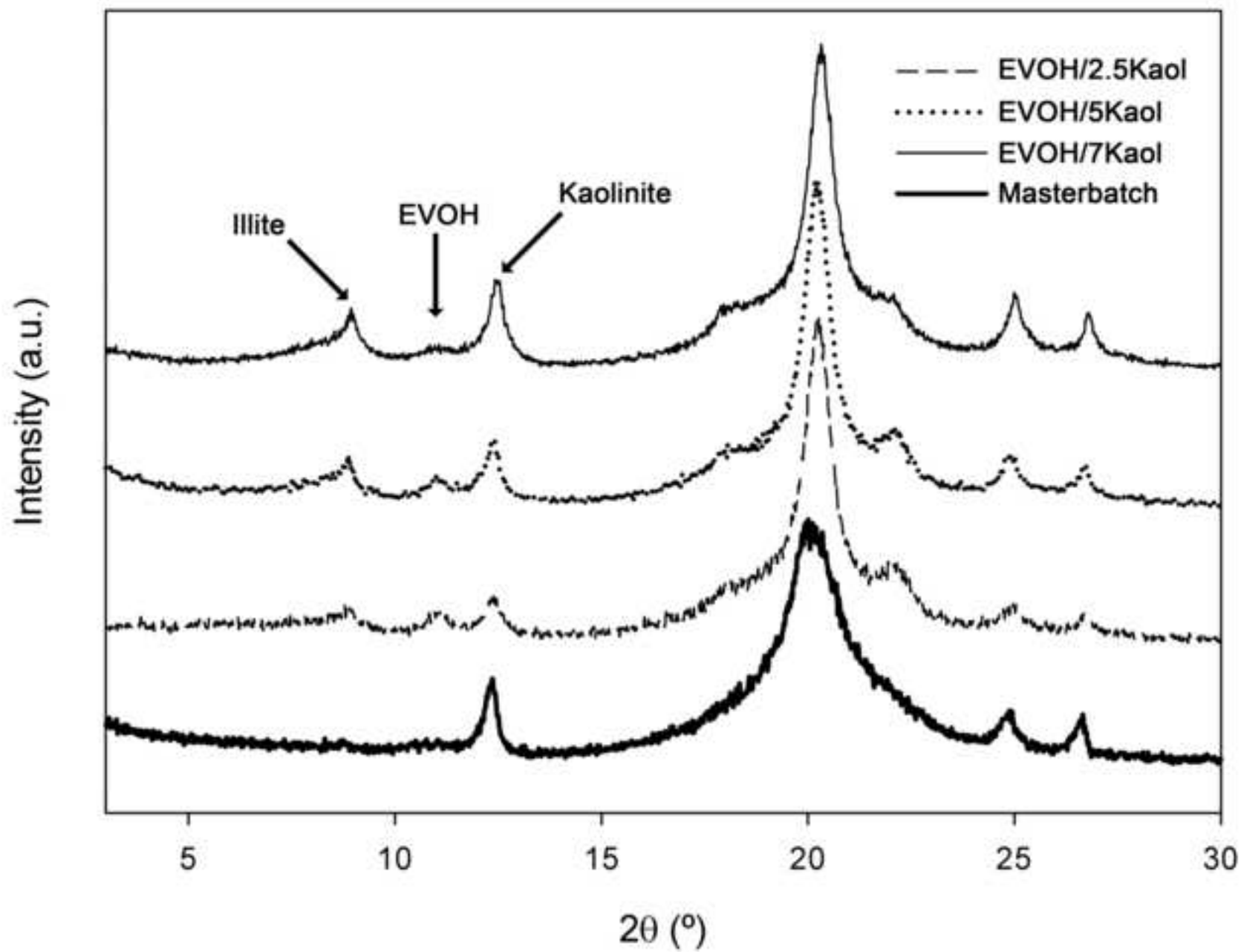




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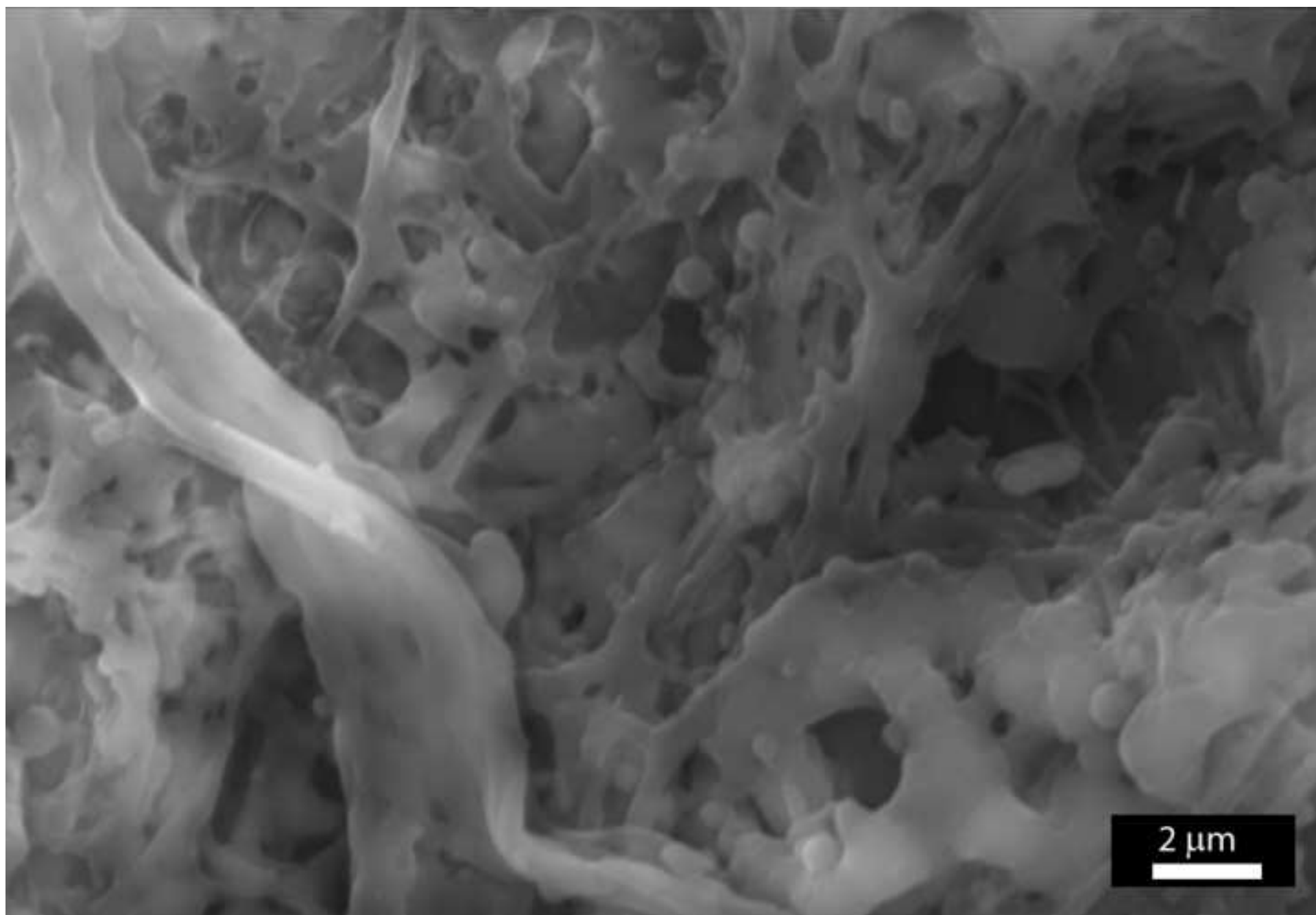


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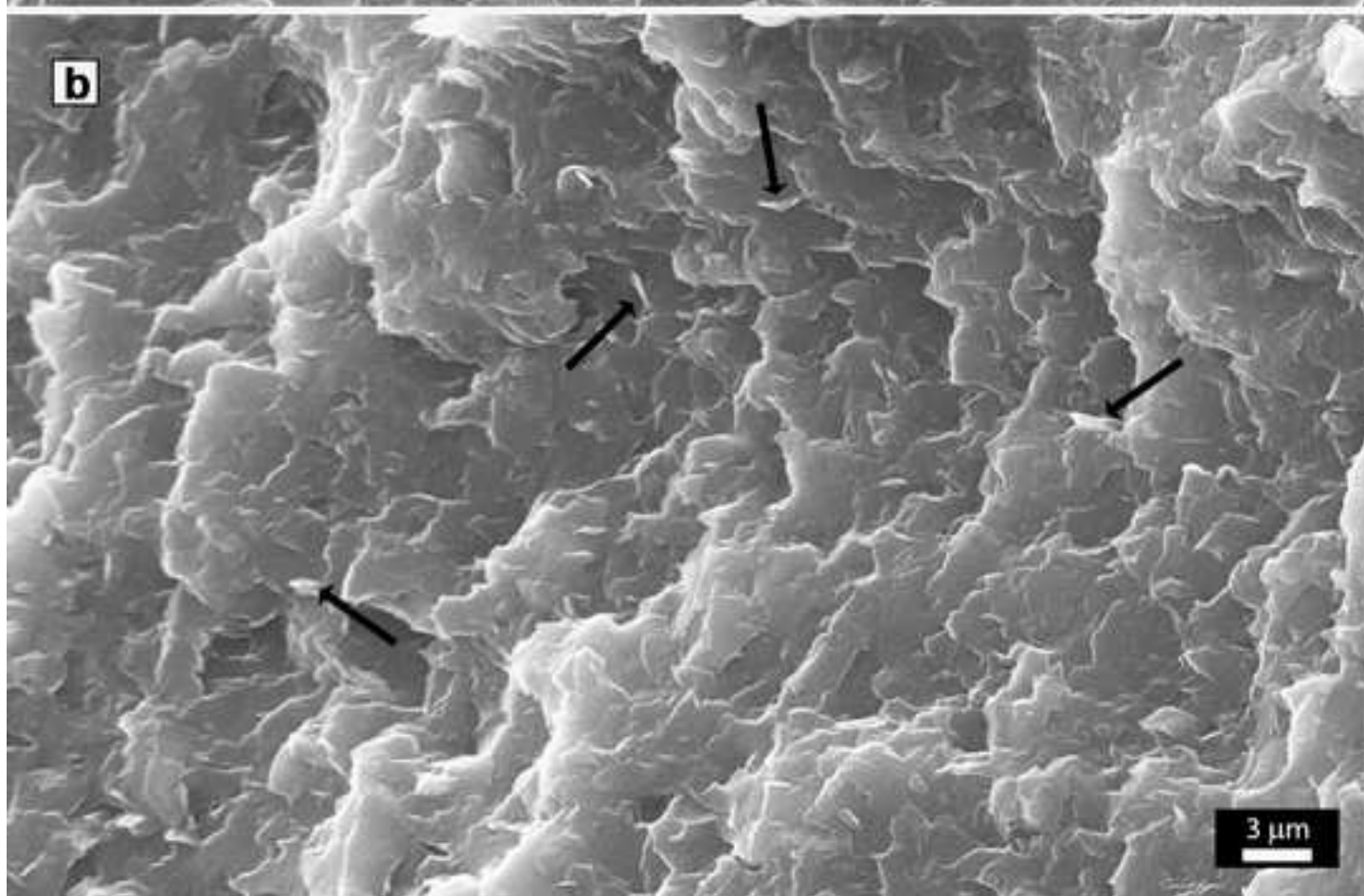
