Sepiolite organic modifiers effect on pet/sepiolite nanocomposites degradation

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A B S T R A C T

In this paper the effect of different organosepiolites on PET matrix was evaluated through the analyses of Melt Flow Index (MFI) and Intrinsic Viscosity (IV) of the nanocomposites. PET/sepiolite nanocomposites were produced through a two-stage process. The masterbatch production was done in a melt compounding extruder, and then these were taken to an injection machine, where different specimens were obtained for characterization purposes. Two types of organomodifiers were tested, silanes in one hand and a quaternary ammonium salt on the other. Thermal analyses were done to determine thermal stability of the organomodifiers. Then, different experiments were carried out increasing the concentration of coupling agents to analyse its effect on PET matrix degradation. As results indicate a high degree of degradation of the nanocomposites matrix, pyromellitic dianhydride (PMDA) was added as chain extender to react with PET molecular chains, with the aim of increasing its molecular weight (Mw).

1. Introduction

Reinforcement of polymers through clay minerals nanocomposites is being study for years. The most widely clays used in nanocomposites are smectites, specially montmorillonite (MMT). However, sepiolite has been getting more and more attention during the past years.

Sepiolite is a hydrated magnesium silicate mineral, with chemical formula $Mg_8Si_{12}O_{30}(OH)_4(OH_2)4 \cdot xH_2O$ (x = 6,8) [1,2] which contains zeolitic water (H_2O) in intracrystalline tunnels and crystal water in its structure (OH_2). Sepiolite has a microfibrous morphology [3–7] with high aspect ratio and two dimensions in the nanometer scale [8]. What makes this clay very attractive to industry is its surface properties [9]; due to its structure, sepiolite has silanol groups (Si–OH) on its external surface, which allow for the preparation of organic-inorganic materials [8,10]. Clays are hydrophilic materials and not very compatible with polymers. Therefore, it is necessary to modify clay surface to convert it into organophilic material, enhancing its compatibility with polymers. So, the modifiers, mainly quaternary ammonium salts and aminosilanes have been added to the nanosepiolite to help in the interaction with PET, allowing a good dispersion of the clay in the matrix and, at the same time, decreasing the amount of adsorbed water.

PET is one of the most widely used polymers due to its low cost and high performance. It has a variety of applications that range from engineering plastics and textile fibres to films and packaging for food and beverage industry. However, the use of PET in industry has some shortcomings, such as low distortion temperature, low rate of crystallization and relatively low barrier to gases for food packaging industry. These, together with the increase use of recycled PET, have made the incorporation of different nanofillers into PET matrix a huge field of interest in the last years [11–17].

However, producing PET/sepiolite nanocomposites faces two handicaps: in one hand PET is a very sensitive polymer to water with very high processing temperatures (260–280 °C) and, on the other hand, sepiolite is a clay that incorporates water in its structure, besides it is a hydrophilic material. During the processing of PET (extrusion or injection), the presence of water produces hydrolysis of PET chains and, above that, these processes themselves could cause thermal and mechanical decomposition of organic molecules modifying the sepiolite clay, such as alkyl ammonium ions, or silanes; which could cause further degradation of the PET matrix. The resultant products could also lead to side reactions between the decomposition products and the polymer matrix, affecting the degradation process [10].

So, it is very important to dry out all the nanocomposite components

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Nomenclature		mm	mili meter
		MMT	Montmorillonite
3MTH	Alkyl trimethyl ammonium chloride	Mw	Molecular weight
CEC	Cation Exchange Capacity	nS	Nano Sepiolite
EFSA	European Food Safety Approval	O-Sep	Organosepiolite
EVOH	Ethylene Vinyl Alcohol Copolymer	PC	Permeability Coefficient
GLYMO	3-glicydilpropyl trimetoxysilane	PET	Poly(ethylene terephthalate)
HS	Aminosilane	PMDA	Pyromellitic dianhydride
IM	Internal Mixer	RH	Relative Humidity
kN	Kilo newtons	Rpm	Revolutions per minute
L/D	Length/Diameter relation	SEM	Scanning Electron Microscopy
LSB	La Seda Barcelona	TEM	Transmission Electron Microscopy
MEMO	γ-methacryloxypropyltrimethoxysilane	TGA	Thermogravimetric Analysis
meq	mili equivalents	TG	Thermogram
min	minute	VTMO	Vinyl trimetoxysilane

before introducing them in the extruder or injection machine. At the same time, it is important to control the processing conditions, such as extruder rpm, to avoid PET chains or sepiolite fibres breaking, and to preserve as much as possible the organic modifiers on the clay.

The objective of this work is to study and develop the best combination of materials that allow the development of a PET nanocomposite to be used in an industrial extruder, for food packaging products. For them, the effect of different types of modifying agents on the final properties of PET nanocomposites will be studied, with special emphasis on minimizing the degradation of the PET matrix.

