

## Rheological and Mechanical Behavior of LDPE/Calcium Carbonate Nanocomposites and Microcomposites

Francesco Paolo La Mantia,<sup>1</sup> Marco Morreale,<sup>2</sup> Roberto Scaffaro,<sup>1</sup> Simona Tulone<sup>1</sup>

<sup>1</sup>Università di Palermo, Dipartimento di Ingegneria Civile, Ambientale, Aerospaziale, dei Materiali - Viale delle Scienze, 90128 Palermo, Italy

<sup>2</sup>Università degli Studi di Enna "Kore", Facoltà di Ingegneria, Architettura e delle Scienze Motorie - Cittadella Universitaria, 94100 Enna, Italy

Correspondence to: M. Morreale (E-mail: marco.morreale@unikore.it)

**ABSTRACT:** The increase of the interest in polymer nanocomposites has been leading to continuous growing search toward nanofillers alternative to the widely known clay-based ones. One of these possible alternatives is represented by calcium carbonate nanoparticles, which have not been widely investigated in such context. In this article, a study on the rheological and morphological behavior of different low density polyethylene-calcium carbonate nanocomposites, compared with a reference calcium carbonate microcomposite, is presented. Several different nanosized calcium carbonates at different amounts were used. The results from the rheological and mechanical tests outlined that only minor changes occur when the amount is up to 2 wt %. The use of higher filler concentrations or the increase in the processing time can significantly affect this behavior. SEM analysis allowed deeper understanding of these phenomena. © 2012 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 000: 000–000, 2012

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### INTRODUCTION

The scientific research about the improvement of specific features in polymer systems has led to an increasing importance of polymer composites.<sup>1</sup> However, it has been soon discovered that the dispersion of the filler inside the matrix and their interfacial adhesion are topical issues. In particular, the formation of agglomerates of filler particles directly leads to the creation of discontinuity zones, where crack initiation processes are facilitated and can thus lead to premature material failure even if the presence of compatibilizing agents or of different flow fields (elongational rather than shear) may drastically and easily overturn those negative effects.<sup>2–8</sup>

During the last years, the research on polymer composites has particularly focused on nanosized fillers. It is known that nanometric-sized fillers display a higher surface area in comparison to traditional, micrometric-sized fillers. This should allow obtaining significant improvements in the mechanical, thermo-mechanical, and barrier properties of the materials<sup>9–13</sup> without significant changes in other important properties such as density, processability, transparency, also because just small amounts of nanofillers are typically sufficient to achieve the above mentioned advantages.

The first extensive studies on the use of nanosized fillers for the production of polymer composites with specific properties were conducted by Toyota Motor Corporation (Japan),<sup>14</sup> using modified lamellar silicates. In the following years, several other investigations with multiple polymer matrices were carried out, outlining interesting results.<sup>13,15–20</sup>

However, not much investigation has been carried out on nanosized calcium carbonate. The importance of this natural inorganic filler is testified by the observation that it is cheap, widely available and constituting approximately the 80% of the fillers commonly used for polymer composites worldwide.<sup>20</sup>

The effects of the addition of microsized calcium carbonate to thermoplastics are well known in literature. Increase of viscosity,<sup>21</sup> dimensional stability,<sup>22</sup> tensile strength,<sup>23</sup> crystallinity,<sup>21</sup> were observed. On the other hand, also negative influences were detected. Saheb et al.<sup>24</sup> found that the addition of calcium carbonate to high density polyethylene (HDPE) caused the decrease of tensile strength, whereas Lazzeri et al.<sup>21</sup> found significant worsening of the impact strength. These negative effects may be mitigated by reducing particle size.<sup>25</sup> However, it is not an easy task to obtain a good dispersion of the nanoparticles inside the polymer matrix. It is well known that calcium

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**Table I.** Main Physical Properties of the Fillers Used in this Study (data taken from Ref. [52])

	Crystal structure	Mean particle diameter (nm)	Specific surface (m <sup>2</sup> /g)	Notes
MVM	Calcite	≈260-33000	-	Natural
Socal <sup>®</sup> 31 (S31)	Rombohedral calcite	50-100	-	Precipitated; crystal shape: cube-like
Socal <sup>®</sup> 312 (S312)	Rombohedral calcite	50-100	16-24	Precipitated; crystal shape: cube-like; hydrophobic coating
Socal <sup>®</sup> P3 (P3)	Scalenohedral calcite	180-240	-	Precipitated; crystal shape: cigar-like

carbonate is poorly active to surfactants or coupling agents commonly used for surface treatment of titanium or silicon oxides.<sup>26</sup> Some researchers have found that *in situ* polymerization can significantly improve filler dispersion,<sup>27-33</sup> however, this method is complicated and not suitable for industrial applications. In this case, in fact, melt processing is obviously the preferred way; therefore, filler dispersion should be obtained directly at the melt state. This method is, obviously, really convenient, but on the other hand, the tendency of the particles to reaggregate is so high that it is often necessary to resort to surface modification. Chan et al.<sup>34</sup> have found that impact strength could be doubled using 9 vol % nanosized calcium carbonate treated with a surfactant. Wang et al.<sup>35</sup> found significant improvements in the mechanical properties of polypropylene (PP) upon adding calcium carbonate treated with stearic acid. Levita et al.<sup>36</sup> showed that calcium carbonate nanoparticles treated with stearic acid and a titanate coupling agent can help to improve the properties at break of polypropylene.

