Effect of Mesoporous SBA-15 Silica on the Thermal Stability of isotactic Polypropylene based Nanocomposites prepared by Melt Extrusion

R. Barranco-García^{1,2}, M.L. Cerrada¹, J.A. Ressa^{3,4}, E.M. Vallés⁴, A. García-Peñas^{5,6}, E. Pérez¹, J.M. Gómez-Elvira¹

¹Instituto de Ciencia y Tecnología de Polímeros (ICTP-CSIC), Juan de la Cierva 3, 28006-Madrid (Spain)

²PhD Program in Industrial Technology: Chemical, Environmental, Energetic, Electronic, Mechanical and Materials at Universidad Rey Juan Carlos, Madrid 28933, Spain

³PLAPIQUI (UNS-CONICET), Camino La Carrindanga km 7, 8000 Bahía Blanca, Argentina

⁴Comisión de Investigaciones Científicas de la Provincia de Buenos Aires (CIC), 1900 La Plata, Argentina

⁵ College of Materials Science and Engineering, Shenzhen Key Laboratory of Polymer Science and Technology, Guangdong Research Center for Interfacial Engineering of Functional Materials, Nanshan District Key Laboratory for Biopolymers and Safety Evaluation, Shenzhen University, Shenzhen 518060, P.R. China

⁶ Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, P. R. China

<https://doi.org/10.1016/j.polymdegradstab.2018.06.006>

ABSTRACT

The influence of mesoporous SBA-15 on the thermal stability of nanocomposites with isotactic polypropylene has been evaluated in detail, both under inert and air conditions, by performing dynamic weight loss measurements and by tracking the evolution of degradation species in materials prepared by melt extrusion. A superior thermal stability has been found in the composites, both under nitrogen and air, compared with that observed in the pristine PP. An almost identical effect has been found under those two atmospheres, in spite that the mechanisms involved in both of them are completely different. The rheological characteristics of these materials turn out the driving aspect in the observed thermal behaviour, prevailing on other specific detrimental parameters.

Keywords: Polypropylene; mesoporous SBA-15 particles; TGA; thermal stability.

INTRODUCTION

The favourable prospect of polymer nanocomposites' emerging market stems from the fact that these materials offer novel or improved properties, merely because a rather small quantity of nanoparticles are dispersed into a polymer matrix (ca. up to 5 wt%). This is especially important in the case of commodities since it is an efficient, quick, and cheap methodology to maintain, even increase, its impact on both daily and high performance applications. The enormous industrial interest on these materials has then promoted a huge basic research, with the purpose of gaining fundamental knowledge about the physicochemical factors involved in the modification of polymer properties.

Silicate and silica based inorganics are undoubtedly the most employed as nanofillers because they are very abundant in nature and because they do not need complicated treatments to be available as particles in the nanoscale. Moreover, they can be supplied in a wide variety of geometries that covers from foils, fibers and spheres. Accordingly, they have been profusely studied from the basic research point of view¹.

New silica materials that are structured as mesoporous networks^{2,3,4}, such as MCM-41, SBA-15, MCM-48 among others, are good alternatives to be used as nanofillers, since they offer an internal volume able to be taken up by polymer chains in the course of preparation from solution, melt compounding or synthesis processes. This phenomenon is expected to favour the disaggregation of rather polar particles within much less polar, even non-polar polymeric matrices and, in that way, to have a deeper impact on material properties.

Beside this, there is another reason that makes mesoporous silica a good choice for the preparation of polymer nanocomposites. These compounds have been already used in cracking of polymers^{5,6,7,8,9,10,11} especially of polyolefins, since they supply a considerable content of acid catalytic centres, spread over a high specific surface, that reduce the activation energy of the process. Due to this characteristic, mesoporous silica compounds have a high potential in all kind of heterogeneous processes. For instance, as supports for catalysts in olefin polymerisation, where much research is currently underway^{12,13,14,15} and where the nanosize could be exploited to modify conveniently the final properties of the material as well. As a matter of fact, these thereby obtained polyolefin grades may be more performant under application conditions and might be also more easily convertible into chemicals by cracking, at the end of the service life. This eventuality would make it possible low-energy

recycling of thermoplastics from the material itself, without adding cracking catalysts. Therefore, the use of mesoporous silica as nanofiller has the added value of contributing to both material and energy savings and, hence, to the sustainability of use and production of thermoplastics.