2. Materials

Virgin PET was supply by Novapet S.A. (Zaragoza, Spain) and had an intrinsic viscosity (IV) of 0.78 dL/g. The sepiolite clay is a commercial Pangel 9 from Tolsa S.A. (Madrid, Spain). It has a cation-exchange capacity (CEC) of 30 meq/100 g. Chemical modification of the sepiolite, done at Tolsa S.A. facilities, was made using different silanes (3-methacryloxypropyltrimethoxysilane, MEMO; 3-glicydilpropyl trimetoxysilane, GLYMO); and a quaternary ammonium salt (alkyl trimethyl ammonium chloride, 3MTH). It has been also used pyromellitic dianhydride (PMDA) as extender of PET molecular chains.

3. Experimental part

Nanocomposites were produced through a two-stage process. The first one being a masterbatch production through direct melt-compounding, introducing the organoclay powder into a laboratory corotating twin screw extruder (MICRO 27 GL-36D, LEISTRITZ) with a L/D relation of 36.

These masters, containing 10% of each organosepiolite, are then taken to an injection moulding machine (KRAUSS MAFFEI KM 200–700/90CZ), where plaques or dumbbell-shaped specimens with 2% nanosepiolite (nS) were obtained. The percentages used to refer general samples are the initial theoretical ones.

PET is a highly hydrophilic material, so it was necessary to dry the pellets out before introducing them into the extruder. The PET used in this study was dried out in a dehumidifier at 120 °C, for 5 h. However, those conditions aren't adequate for the nanocomposites, which have been dried at 80 °C for 7 h (CRAMER-TROCKNER, PK 100/300F) due to the sepiolite nucleation effect onto PET matrix, that affects its crystallization [18,19]. The drying step of the PET nanocomposites is key for achieving good reproducibility in the processing process, as well as for minimizing PET degradation.

3.1. Characterization techniques

3.1.1. Thermal analysis (TGA)

Thermogravimetric Analysis (TGA) was used to determine percentage of modifying agent within the nanosepiolite and their decomposition temperatures. The analyses were performed in a Mettler Toledo 851e equipment, under a nitrogen atmosphere, in a temperature range of 25 °C–850 °C using a heating speed of 10 °C/min. At the same time, it was also calculated by TGA the amount of sepiolite in the nanocomposites, using two steps:

1st step: from 50 °C to 600 °C at 20 °C/min under nitrogen atmosphere.
2nd step: from 600 °C to 900 °C at 20 °C/min under air atmosphere.

3.1.2. Melt fluid index

Melt Fluid Index (MFI) is the amount of plastic material, in grams, that comes out from a standardized die for 10 min, under a fixed load and constant temperature. The equipment used has been a Tinius Olsen, MP600 Extrusion Plastometer (LINPAC PACKAGING S.A.U.). In the case of PET and its nanocomposites, both in pellets and in sheet, load was 2.16 Kg and the temperature was kept at 270 °C [20].

3.1.3. Intrinsic viscosity

Intrinsic Viscosity (IV) analysis were done on extruded pellets. The equipment used was an Ubbelohde Viscosimeter, following the standard ASTM D4603 [21]. A main solution is prepared, and five different dilutions are taken: 2×10^{-3} g/ml, 4×10^{-3} g/ml, 6×10^{-3} g/ml, 8×10^{-3} g/ml and 10×10^{-3} g/ml. The solvent used for PET is phenol/1,1,2,2-tetrachloroethane at 60/40% in weight respectively. The materials must be dried before producing the corresponding solutions. The viscosimeter is situated inside a thermic bath at 30 °C, and five measures for each aliquot have been analysed.

3.1.4. Capilar rheometry

In order to determine shear speed effect on the PET nanocomposites IV, capilar rheometry analyses were performed in a CEAST equipment (twin bore 5000) with a maximum force of 50 kN, a shear speed range of 0.3–30000 s^{-1} (capillaries with L/D of 5, 10 and 30) and maximum temperature of 450 °C.

3.1.5. Optical microscopy

Samples for optical microscopy (OM) were prepared in a mounting press and polished prior to their observation under an OLYMPUS BX 60 M microscope, using a specific software (OMNIMET) for the pictures acquisition.

3.1.6. Young Modulus

These tests were performed in a universal MTS 831-59 machine under the following standard UNE-EN ISO 527-2 [22]. The specimens used were dumbbell like (type 5), and five samples were analysed in each direction (longitudinal and transversal) at 100 mm/min.

3.1.7. Heat deflection temperature (HDT)

The heat deflection temperature was measured using a CEAST HDT3 VICAT P/N 6911/000 under the standard UNE-EN 75-1. The dimensions of the specimens were 80 x 10 × 4 mm and were submitted to 1.8 MPa load with a heating temperature of 120 °C/h.