As regards the rheological behavior, nanocomposites show a significant increase of viscosity even at low filler content.<sup>37-41</sup> Li and Masuda<sup>38</sup> have attributed this behavior to the formation of agglomerated and crosslinked structures. Wang et al.<sup>40</sup> suggest that the viscosity raise is due to the presence of a considerable number of agglomerates and aggregates in the composites, forming a “filler network.”

The particle shape has also an important role. Xie et al.<sup>42</sup> reported for a poly(vinyl chloride) (PVC)-nanosized CaCO<sub>3</sub> system that the viscosity is higher than for neat PVC at low frequencies, whereas it is lower at higher frequencies, a completely different behavior in comparison to that typically observed in layered silicate-based nanocomposites.<sup>43,44</sup> The reason for this different behavior should be sought in the different geometry of calcium carbonate particles and layered silicates.

Osman and Atallah<sup>45</sup> found that permeability does not change much upon using CaCO<sub>3</sub> particles, while nanocomposites filled with montmorillonite have permeability coefficients lower than those of the neat polymer.

Avella et al.<sup>46</sup> have carried out an investigation on the influence of filler shape on thermal behavior of isotactic polypropylene. Thermogravimetric analysis (TGA) tests showed that needle-shaped particles allowed obtaining an increase in the decomposition temperature.

Few investigations are also available in the scientific literature with concern to the environmental stability of polymer/calcium carbonate nanocomposites. Li et al.<sup>47</sup> studied natural photo-age-

ing of PP/calcium carbonate nanocomposites, finding that the filler significantly increased the natural photo-oxidation rate, however, the overall photodegradation mechanism did not change significantly and included several proposed aspects. Morreale et al.<sup>48</sup> investigated the accelerated weathering behavior of PP/CaCO<sub>3</sub> microcomposites and nanocomposites, finding increases in the photo-oxidation rates and to different photodegradation products distribution in comparison to neat PP or PP/clay nanocomposites, as well as a significant increase in crystallinity.

To our best knowledge, there are not many papers available about low density polyethylene (LDPE)-based CaCO<sub>3</sub> nanocomposites. In this work, therefore, we performed an investigation on the mechanical and rheological behavior of LDPE-based systems on using nanometric CaCO<sub>3</sub> with different particle size and crystal shape. The results were compared with those obtainable using an ordinary micrometric, natural calcium carbonate, which was taken as “reference” composite.

## EXPERIMENTAL

### Materials

The LDPE used in this work was a Riblene<sup>®</sup> FC30 produced by Polimeri Europa, Italy. Its main properties are: melt flow index = 0.27 g/10 min (at 190°C, 2.16 kg load), density = 0.922 g/cm<sup>3</sup>, melting temperature ≈113°C.

Four different calcium carbonate types were used in this work. They were kindly supplied by Solvay (Belgium) and the main properties (according to the Producer) are summarized in Table I.

### Processing

The composites were prepared by means of a Brabender (Germany) PLE330 batch mixer running at 60 rpm for a 4-min mixing time at T = 190°C. To evaluate the effect of the mixing time, some systems were prepared also at an increased mixing time, equal to 9 min. The effect of a relatively high filler content was investigated by preparing some systems also with a 10 wt % filler amount. All of the investigated systems are summarized in Table II.

The specimens for the following characterizations were obtained by compression molding using a Carver (USA) laboratory press set at T = 190°C, compression time ≈4 min, pressure ≈100 bar.

Mechanical characterization was carried out on at least seven specimens cut off compression molded sheets according to ASTM D882 (specimen size: 90 mm × 10 mm × ≈1 mm), with a crosshead speed of 5 mm/min, by means of an Instron

**Table II.** Composition and Processing Time of the Samples Tested in this Study

Mixing time (min)	Matrix/filler (wt %)	FC30	MVM	P3	S31	S312
4	100	*				
	99.5/0.5		*	*	*	*
	99/1		*	*	*	*
	98/2		*	*	*	*
9	90/10		*		*	
	100	*				
	99/1				*	*
	90/10				*	*

\*prepared blends.

(USA) 3365 apparatus. Reproducibility of the results was fairly satisfactory, as it never exceeded  $\pm 7\%$ .

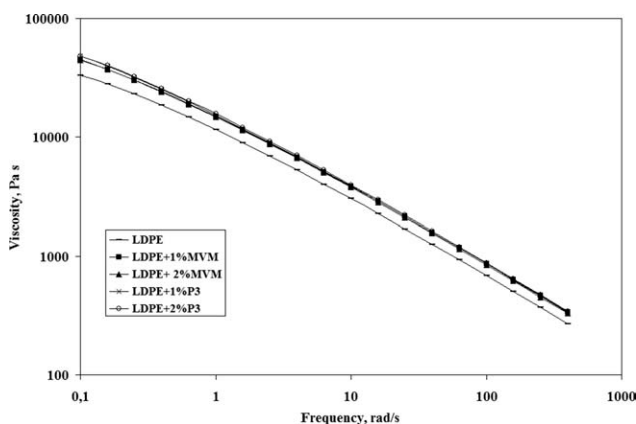
Rheological curves were obtained with the aid of a Rheometric Scientific (USA) RDA II plate-plate rheometer, at  $T = 190^\circ\text{C}$  and with a 5% applied strain in the range 0.1–500 rad/s. Morphological characterization on samples fractured in liquid nitrogen (fracture surface in the transverse direction) was performed using a Philips (Netherlands) XL30 ESEM, operating with a 30 kV acceleration voltage; samples were gold-sputtered to make them electrically conductive.