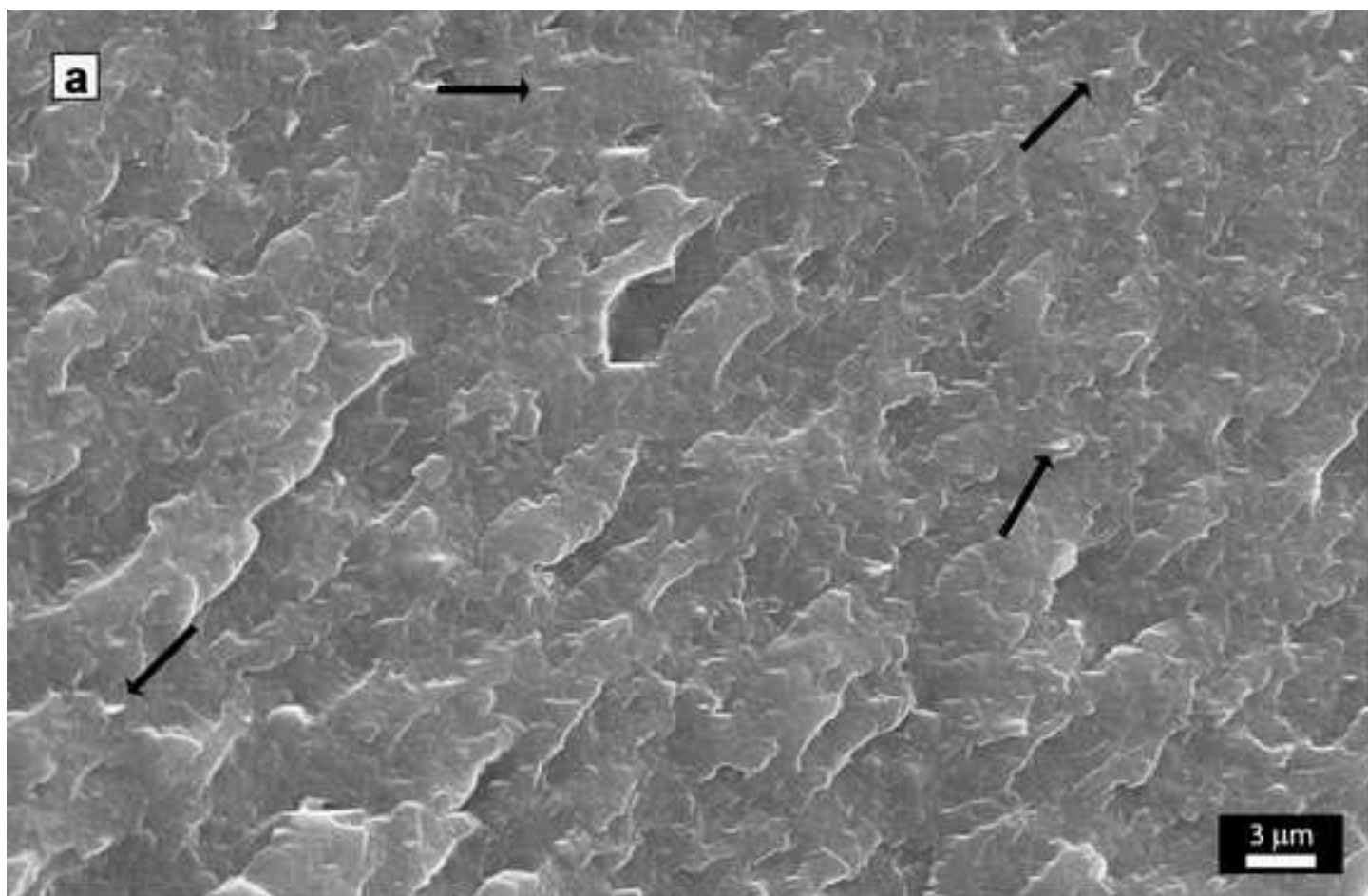


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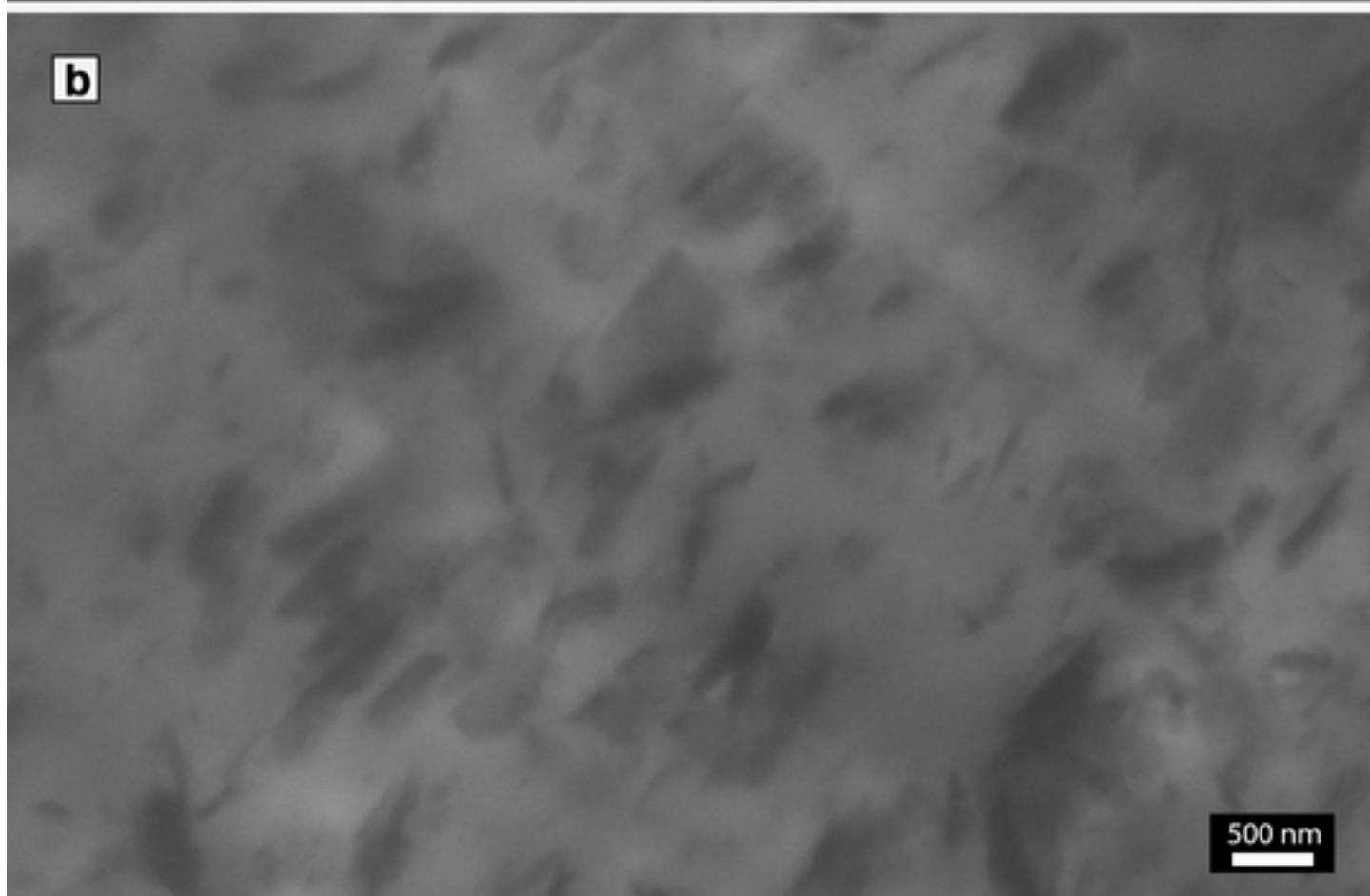


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