4. Results and discussion

When processing PET in an extruder or injection machine it is very important to have good quality raw materials. One of the main things that define a good quality material, in this case, is its melt viscosity. However, during PET extrusion and injection, a reduction of its viscosity takes place, due to mechanical and thermal degradation [23]. At the same time, PET is very sensitive to water. This water can hydrolyse PET at high temperatures, breaking down its molecular chains and decreasing its viscosity. Therefore, it is of great importance to introduce PET raw material completely dry in an extruder. When producing PET nanocomposites, the surface of the clay needs to be modified in order to have a more hydrophobic structure and more compatibility with the polymer chains. However, introducing organosepiolite into the PET matrix generates further degradation of the polymer during processing [24,25]. The objective of this work is to find the best clay organo-modifier to reduce this matrix degradation.

4.1. Organomodifier effect in the nanocomposite viscosity

In order to examine the effect of the different surfactants used into the PET nanocomposites, melt fluid index (MFI) and intrinsic viscosity (IV) were measured.

The materials used in this study are two silanes and an ammonium salt (Table 1). Silanes are grafted to the hydroxyl surface of the sepiolite [26] while the ammonium salt is physisorbed onto those hydroxyl groups.

Table 2 shows MFI and IV values of the extruded nanocomposites. IV analysis were done for the silane containing sample with lower MFI and for the ammonium one, apart from the PET sample. It can be observed that extrusion process does not affect the PET matrix. However, it is greatly affected by the introduction of organosepiolite into the matrix, increasing its MFI no matter the modifier chosen.

In a first analysis, it was observed a huge decrease in the IV of all the samples, higher for those nanocomposites modified with silanes, compared to those modified with a quaternary ammonium salt. This could be due to a lower percentage of silane modifiers, which make those samples less hydrophobic (more hydrophilic), to a thermal degradation of the silane composites and/or to the hydrolysis of the organosilanes by adsorbed water on the external clay surfaces [27].

At this point, it is clear that the matrix viscosity is highly influenced by the organic compound used to modify the sepiolite.

Table 2
MFI and IV results for the organomodified nanocomposites (extruded masterbatch).

Samples	MFI (g/10 min) 270 °C, 2.16 Kg	IV (dl/g)
Pure PET	30.6 ± 0.4	0.778 ± 0.004
Extruded PET	31.0 ± 2.0	
LPC1	177 ± 7	0.385 ± 0.005
LPC2	214 ± 11	
LPC3	141 ± 15	0.486 ± 0.006

4.2. Thermogravimetric analysis

In order to investigate the thermal stability of the PET–organosepiolite nanocomposites, thermogravimetric analysis (TGA) was performed. PET processing temperature is high (around 270 °C), and at that temperature the organic modifiers can be degraded. Thermal stability has been studied at the same time that the amount of modifying agents incorporated with the sepiolite.

Fig. 1 shows pristine sepiolite thermogram (TG), in which it can be seen four transitions:

- At low temperatures range (from room temperature to 125 °C) a huge endothermic pick is observed, which is justified due to loss of superficially adsorbed water, together with zeolitic water that is less strongly bonded [28,29]. Weight loss in this range is nearly 5%.
- As the temperature increases, a less severe weight loss is observed. In the range from 125 °C to 350 °C a weight loss of 3% (3.08%), corresponding to residual zeolitic water [30] and a first part of structural water, is obtained.
- Between 350 °C to 650 °C, the second half of structural water gives another 3% (3.25%) weight loss. This agrees with what has already been indicated by Jones and Galan [31], who had already mentioned that the loss of structural water in the sepiolite had place in two stages; each indicated by different endothermic peaks (different reactions) and similar weight losses. This broad temperature ranges involving water reflects the numerous environments of this compound in the sepiolite structure.
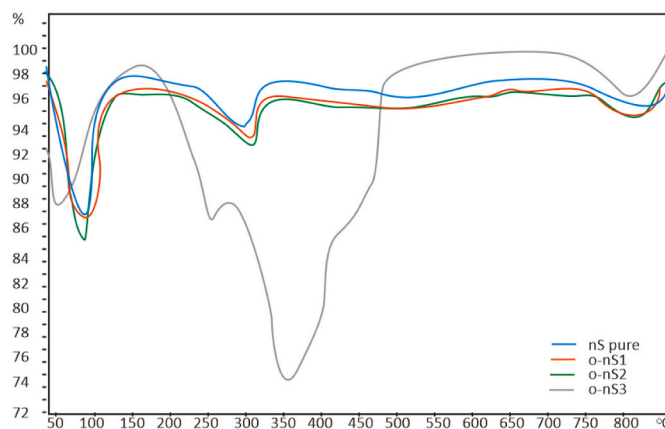

Fig. 1. Pure sepiolite thermogram, TG.

Table 1
Materials used to produce the PET/O-Sep nanocomposites.