## RESULTS AND DISCUSSION

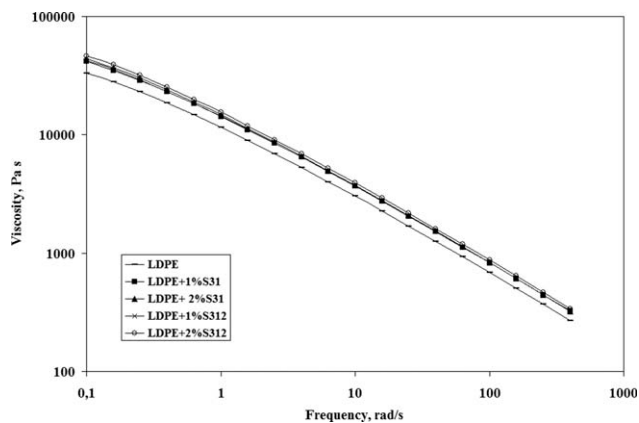
### Rheological Characterization

Figures 1 and 2 report the rheological curves of 4-min processed nanocomposites, respectively filled with MVM, P3, S31, and S312, together with the neat matrix for comparison.

The results clearly show that limited changes in the viscosity occur upon adding the fillers, regardless of their different characteristics, especially at the higher shear rates which are representative of the usual processing conditions. This can be partially explained considering the small amount used, and is in agreement with the results found from other researchers<sup>49,50</sup> on



**Figure 1.** Rheological curves of LDPE, LDPE-MVM, and LDPE-P3 systems.



**Figure 2.** Rheological curves of LDPE, LDPE-S31, and LDPE-S312 systems.

relatively similar systems based on polypropylene and nanosized  $\text{CaCO}_3$ .

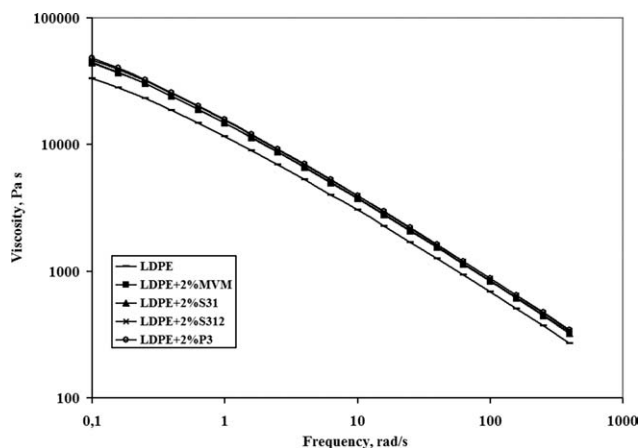
The effect of the different fillers used at the highest filler content is shown in Figure 3. It can be observed again that only small differences are present between the fillers used.

With concern to the effect of increasing the filler content on the rheological properties, Figure 4 reports the viscosity of the composites filled with P3 as a function of filler content.

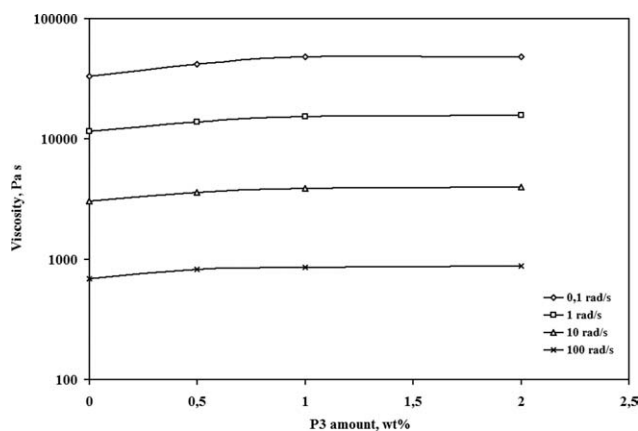
The results clearly indicate that no significant changes in the viscosity at specific frequency values occur upon increasing the filler content. This also applies to the other fillers here investigated, therefore, the curves are not reported for sake of conciseness.

Thus, to assess the effect of higher filler amounts on the processability, rheological analysis was performed on selected, representative samples filled with 10 wt % MVM or S31 and processed for 4 min. The corresponding rheological curves are reported in Figure 5.

It can be observed that in this case, where more significant amounts of filler are used, the increase in the viscosity going from the neat polymer to the composites is significant as well. This is in agreement with the results found by other



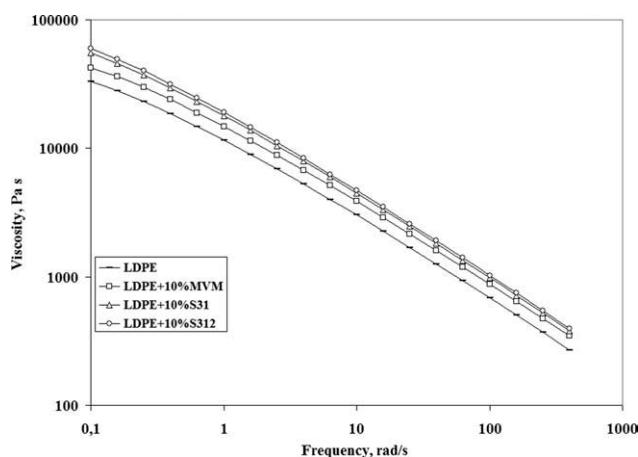
**Figure 3.** Comparison of the rheological curves of the microcomposites and nanocomposites filled with the highest (2 wt %) filler amount.