Despite the growing interest in the application of mesoporous silica for the preparation of polyolefin nanocomposites, either as supports of metallocene catalysts^{12-15,16,17,18,19} or by melt compounding^{20,21}, not much attention has been paid on the impact of these particles on the stability of the polymer matrix. This study aims to contribute to this critical issue by presenting a basic evaluation about the influence of pristine SBA-15 on the stability at high temperature, under both pyrolytic and oxidative conditions, of isotactic polypropylene (PP) and its based nanocomposites (PP/SBA) obtained by melt compounding. In fact, if one of the expected effects of presence of SBA-15 particles is to catalyse polymer chain scissions, it seems mandatory to evaluate the impact of this inorganics on the stability at high temperatures. This study will allow, on one hand, drawing conclusions about the suitability of replacing pristine PP by its SBA-15 based nanocomposites and, on the other, it will provide essential knowledge about the factors driving the modification of the material's thermal performance.

EXPERIMENTAL

Materials and preparation of samples

A commercially available metallocene-catalyzed isotactic polypropylene, iPP (Metocene HM562P: melt flow index of 15 g/10 min, ISO 1133, kindly supplied by Lyondell-Basell) was used in the present research as polymeric matrix. The mesoporous SBA-15 particles were purchased to Sigma Aldrich.

The PP/SBA nanocomposites were prepared by extrusion of the iPP and the inorganic SBA-15 particles at different ratios in a co-rotating twin-screw microextruder (Rondol). A screw temperature profile of 115, 170, 180, 185 and 190°C was used from the hopper to the die, being the length to diameter ratio 20:1.

The resulting materials were processed into films by compression moulding in a Collin P-200-P press between hot plates at 190°C for 3 min without pressure and, then, 3 min at 30 bar, and subsequent rapid cooling between refrigerated plates for 3 min under the same pressure.

Nanocomposite samples are referred in this study as PP followed by the weight percentage value in SBA-15 particles. Thus, for instance, PP2 and PP13 stand for PP/SBA nanocomposites with a weight content in SBA-15 of 2 and 13 wt.%, respectively.

Two additional samples, PP43 and PP80, were synthesised using a metallocene catalyst immobilised on the SBA-15 particles, acting as support, under different reaction conditions, in order to get nanocomposites in which either most or a significant fraction of the polymer could reach the internal mesoporous network of the SBA-15 particles. For this synthesis, the SBA-15 was impregnated with the $\text{Me}_2\text{Si}(\text{In})_2\text{ZrCl}_2$ catalyst (Strem) using glove-box and Schlenck techniques, according to the following procedure: The metallocene catalyst was dissolved in freshly distilled toluene at room temperature and the solution was subsequently mixed with the SBA-15, previously dried under vacuum at 350°C overnight. After 3 hours of contact time, the suspension was filtered under N_2 , washed with 10 mL of toluene and finally dried under vacuum. The so-prepared SBA-15 supported metallocene was directly introduced in the reactor, as a suspension in toluene, where it undergoes the in-situ activation with the modified MAO (MMAO-12, Aldrich 7 wt.% Al in toluene) present in the medium. The polymerisation conditions for both samples are specified in table I.

Table I. Reaction conditions for the synthesis of samples PP43 and PP80 and final PP/SBA ratio in the samples

Sample	Temp. (°C)	Time (h)	Propylene (bar)	[Al]/[Zr] (molar ratio)	Catalyst/SBA-15 (weight ratio)	PP/SBA-15 (weight ratio)
PP43	20	24	0.99	544	0.049	1.32
PP80	25	24	0.41	969	0.036	0.25

DSC characterisation

The DSC analysis of the films was carried out in a TA instruments DSC Q100 apparatus connected to a cooling system and calibrated with Indium and Zinc. The samples were heated under N_2 , from 0°C to 220°C at a heating rate of 20°C/min. The melting temperatures are collected in table II.