Materials	Compounds	Acronyms	Nanocomposites (% modifier)	Sepiolite
Polymer	Polyethylene terephthalate	PET		
Clay	Pristine sepiolite (Pangel S-9)	nS		
Clay Modifiers	3-methacryloxypropyltrimethoxysilane (CAS 2530-85-2)	MEMO	PET + 2% nS (2%) - LPC1	o-nS1
	3-glycidilpropyl trimethoxysilane (CAS 2530-83-8)	GLYMO	PET + 2% nS (2%) -LPC2	o-nS2
	Alkyl trimethyl ammonium chloride (CAS 68002-62-0)	3MTH	PET + 2% nS (3%) - LPC3	o-nS3

- Then, from 650 °C to 850 °C, sepiolite dehydroxylation takes place with a weight loss of 2.1% and becomes amorph [32,33].

The information obtained from the pristine sepiolite thermal analysis was used to investigate the thermal stability of the organomodified sepiolite. Pink and green lines in the same Fig. 1 show the TG of a MEMO modified sepiolite (o-nS1) and a GLYMO modified one (o-nS2). It can be observed that these TG are quite like that of pristine sepiolite. Analysing different temperature ranges it is obtained the total amount of modifier grafted to the sepiolite as well as its thermal stability. If there was non-grafted silane this should be noted at around 200 °C, as it has been shown in previous works [34]. However, this effect cannot be seen in neither of the TGs, not in o-nS1 nor o-nS2, the small amount of non-grafted silanes in these samples is shown in Table 3.

The TG obtained for a sepiolite modified with an ammonium quaternary salt (o-nS3), is quite different from that of the pristine clay as seen in Fig. 1. In this TG (grey line) four temperature ranges can be distinguished again. The first one (from room temperature to 150 °C) corresponds, as in the case of pristine sepiolite, to adsorbed water and some zeolitic water as well. Observing this first step, sepiolite is more hydrophobic when modified with both coupling agents (silanes and quaternary ammonium salt) than its pristine form, being the least hydrophilic ones those modified with ammonium salt (3.47%) and MEMO (3.49%). The second part (from 150 °C to 280 °C) includes and endothermic peak at 250 °C which corresponds to the loss of structural water in the sepiolite and, perhaps, some loose modifier. The beginning of thermal dissociation of the quaternary ammonium salt matches with PET melt processing temperature [35]. A third range could be between 280 °C to approximately 430 °C, with another peak at 350 °C associated to the loss of ammonium salt adhered to the sepiolite surface. In the next range, form 430 °C–650 °C, correspond to the decomposition of the surfactant and loss of the remaining structural water [36,37]. And last, the dehydroxylation of sepiolite takes place (as mention before).

The amount of modifier grafted to these organoclays (Table 3) vary as a function of the compound used. On the other hand, when using sepiolite o-nS3, it can be seen an amount of nearly 13%, 4% of that (belonging to sepiolite and modifying agent) is decomposed under 270 °C, which is PET processing temperature.

Thermal stability of the modified sepiolites has been investigated with the TG curves. Fig. 2 shows that the nanocomposite modified with silane have less thermal stability than that modified with ammonium salt. On the other hand, it is also observed a decrease in thermal stability in extruded PET compared to pure PET (Fig. 2b).

4.3. Capilar reometry

Nanocomposites degradation has been also seen in the capillary rheometry results. For these analyses, four samples have been chosen: Virgin PET, extruded PET, and two nanocomposites modified with a silane (GLYMO, LPC2) and an ammonium salt (3MTH, LPC3).

Results obtained for the nanocomposite samples show a decrease in viscosity with increasing shear rate up to 200 s^{-1}, where there is a change in that tendency (Fig. 3). This variation is lower for both PET samples (extruded and virgin PET) than for the nanocomposites. Being the most abrupt of all variations seen in the sample modified with the

ammonium salt. This variation has been attributed to a crystallinity change in the samples. In Fig. 4 it can be seen how a PET sample goes from amorph (transparent) to crystalline (opaque) as a function of the shear rate. It is known that when degradation occurs in a polymer, a decrease in its molecular weight (MW) happens which is associated to an increase in crystallization speed. Silanization of clays has also been known to have an important impact on increasing crystallinity formation speed during injection moulding [38].

4.4. Mechanical properties

Table 4 shows an increase in Young modulus of 11–12% in those nanocomposites modified with a silane agent compared to that of pure PET. On the other hand, when the modifier is an ammonium salt that increase is 16%. It can be also observed a small increment of 4% in HDT for these nanocomposites, whilst when silane agents are used the HDT doesn't improve over that of pure PET.

During injection of the nanocomposites, it has been observed some stability problems due to the degradation observed in the masters. This reflects that these materials are very sensitive to a second processing, and that it is necessary to control humidity and process conditions as much as possible to avoid an increase in matrix degradation.

Although there is an improvement in mechanical properties, it is necessary to say that those results are influenced by a matrix which has suffered some degradation. Thus, it would be expected to achieve higher modulus values if it wasn't for that intrinsic viscosity decrease seen in the nanocomposites [39].