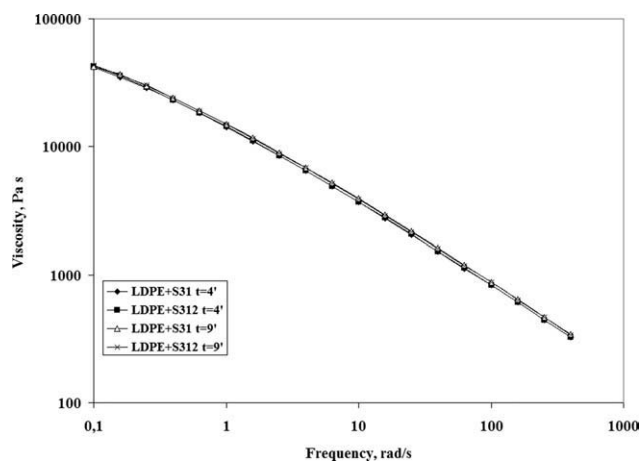
**Figure 4.** Viscosity of the LDPE-P3 systems at different frequencies, as a function of filler content.

researchers<sup>21,40,41</sup> on HDPE or PP-based systems filled with calcium carbonate fine particles and attributed to the formation of particle agglomerates and networks. Furthermore, rheological curve of S31 nanocomposite is higher than that of the MVM microcomposite in the whole frequency range. This result is a proof of a higher synergistic effect between the polymer matrix and the nanosized filler, rather than the microsized filler and is clearly due to the higher surface area of the nanofiller. This synergistic interaction is further increased on using the coated S312 nanometric calcium carbonate.

To assess the significance of mixing time, some systems were also prepared, with a mixing time of 9 min rather than 4. The overall results (not reported here in detail, for sake of conciseness) pointed out that significant differences between the neat polymer and the nanocomposites occurred only at low frequencies, whereas only small differences were found between the nanocomposites investigated. On the other hand, on increasing the filler content to 10 wt %, a significant increase of the viscosity upon adding the nanosized fillers was found, although the investigated nanofillers behaved in a very similar way.



**Figure 5.** Rheological curves of 10 wt % filled systems.

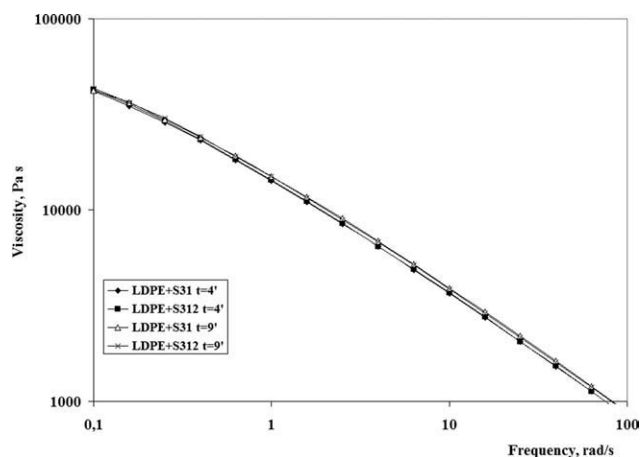


**Figure 6.** Rheological curves of nanocomposites processed for 4 or 9 min, respectively.

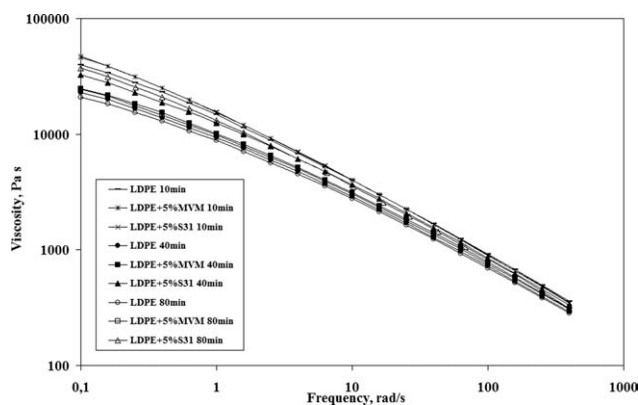
In particular, a direct comparison can be done with regard to the nanocomposites (1 wt %) processed for 4 and 9 min, respectively, as reported in Figure 6.

It can be observed that, on average, the samples processed for 9 min have rheological curves higher than those of the corresponding samples processed for 4 min, and this can be attributed to a superior dispersion of the nanofiller in the matrix due to the longer mixing time. This can be better seen in the magnification reported in Figure 7. However, it must be pointed out that the differences are quite small. A similar behavior was found also on 10 wt %-filled nanocomposites (not reported here for sake of brevity).