TGA measurements

TGA measurements were carried out in a Thermal Analysis TGA-Q 500 device. The samples used were 4 mm discs of approximately 5mg cut from the film with a calibrated die. Heating ramps from 40°C up to 750°C at 2, 5, 10 and 20°C/min were used, under a 90 mL/min flow of either nitrogen or air.

The TGA curves obtained were used to calculate the apparent activation energy (henceforward referred as E_a) of the weight loss process, by using the isoconversional method proposed by Friedman²². The analysis of changes in E_a was mainly focused on the initial stages of the degradation.

Degradation of samples

The controlled degradation, up to the selected final temperature, of the virgin PP and their PP/SBA nanocomposites was performed under N₂, in a tubular furnace. Initial quantities between 10 and 20 mg of the films were heated into a glass test-tube, properly modified to be fed by a laminar flow of the inert gas. The pyrolysis heating ramp within the cell was checked to be between 8 and 9°C/min, by means of a K type thermocouple/data logger (Lascar Electronics), which tracked the actual temperature value every 10 s. After a 15 min purging stage with Nitrogen (250 mL/min), the pyrolysis cell was let equilibrate at room temperature and, then, the heating ramp was started in the Nitrogen stream. Finally, the sample was cooled down under N₂ at room temperature.

In the case of degradations in air, all samples were isothermally oxidised in a fan-oven at 160°C, at increasingly residence times.

FTIR analysis of degradation kinetics

The FTIR spectra of both the reference and the degraded samples were recorded from the films, by performing 4 scans in a Perkin Elmer Spectrum Two, in the 4000-450 cm⁻¹ range, at a resolution of 2 cm⁻¹. The absorbance of the spectra were normalised to the intensity of the 2722 cm⁻¹ peak.

Measurement of the zero shear viscosity (η_0)

Rheological characterization of dynamic viscosity η' was carried out in a dynamic rotational rheometer, TA Instruments ARG2 (New Castle, USA). The experiment was performed under a nitrogen atmosphere using 25 mm diameter parallel plates. This viscoelastic parameter was measured in small-amplitude oscillatory shear flow as a function of frequency and temperature. The frequencies covered were in the 0.01 s^{-1} to 100 s^{-1} range. The temperature interval evaluated was ranging between 160 and 200 °C. To ensure the linear relation between stress and deformation, small stresses were used in all the dynamic tests. Zero shear viscosity (η_0) values were assessed by extrapolation of the dynamic viscosity η' values to a frequency of 0 Hz, with the exception of PP13. In this material, the reported data are those experimental results at a frequency of 0.63 rad/s, because of an extrapolation cannot be applied since percolation seems to be reached in this PP13. The viscosity values at lower frequencies would turn out without physical sense because presence of SBA-15 at that content does not allow achieving the Newtonian plateau.

Table II. Weight content in SBA-15 particles determined by TGA; melting temperatures (T_m) obtained from DSC experiments; and, values of zero shear viscosity (η_0) at different temperatures above T_m

Sample	SBA-15 wt. %	T_m^{DSC} (°C)	$\eta_0^{160^\circ\text{C}}$ (Ps·s)	$\eta_0^{180^\circ\text{C}}$ (Ps·s)	$\eta_0^{200^\circ\text{C}}$ (Ps·s)
PP	0	142.0	1750	1180	880
PP2	2	143.0	1830	1150	885
PP4	4	143.0	1780	1180	890
PP8	8	142.5	1980	1380	1040
PP13	13	142.5	5880 ^a	5400 ^a	5220 ^a

^aReported data are the experimental results at a frequency of 0.63 rad/s.

RESULTS AND DISCUSSION

Thermal stability under N₂

The presence of SBA-15 has been found to improve the thermal stability of the PP under inert atmosphere. Figure 1a shows that this effect is remarkable for sample PP13, as noticed by comparing their TGA curves at different heating rates with those ones from the reference PP. The stabilizing effect is also noticed from Figure 1b, where the corresponding DTGA curves have been represented. Figure 1a also displays some qualitative changes in the weight loss trend, which can be ascribed to the SBA-15 presence. As a matter of fact, the initial curved weight loss shape observed in the virgin PP changes to a faster initial evolution of volatiles in the PP13 specimen. Additionally, the temperature gap, caused by the increase of the heating rate in the 2-20°C/min range, is reduced at low weight losses in the case of the PP13 nanocomposite. These two facts by themselves allow predicting an increase of the apparent E_a of the pyrolysis at low degradation stages.