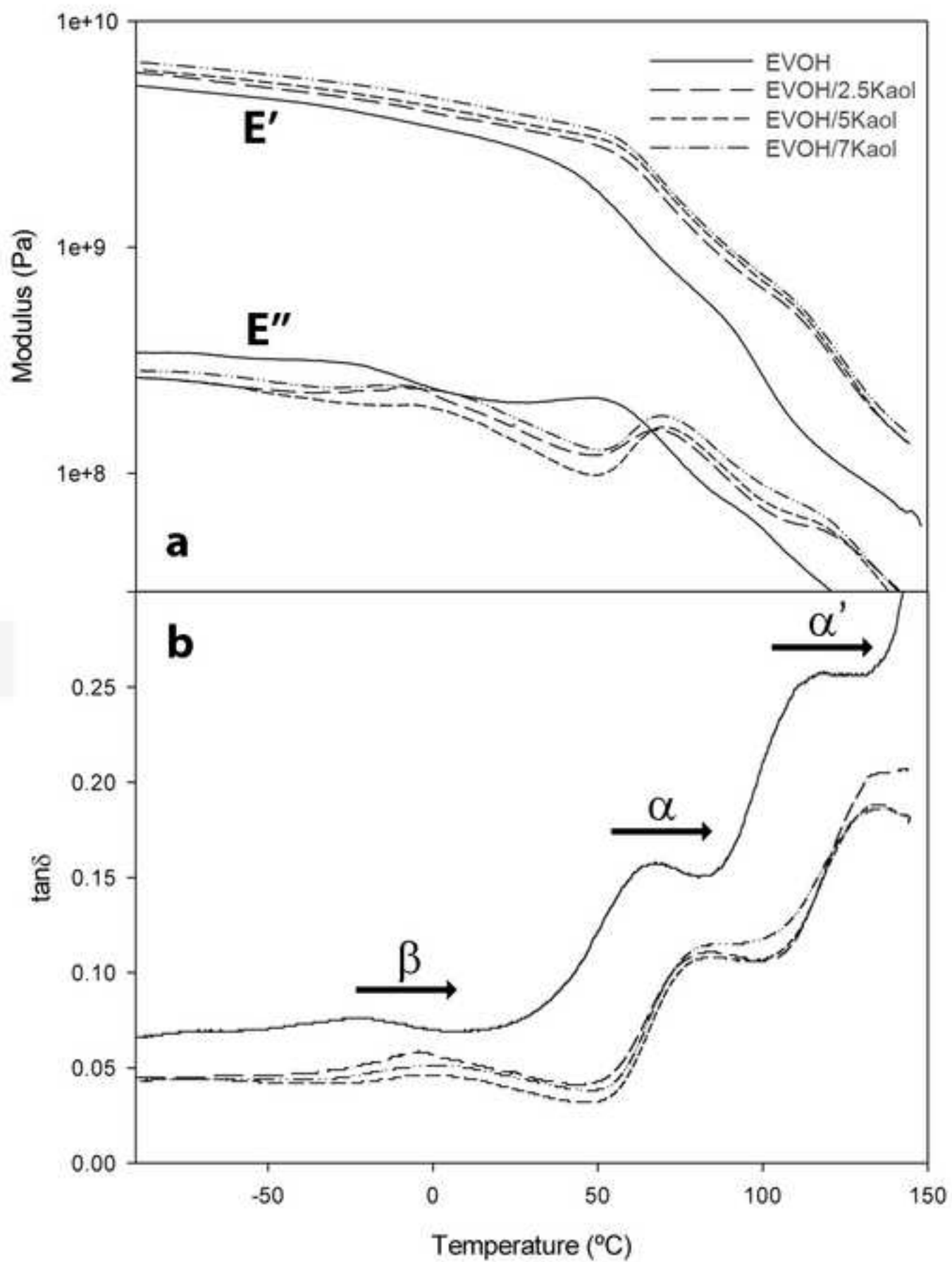


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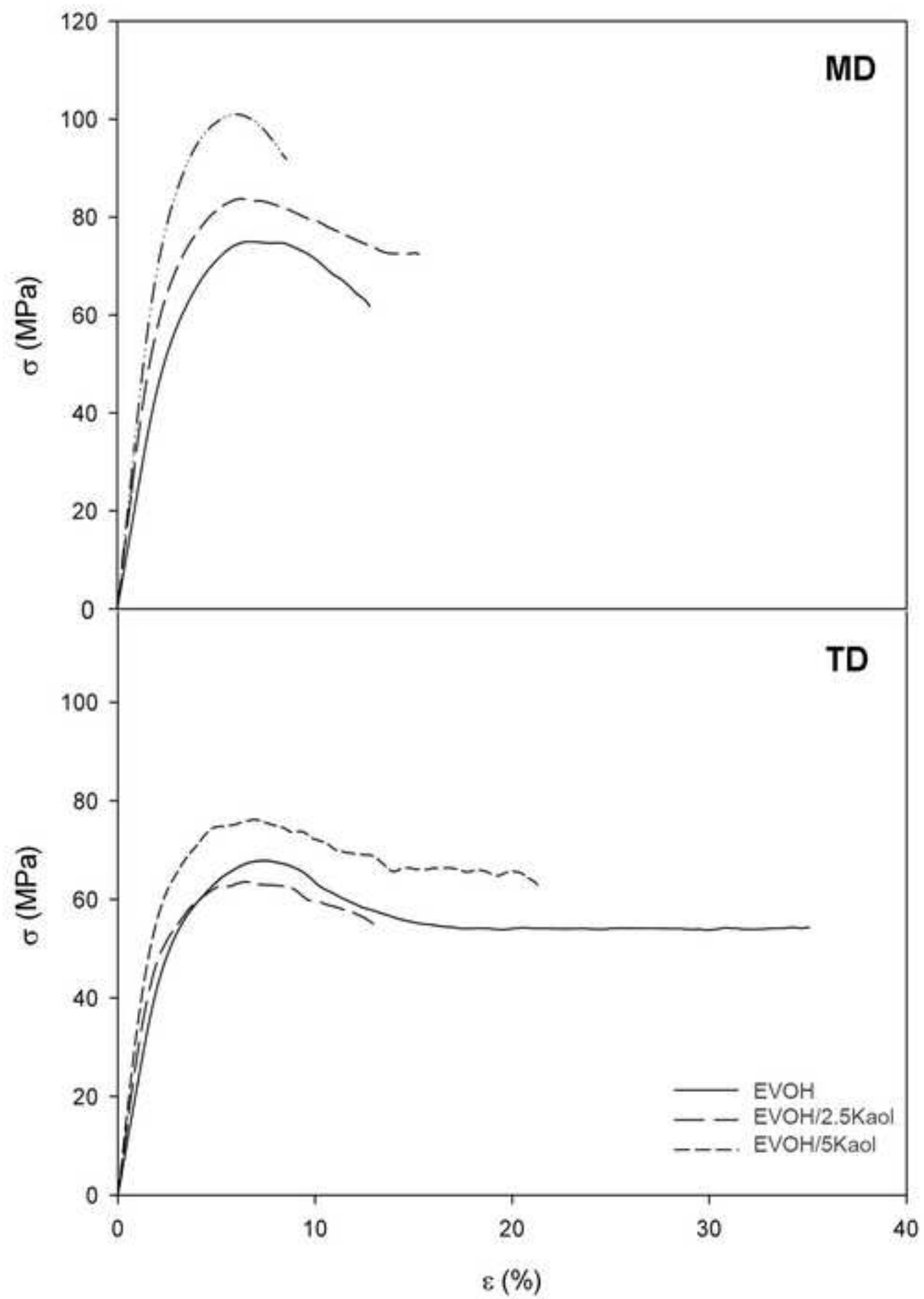
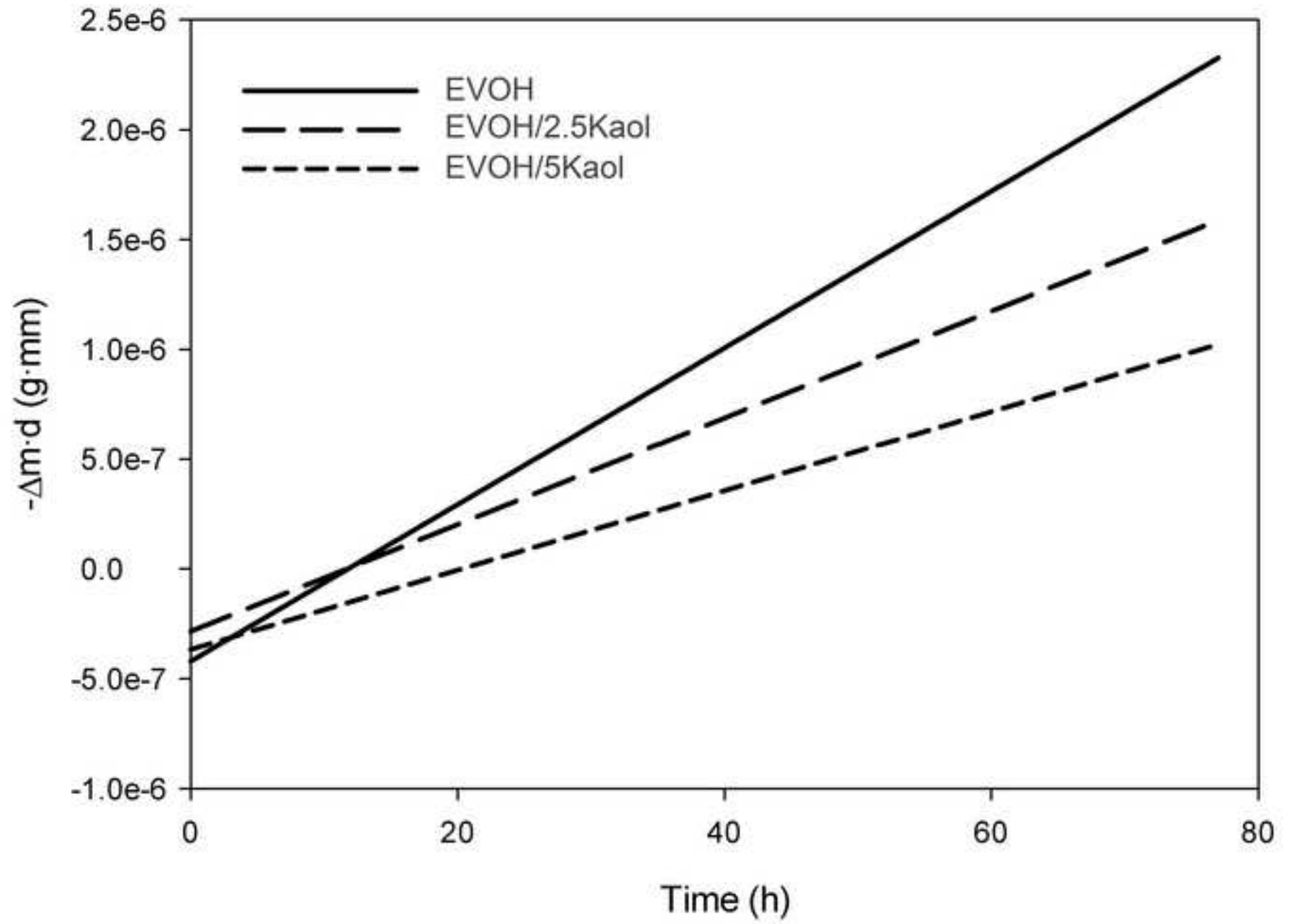




Figure 8  
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## Abstract

Nanocomposites of unmodified kaolinite (Kaol) / ethylene-vinyl alcohol copolymer (EVOH) with different Kaol contents have been obtained by a two-step process: melt blending in an internal mixer and film processing by co-extruding the obtained clay polymer nanocomposites pellets in between two low-density polyethylene (LDPE) layers. The addition of the clay mineral to the molten polymer has been carried out by using a Kaol/EVOH masterbatch containing 15mass% Kaol. The so-obtained samples have been analysed by means of WAXS, SEM, TEM, DMA and tensile tests. Finally, barrier properties to water vapour and oxygen at two relative humidities have been assessed. Morphological analysis has revealed high degree of dispersion and distribution of the Kaol within the EVOH matrix. A considerable increase in the mechanical and in the barrier properties has been found. The present work puts forward the effectiveness of an unmodified kaolinite for obtaining ultra-high barrier clay mineral / polymer nanocomposites.