It is interesting to deepen the investigation on the effect of gradually increasing the mixing time on the rheological properties of the composites. In fact, as discussed above, an increase of the processing time should lead to a higher degree of filler dispersion in the matrix, and thus higher viscosity and overall better properties of the composites. However, longer mixing times lead necessarily to more intense degradation phenomena due to thermomechanical stresses. Therefore, some systems were



**Figure 7.** Detail of the rheological curves of nanocomposites processed for 4 or 9 min, respectively.

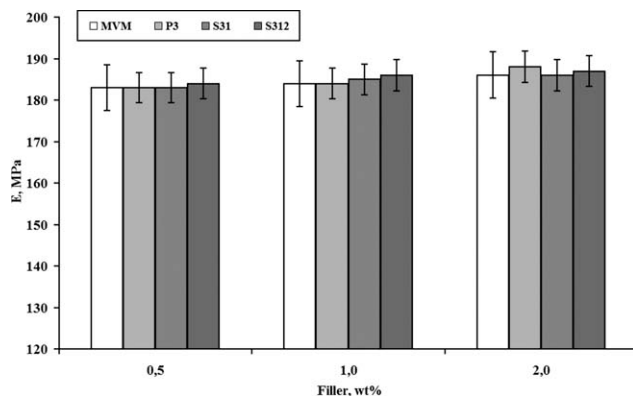


**Figure 8.** Rheological curves of neat LDPE, MVM microcomposites, and S31 nanocomposites at increasing processing times.

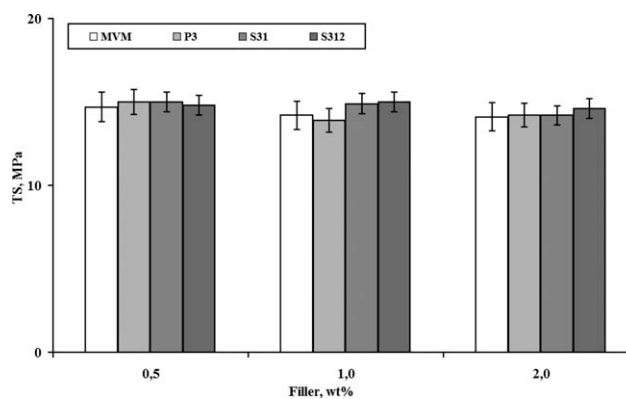
prepared with 5 wt % S31 and MVM, processed for 10, 40, and 80 min, respectively. The samples were subjected to rheological tests as above, and the obtained rheological curves are shown in Figure 8. These allow making some considerations.

As long as the processing time is just 10 min, the differences between the microcomposite and the nanocomposite are very small, with a moderate increase of the viscosity if compared with the neat LDPE, in agreement with the results discussed previously for 2 wt % filled systems.

The increase of the mixing time to 40 min leads to significant degradation phenomena, as highlighted by the decrease of the viscosity of the LDPE, as well as the composites. On the other hand, significant differences appear between the nanocomposite and the microcomposite, with the former showing considerably higher viscosity values than the latter. This is due to the higher degree of dispersion attained by the nanosized filler upon increasing the processing time. At 80-min processing time, the degradation phenomena further decrease the LDPE viscosity values, but the increased degree of filler dispersion allows the microcomposite to displaying almost the same rheological behavior as the 40-min processed one. This effect is even superior with regard to the nanosized filler, to such a degree that the 80-min processed nanocomposite has viscosity values which



**Figure 9.** Elastic modulus of the investigated systems as a function of filler content.



**Figure 10.** Tensile strength of the investigated systems as a function of filler content.

are practically equal, or slightly superior, to those of the 40-min processed one.

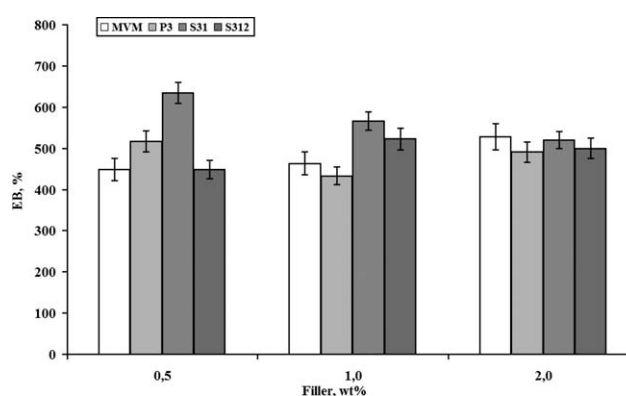
### Mechanical Characterization

The tensile properties (elastic modulus, tensile strength, elongation at break) are reported in Figures 9–11, respectively (the values for the neat LDPE are reported in Table III). The first observation to be done regard the elastic modulus. The variations of this property are not significant on adding 1 wt % filler, whereas the trend begins to appear significant at 2 wt % filler load, with an increase in the rigidity of all the investigated composites, in particular upon using the P3 nanofiller. This is likely to be due to its elongated shape.

With regard to the tensile strength, the general trend is that the property keeps practically unaltered, or slightly enhanced, upon adding the fillers, especially with regard to the S312 nanocomposites. As regards the elongation at break, only limited reductions are observed.

To assess the effect of higher filler contents, some 10 wt % filled systems were prepared and the results are reported in Table III.

It can be clearly observed that the use of the fillers increases the modulus, while tensile strength and elongation at break experience only small reductions. The result is particularly interesting



**Figure 11.** Elongation at break of the investigated systems as a function of filler content.



**Table III.** Mechanical Properties of 10 wt % Filled Nanocomposites and Microcomposites

	E (MPa)	TS (MPa)	EB (MPa)
LDPE	182 ± 4	14 ± 0.1	550 ± 50
LDPE+10%MVM	215 ± 9	12.5 ± 0.1	540 ± 8
LDPE+10%S31	220 ± 8	12.1 ± 0.1	500 ± 6
LDPE+10%S312	225 ± 4	10.1 ± 0.2	417 ± 7

with regard to the S31 nanofiller, which proves to assure the best mechanical properties at relatively high filler contents.