In order to produce more hydrophobic samples, it was decided to produce a batch of nanocomposites increasing the amount of organomodifiers used. The objective here was to occupy as much hydroxyl groups as possible since, usually, the higher the amount of free hydroxyl groups the higher the matrix degradation during processing [40]. This has been seen in these samples: LPC4 and LPC5 show better viscosity and fluidity values than that obtained with just 2% of modifier MEMO, and 3% of 3MTH respectively. However, the improvement in the samples containing 100% 3MTH is not much, observing that when adding a higher quantity of 3MTH to the nanocomposites, viscosity values do not change accordingly to the amount of organomodifier added. This could be due to secondary reactions produced by the organomodifiers excess, which could catalyse PET hydrolysis. At the same time, an excess of the surfactant could act as plasticizer in the matrix, decreasing its IV and increasing its MFI (Table 5).

4.5. Molecular weight and chain extenders

Due to thermal and hydrolytic degradation of PET nanocomposites, PET molecular chains are broken, therefore reducing its molecular weight (Mw) which is reflected in its IV [41]. The aim of this study is to use a chain extender to counteract PET matrix degradation. Pyromellitic dianhydride (PMDA) is the compound used, since it is already been proven effective in increasing PET IV [42–44]. PMDA is thermally stable and doesn't produce side reactions when reacting with PET. This additive is expected to react with the PET terminal hydroxyl groups, extending its molecular chains. It is added, together with the nanocomposite master and the virgin PET, in a twin-screw extruder (MICRO 27 GL-36D from LEISTRITZ), which has a maximum flow of 30 kg/h and L/D of 36.

The concentration of the chain extender added is key for achieving good results, since an excess of this compound could cause crosslinking within PET polymeric chains, and too little quantity wouldn't produce the reaction require for increasing PET molecular weight. Table 6 shows concentrations of chain extender used which are based in previous studies [40–42,45,46]. It is also very important the residence time of the additive in the process, since it needs an activation time and a certain period in contact with the PET. In order to analyse the chain extender effect on PET nanocomposites, it will be used the same amount of
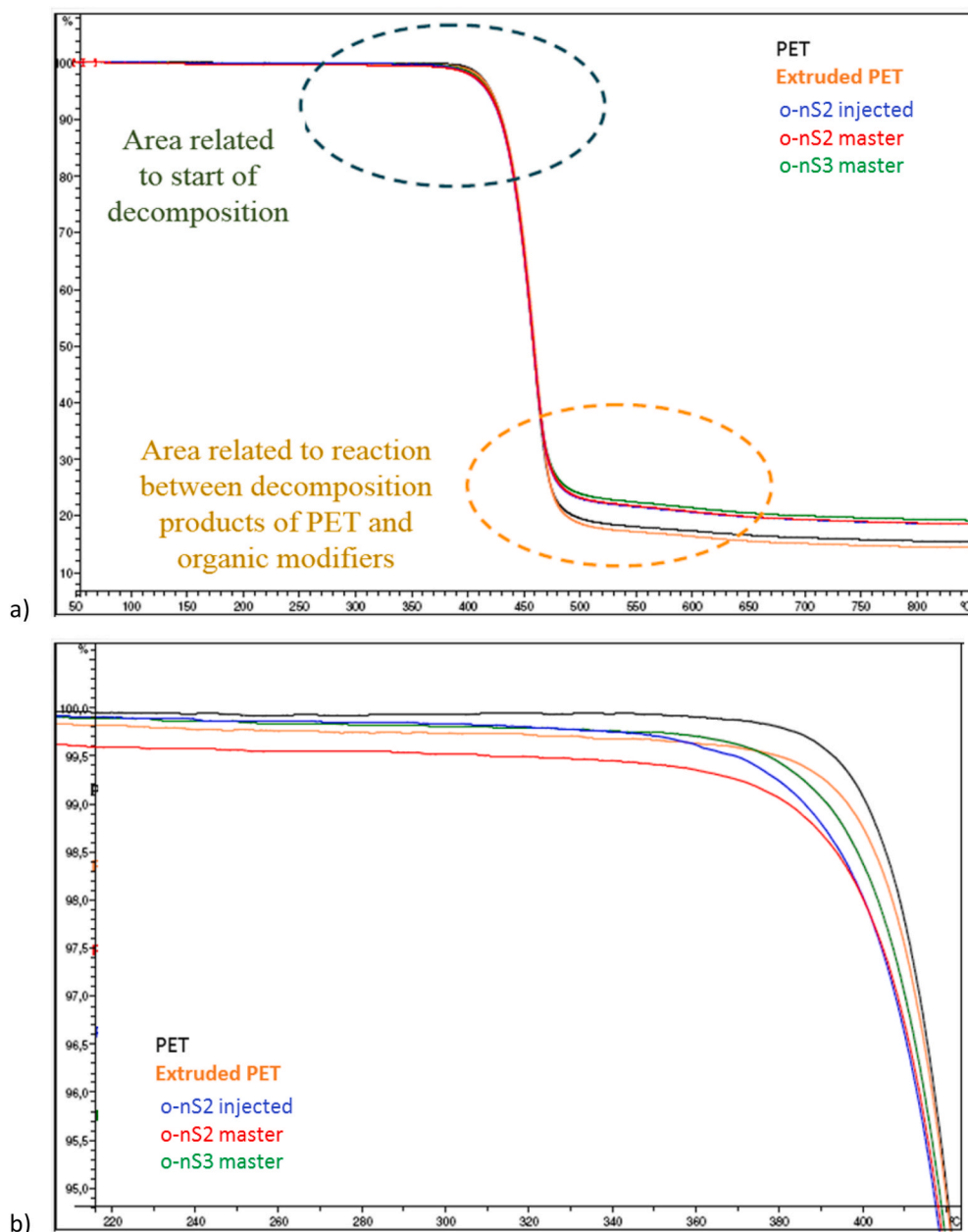
Table 3
Total and grafted amount of modifying agent between 125 and 650 °C.