The superior thermal performance conferred by the mesoporous SBA-15 particles is also dependent on their content, as deduced from the comparison of the TGA curves corresponding to the different samples at the same heating rate (10°C/min) represented in Figure 2a. It is worth noticing that the stabilizing influence is somewhat visible at 2 wt.%, increasing with the SBA-15 incorporation up to 8 wt.%. At the highest 13 wt.% content, that enhancement is hardly raised. The limit of the stabilization effect at high temperatures seems to appear, then, at a content of 8 wt.% of SBA-15 particles. This fact can be easily seen in the corresponding derivative curves of TGA runs at 10°C/min for the different SBA-15 contents (Figure 2b). This figure depicts that rather similar curves in shape and position are observed in the samples with SBA-15 contents of 8 and 13 wt.%, respectively.

Figure 1. (a) TGA and (b) DTGA curves in N₂ for the PP (black) and PP13 (blue) films at different heating rates: 2 (solid thick lines), 5 (solid thin lines), 10 (dashed lines) and 20 °C/min (dotted lines).

According to the above-mentioned changes in the features of the TGA curves, caused by the presence of SBA-15 particles, it seems mandatory to assess if apparent E_a variations occur and, what is more important, if it really implies a change in the pyrolysis mechanism or it simply reflects changes in the kinetics of the evolution of volatiles. For this reason, the Friedman's approach²² was used to evaluate the apparent E_a values.

Figure 2. (a) TGA and (b) DTGA curves in N₂ for the different samples at 10°C/min. A colour code is inserted into the plots.

Variations of the apparent E_a with the pyrolysis conversion, for the virgin PP and the different nanocomposites, are shown in Figure 3. As previously indicated, the analysis is mainly focused on the initial and medium pyrolysis stages (ca. up to a 50 weight loss percentage). It is clear that the typical initial increase in the E_a for the PP is also observed in films with SBA-15 particle compositions of 2, 4 and 8 wt.%. Nevertheless, the slope of this rise is getting sharper and its starting value becomes superior with increasing SBA-15 content. As far as the PP13 material is concerned, it displays an anomalous decreasing shape that allows suspecting a driving role of the SBA-15 particles in the kinetics of the weight loss process. At this particular concentration, the process starts with an unexpectedly high value of

the E_a that is reduced significantly to lower values, these being similar to those found at the other compositions in the 20-50 wt.% range.

Figure 3. Dependence of E_a on the weight loss for the different materials under analysis. The colour code is inserted into the plot.

The E_a of the PP pyrolysis is an apparent magnitude since it reflects the energy requirements of a great number of radical chain processes, which make up the mechanism. Additionally, the E_a has been reported to be apparent not only from the chemical point of view but also from the physicochemical standpoint, due to the fact that it is also sensitive to physical or physicochemical features that might have a significant influence in chain scission processes happening in the molten state, e.g. factors controlling chain flexibility. In this sense, several features have been reported to make the difference in the apparent E_a required for the pyrolysis of PP. Among them, the influence of specific chain conformations associated with distinctive tacticity^{23,24} together with that ascribed to changes in molecular weight²⁵ and the presence of comonomer units, acting as interruptions in the PP sequences²⁶. Anyway, variations in the apparent E_a should be related to an alteration in the most energy demanding step, this being either a chemical or physicochemical stage.

In order to elucidate the true nature of the factors underlying the SBA-15 role, onto the variations of E_a , a more detailed analysis of the species generated in the remaining solid after the pyrolysis, as well as of their build-up kinetics, has been performed by means of the FTIR technique. Some species are a fingerprint of the chain scission mechanism, through which polyolefins generally degrade under an inert atmosphere^{27,28,29,30}. The resulting functionalities

formed are end-chain double bonds, whose distinctive IR absorptions and their relative intensities allow tracking the advance of the pyrolysis.