The effect of longer processing times on the mechanical properties was investigated by performing mechanical tests on 1 wt % and 10 wt % samples processed in the mixer for a 9-min time. The results are reported in Table IV.

As regards the elastic modulus, an increase between 15% and 20% was observed upon adding a 10 wt % filler amount, while no significant enhancement was observed with 1 wt % filler content. With reference to the tensile strength, a small increase was obtained upon using 1 wt % S312; however, upon increasing the filler content up to 10%, tensile strength decreased to values comparable to those of the unfilled system. A similar trend was observed also with concern to the elongation at break.

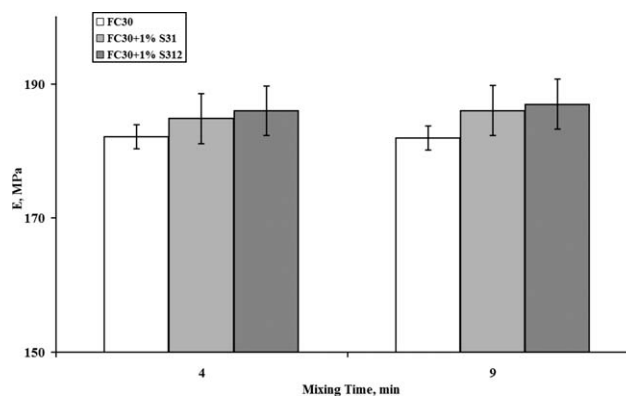
It is interesting to point out that such variations in the mechanical properties can be detected, when using microsized fillers, only with much higher amounts (~40 wt %).<sup>51</sup> This further proves the better interfacial interaction between matrix and filler assured by the nanosized particles here investigated.

It is interesting to compare directly the results obtained by increasing the mixing time from 4 to 9 min. Figures 12–14 show, respectively, the elastic modulus, tensile strength, and elongation at break of the samples after 4-min or 9-min processing.

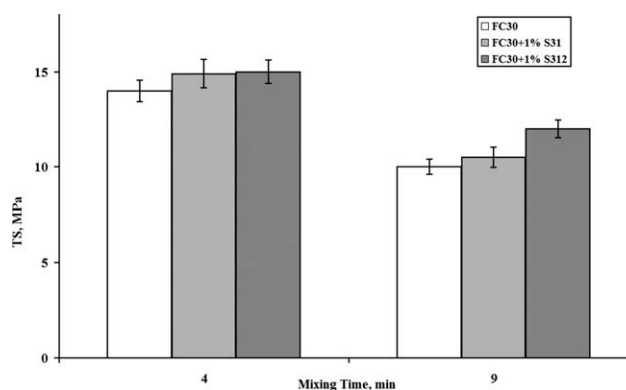
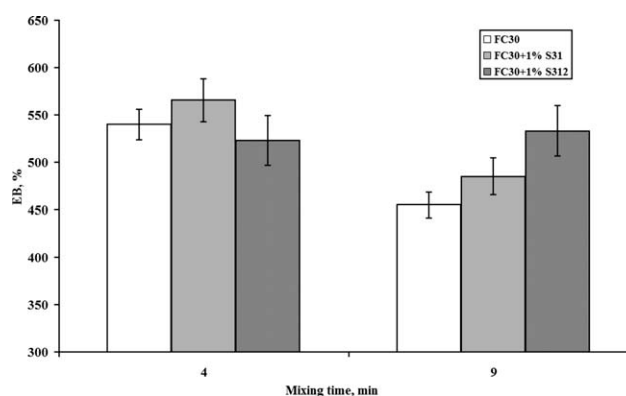
It can be observed from Figure 12 that practically no significant differences exist between the two batches. As regards the tensile strength, the values slightly decrease as the mixing time increases. This is probably due to degradation phenomena, as a significant decrease was already found in the neat LDPE, where tensile strength reductions upon increasing processing time can be explained by a reduction of the molecular weight (obviously, no effect related to the fillers can be present). Furthermore, the decrease is higher in the neat LDPE rather than in the nanocomposites and the average increase going from LDPE to the

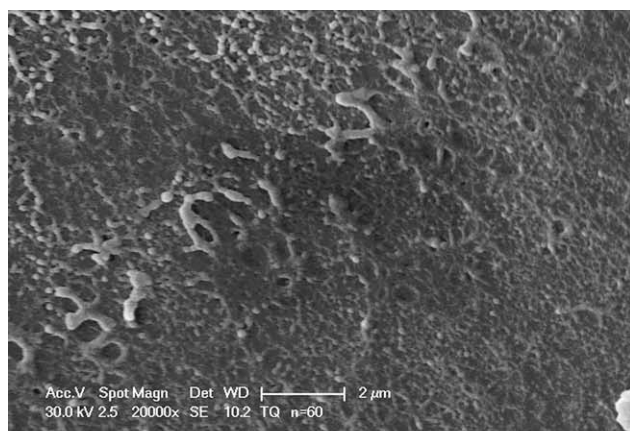
**Table IV.** Comparison of the Mechanical Properties of 1 wt % and 10 wt % Nanocomposites