Organoclay	Zeolitic water 50–150 °C (weight %)	Volatilized mass 150–650 °C (weight %)	Grafted Modifying agent (weight %)
Pure Sepiolite	4.96	6.33	–
o-nS1	3.49	7.53	1.01
o-nS2	4.25	7.78	1.17
o-nS3	3.47	19.57	13.24

Fig. 2. a) TG area showing the thermal stability of PET and its nanocomposites; b) curve amplification.

sepiolite than before (2% nS), varying the amount of PMDA. LPC1 nanocomposite is used as control sample.

Dispersion of the nanosepiolite is worse in those samples containing 0.15 and 0.45% of PMDA than in the control sample, and a little better when adding 0.30% PMDA (Fig. 5).

In order to analyse PMDA effect on the PET matrix, it was measured the intrinsic viscosity of the master batches (after the extrusion process, before injection). In Table 7 it can be seen the results obtained together with the inorganic content of the samples, determined by TGA.

IV of these samples are better but quite like those previously obtained. Sample with 0.15% PMDA (LPC7) presents 30% IV increase over sample LPC1. However, as seen in Fig. 5, the dispersion is much worse. The more chain extender added to the nanocomposite, the lower the IV (Table 7). It was expected a higher viscosity increase in the nanocomposites when using PMDA. One of the reasons for these results could be a short residence time of the additive in the extruder (45 s). It is also necessary to note that the system shown here is more complex than a pure PET one; in this case, PMDA can not only react with the PET

hydroxyl groups but also with the sepiolite ones. This reaction could cause sepiolite agglomeration, as it has been seen in Fig. 5, instead of PET chains extension. In Fig. 6 it is shown the actuation mechanism of PMDA with the end hydroxyl groups in PET, proposed by Khemami [47], which are the ones that should be reacting to induce chain extension.

Next, some experiments have been made in an internal mixer (Haake Rheomix 3000P) to determine if processing time is the key point in this case. The trials consist of processing three different samples which have been produced in the laboratory extruder:

- PET/ns_MEMO nanocomposite (LPC1) is taken for comparison purposes,
- LPC8, where the PDMA is added during the extrusion process to obtain the masterbatch,
- LPC10 is the result of mixing sample LPC1 with PDMA in the IM for 3 min.

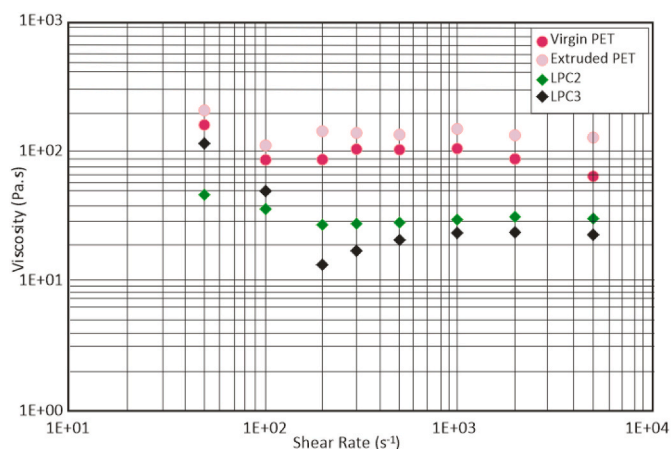Torque values give an idea of the existence of chain extension

Fig. 3. Capillary rheometry of samples PET_ext, o-nS2, o-nS3, PET_virgin

reactions, since when this happens torque increases with time. In the work done by Incarnato et al. [48], torque reaches a maximum of 13–14 Nm Looking at approximately 200 s. This is the time needed for the PMDA to react with recycled PET. In Fig. 7 it can be seen a pick at approximately 3 min, which is a similar activation time to that obtained in the mentioned work. The low activation pick could mean that part of the PMDA is reacting with sepiolite hydroxyl groups and not with the PET. However, it is seen that torque values for both samples with PMDA (added during extrusion or in the mixing chamber) is three times that of PET nanocomposite (LPC1). This means that the PMDA has promoted PET chain extension to a certain degree, besides the agglomeration of sepiolite particles. Intrinsic viscosity of these samples has been analysed, and as it can be seen in Table 8, the addition of the additive in the mixing chamber produces and increase in IV of 59% versus the first sample containing sepiolite modified with MEMO.