	E (MPa)	TS (MPa)	EB (MPa)
LDPE	182 ± 2	10.1 ± 0.4	445 ± 12
LDPE+1%S31	186 ± 5	10.7 ± 0.4	475 ± 20
LDPE+10%S31	216 ± 6	9.7 ± 0.3	361 ± 19
LDPE+1%S312	187 ± 3	12 ± 0.3	533 ± 25
LDPE+10%S312	218 ± 4	10 ± 0.6	440 ± 18

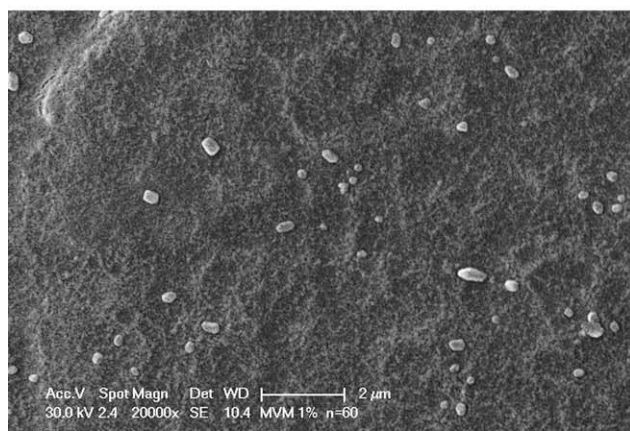
**Figure 12.** Elastic modulus comparison between 4-min and 9-min processed systems.

nanocomposites is higher in the 9-min samples. This means that degradation phenomena obviously occur also in the nanocomposites, but these are counterbalanced by a slightly more intimate mixing between matrix and nanofillers, which can improve the tensile strength; also the overall reduction in the elongation at break confirms the previous considerations. This is in complete agreement with the results from rheological characterization, where the curves of 9-min processed samples were

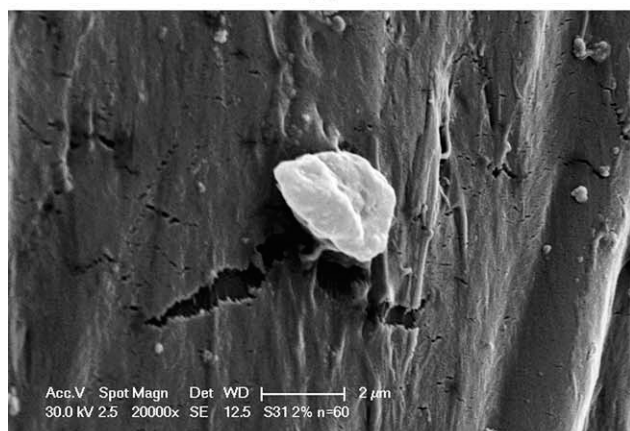
**Figure 13.** Tensile strength comparison between 4-min and 9-min processed systems.**Figure 14.** Elongation at break comparison between 4-min and 9-min processed systems.



(a)



(b)

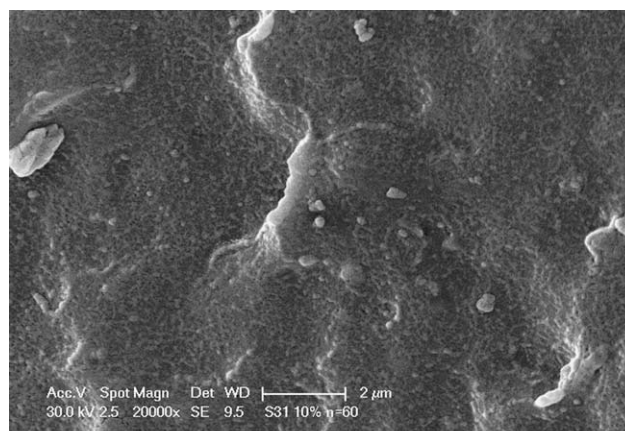


(c)

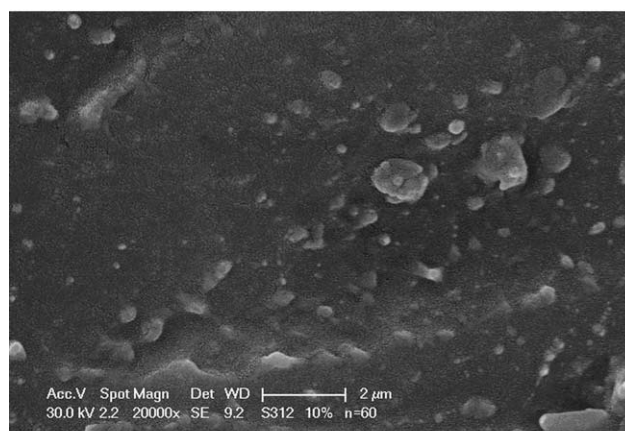
**Figure 15.** SEM images of neat LDPE (a), MVM 2 wt % microcomposite (b), S31 2 wt % nanocomposite (c).

slightly higher than those of 4-min processed ones. The latter result is, in fact, due to the simultaneous presence of two opposite factors: polymer degradation (which leads to a decrease in viscosity) and improved dispersion of the nanofiller (which leads to an increase in viscosity). However, with regard to the tensile strength of the 9-min samples, it appears that the influence of degradation was higher than that of dispersion.