5. Conclusions

In this paper it is analysed the effect of the organomodifier into the PET matrix, observing an increase in PET fluidity and decrease in viscosity. Since processing temperature of PET is high, some thermogravimetric analyses were done to observe the stability of the coupling agents at high temperatures. It has been shown that thermal dissociation of 3MTH starts at PET processing temperature, however, in those sepiolites modified with silanes there is no appreciable degradation at that temperature.

Due to this degradation, the nanocomposites properties are not as good as expected, with an improvement in Young Modulus of approximately 10–14% when 2% of silanes are used and 16% when an ammonium salt, at 3%, was added as sepiolite surface. There is nearly no variation in HDT in those nanocomposites, finding an increase of 2 °C when the ammonium salt is used.

The increase in the amount of organomodifier used with the sepiolite produce an improvement in intrinsic viscosity, verifying the importance

Table 4
Nanocomposites mechanical properties (Young Modulus) and heat distortion temperature (HDT).

Sample	Nanocomposite	TGA (% nS)	Young Modulus (MPa)	HDT (°C)
Extruded PET	–	0.19	2520 ± 17	60.6 ± 0.14
Injected PET	–	0.22	2490 ± 30	61.5 ± 0.24
	LPC1	1.71	2800 ± 87	61.0 ± 0.26
	LPC2	1.82	2800 ± 18	60.4 ± 0.24
	LPC3	1.60	2920 ± 27	62.4 ± 0.33

Table 5
MFI and IV results for the organomodified nanocomposites (extruded masterbatch).

Nanocomposite		MFI (g/10 min) 270 °C 2,16 Kg	IV (dl/g)
PET + 2% SEP-LPC4 (MEMO-25)	LPC4	104.9 ± 1.6	0.584 ± 0.028
PET + 2% nS-LPC5 (3MTH-50%)	LPC5	115.6 ± 4.5	0.491 ± 0.006
PET + 2% nS-LPC7 (3MTH-100%)	LPC6	141.1 ± 1.4	0.523 ± 0.006

Table 6
Materials used for the chain extender process and its concentrations.

Samples	Nanocomposite
PET +2% nS(MEMO)	LPC1
PET + 2% nS(MEMO2) + 0.15% PMDA	LPC7
PET + 2% nS(MEMO2) + 0.30% PMDA	LPC8
PET + 2% nS(MEMO2) + 0.45% PMDA	LPC9

Fig. 4. Pictures of extruded material through capillary rehometry, obtained as a function of shear rate.

PET + 2 % nS(MEMO)
LPC1

PET + 2% NS(MEMO2) + 0.15% PMDA
LPC7

PET + 2% NS(MEMO2) + 0.30 % PMDA
LPC8

PET + 2% NS(MEMO2) + 0.45 % PMDA
LPC9

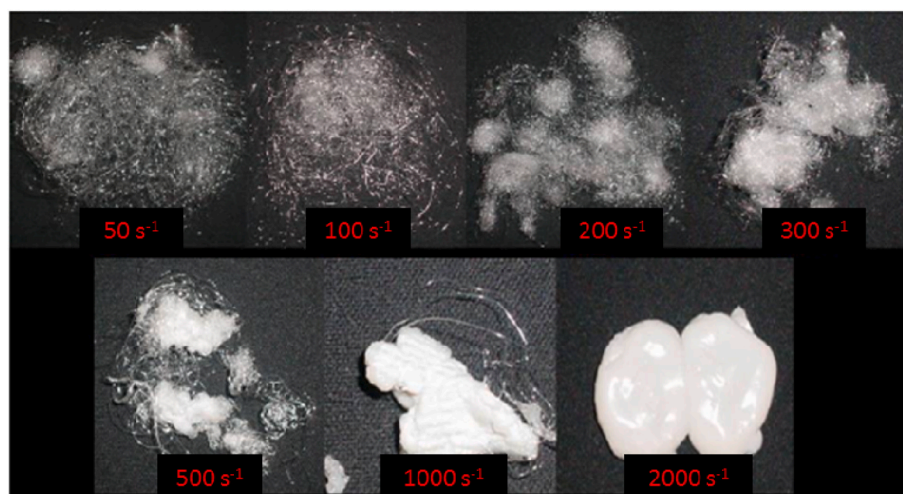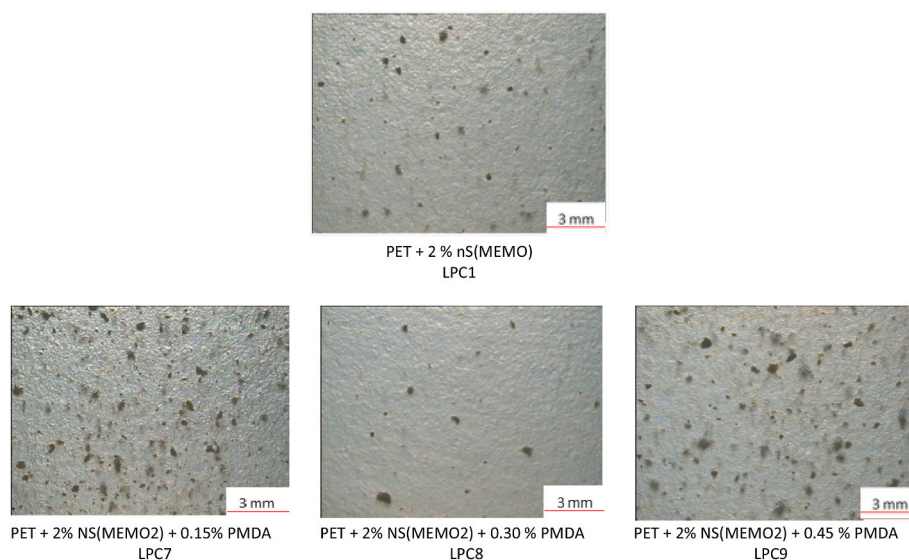**Fig. 5.** OM pictures of the PET nanocomposite with and without chain extender (PMDA).

Table 7
Intrinsic viscosity results for the new nanocomposites.

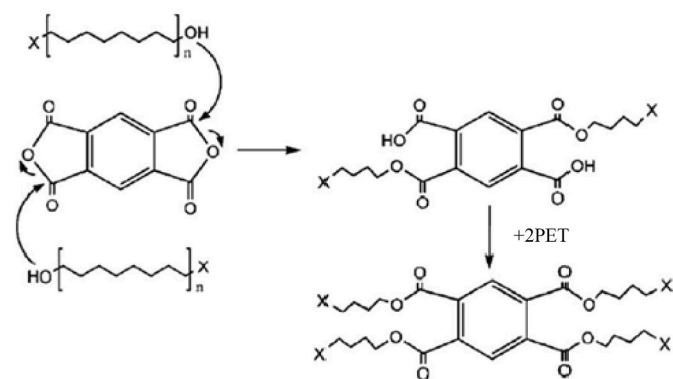| Samples	Nanocomposite	% nS (TGA)	IV (dl/g)
PET + 2% nS(MEMO)	LPC1	2.01	0.385 ± 0.005
PET + 2% nS(MEMO) + 0.15% PMDA	LPC7	3.24	0.501 ± 0.013
PET + 2% nS(MEMO) + 0.30% PMDA	LPC8	2.82	0.453 ± 0.013
PET + 2% nS(MEMO) + 0.45% PMDA	LPC9	2.80	0.414 ± 0.014

Fig. 6. Chain extension reaction between PMDA and PET hydroxyl (-OH) groups [46].

of covering the hydroxyl end groups on the clay surface to minimize PET degradation.

The use of PMDA has been proven to be effective in increasing nanocomposite IV with a concentration of 0.15%. However, that increase is too low, and both the low residence time and the presence of hydroxyl groups on the sepiolite are the main causes why the chain extender did not work as expected. It has been found that an increase of PMDA (0.30%), together with a low residence time in the extruder, does not improve viscosity values but generates bigger agglomerates. However, when that same amount of polymer extender is added, together with the nanocomposite in a mixing chamber, 3 min, viscosity values reach nearly those of pure PET.
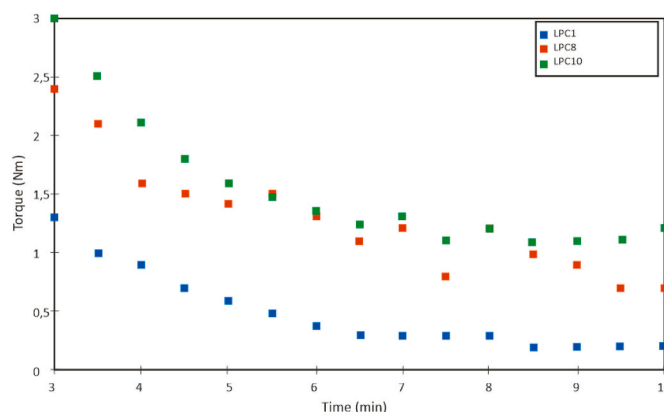

Fig. 7. Torque versus time for PET/sepiolite nanocomposites containing PMDA.

Table 8
Intrinsic viscosity results for samples used to analyse residence time.

Samples	Nanocomposite	IV (dl/g)
PET + 2% nS(MEMO)	LPC1	0.442 ± 0.005
LPC1 + 0.30% PMDA_extruded	LPC8	0.532 ± 0.022
(LPC1 y 0.30% PMDA) - IM	LPC10	0.701 ± 0.030

Author statement

T. Fernández-Menéndez: Investigation, Writing-Original draft preparation, D. García-López: Validation. A. Argüelles: Formal analysis. A. Fernández: Resources, Project administration. J, Viña: Writing-Review & Editing, Supervision.

Declaration of competing interest

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