A general comment which may be done with regard to all of the above shown results concerns the two nanosized fillers, uncoated and coated. The hydrophobic coating should, in general, lead to higher degree of interaction between the hydrophilic  $\text{CaCO}_3$ -based nanofiller and the hydrophobic polyolefin based matrix. This was observed in the mechanical properties, especially for those which significantly reflect the degree of mutual interaction between the filler and the matrix, such as the tensile strength: the S312-filled samples showed slightly better values than the S31-filled counterparts. On the other hand, this enhancement was, on average, lower than expectable on the basis of the previous considerations. This can be attributed mainly to aggregation phenomena which can involve the nanoparticles (even in the case they were coated) and, therefore, reduce the surface area of the nanoparticles available to mutual interaction with the polyolefin matrix. In fact, upon increasing the processing time, some aggregates were disrupted and a higher degree of dispersion was attained, as shown by the results discussed previously. This improved dispersion of the filler particles upon increasing the processing time was also proved by morphological characterization through SEM analysis.



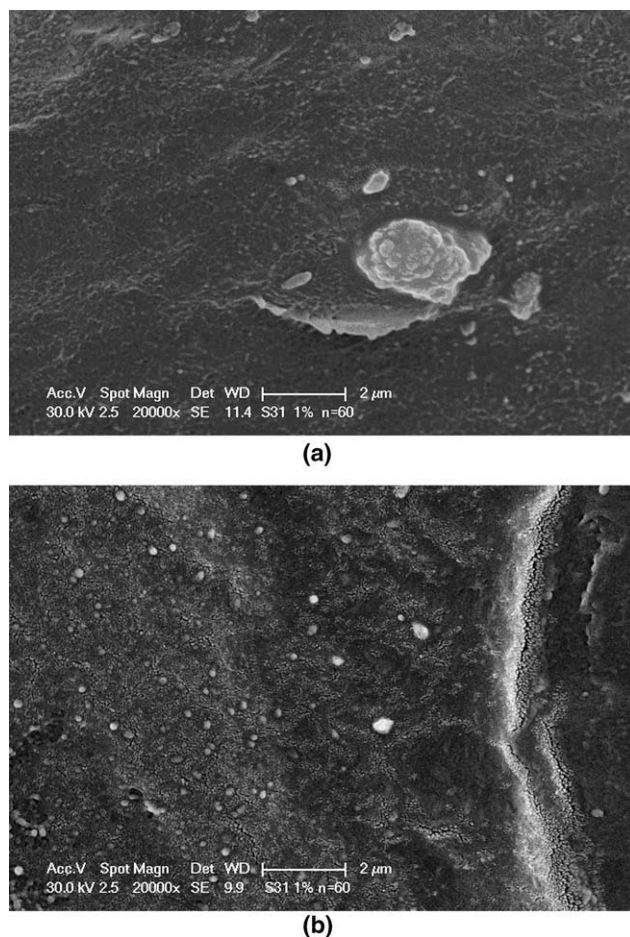
(a)



(b)

**Figure 16.** SEM images of S31 10 wt % (a) and S312 10 wt % (b) nanocomposites.





**Figure 17.** SEM images of S31 1 wt % nanocomposites processed for 4 (a) and 9 (b) min.

### Morphological Characterization

SEM micrographs of neat LDPE and composites filled with MVM and S31, respectively, are shown in Figure 15(a–c).

The first consideration to be pointed out is the tendency of the nanofiller to form random isolated agglomerates, as the one shown in Figure 15(c). This, in fact, can negatively influence the mechanical properties and thus can give an explanation of some values found for the tensile strength and the elongation at break, as discussed in the Mechanical Characterization section. In particular, the aggregates can significantly lower the tensile strength. Furthermore, the average tendency to form agglomerates is higher upon increasing the filler content, as shown in Figure 16(a, b), where micrographs of 10 wt % filled S31 and S312 nanocomposites are displayed. These pictures show an increased presence of aggregates, whereas these were barely isolated in the 2 wt % filled samples.

As regards the effect of longer mixing time, the micrographs in Figure 17(a, b), clearly show that increasing the processing time of a S31 nanocomposite from 4 min (a) to 9 min (b) led to a significantly better dispersion of the filler in the matrix, with a reduction of the number and size of agglomerates. This can, therefore, justify the improvements in the mechanical properties discussed in the previous section.

### CONCLUSIONS

In this work, the rheological and mechanical behavior of different LDPE-calcium carbonate nanocomposites has been investigated and compared to a reference calcium carbonate microcomposite.

Rheological analysis showed that no significant variations occur upon using filler amounts up to 2 wt %, while it is required to add 10 wt % to observe significant increases of the viscosity, especially for the nanocomposites, in comparison to the microcomposite. Rheological tests at high processing times showed that the increase of processing time (at least 40 min) can improve the dispersion and the synergistic effects between the polymer matrix and the nanofiller, to an extent which can overcome the polymer chains degradation.

Mechanical analysis highlighted only small improvements of the elastic modulus and the tensile strength upon increasing the filler content, with some enhancement of the elastic modulus at 2 wt % filler loading, especially in the case of the elongated-shape nanofiller. Use of 10 wt % filler loading significantly increased the elastic modulus, with limited decreases of tensile strength and elongation at break. The increase of the processing time from 4 to 9 min allowed obtaining moderate improvements of the filler dispersion in the matrix, which was observed also by SEM analysis. The latter factor provided also a further understanding of the causes for the small variations observed between the neat polymer and the nanocomposites.

### ACKNOWLEDGMENT

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