Figure 4a shows the evolution of intensity corresponding to the out-of-plane deformation mode of end-chain vinyliden protons generated during the pyrolysis of the virgin PP^{31,32}. The FTIR analysis performed in every other case reveals that the same species are produced and, then, that the chain scission mechanism does not change because of the presence of SBA-15. Nevertheless, the kinetics of this peak's growth is remarkably different, as deduced by the semi-quantitative analysis depicted in Figure 4b. The induction temperature range strongly depends on the SBA-15 content. This fact allows asserting that the well-known chain scission process really takes place, but it is increasingly delayed as the SBA-15 content is raised.

According to these results, the differences observed in the apparent E_a with the SBA-15 content (Figure 3) do not correspond to a change in the chemical mechanism, but to physical and/or physicochemical features associated with the SBA-15 particles. One of the most important effects could be a shielding in retention of volatiles or in some protection against heating derived from the presence of those SBA-15 particles, which eventually would shift the TGA curves towards higher furnace temperatures. Another factor could be the specific PP/SBA interaction at the interface or some restrictions in the molten PP chain dynamics as a result of the presence of SBA-15.

Figure 4. (a) Evolution of the FTIR out of plane deformation mode of terminal vinyliden protons in the pyrolysis of the virgin PP. (b) Kinetics of growth for the 887 cm^{-1} peak in the PP homopolymer and the different SBA-15 nanocomposites. Degradation times and samples are identified in the graphs a) and b) respectively by a colour code.

Concerning an eventual barrier effect of the particles, such possibility has been indeed proven, but for the access of oxygen to the polyolefin at high degradation stages and for laminar and fibrous silicate particles^{33,34,35,36}. In those particular cases, a somewhat continuous inorganic layer hinders the diffusion of the oxygen and causes a raise of the E_a , since the degradation becomes anaerobic. Quite on the contrary, an effective barrier effect of SBA in the pyrolysis of our samples would imply a blocking role of particles in the early loss of volatiles. This scenario can be discarded, especially if kinetic results are taken into account, since FTIR results shows that the progress of the pyrolysis is really delayed by the presence of SBA-15 (figure 4b).

Regarding thermal isolation, SiO_2 particles are considered as a poor insulator, with thermal conductivities over 0.721 W/mK ³⁷ (ca. 1.2 W/mK and 1.435 W/mK)³⁸ and they are not expected to restrict the heat flux when mixed with a much lower thermal conductive material like PP, both in the solid and in the molten state (ca. < 0.24 W/mK)³⁹. In fact, SiO_2 has been used to increase somewhat the thermal conductivity other polymer materials like epoxy resins⁴⁰.

Among the physicochemical factors mentioned, PP/SBA interactions at the interphase are expected to lower the E_a , because of the existence of Lewis acid centres on the particle surface that promote chain scission^{7,8,9,10,41}. However, the reality is just the opposite and both

temperature and E_a of the pyrolysis increase with the SBA content. From the few works available in related literature that report a stabilisation effect of mesoporous silica in PP nanocomposites⁴², such an influence would be related with those parameters affecting the dispersion efficiency of particles, e.g. processing conditions and polymer/filler interaction at the interphase. In our case, on the basis of the little impact of the above commented parameters, a rise in viscosity of the molten material is suggested to play a key role in the observed stabilisation. In other words, restrictions to chain dynamics may make thermally activated scissions more difficult. It is obvious that a comparative rheological study of the materials is not possible at temperatures far higher than the melting point, but the analysis of the viscosity at temperatures over the melting point may be helpful to withdraw conclusions about dissimilar chain dynamics, depending on the SBA-15 content (see Figure 5).

Figure 5. Dependence of zero shear viscosity on the SBA-15 content at different temperatures: 160°C, 180°C and 200°C.

This rheological analysis shows rather interesting characteristics. There is a noticeable influence of presence and content of SBA-15 particles in the zero shear viscosity values (see Table II and Figure 5). Thus, viscosity of the molten materials (whose T_m values listed in Table II) slightly increases up to 8 wt.% and very sharply at the highest content (PP13 specimen) because percolation is close to be reached at that SBA-15 amount. These variations in η_0 point out that restriction in chain dynamics can play a significant role onto the energy required for chain scission. This dependence correlates rather well with the progressive

increment found for *Ea* up to the PP8 sample and with the surprisingly superior *Ea* of the initial stages in the PP13 pyrolysis. Therefore, the hindrance of polymeric chain mobility caused by the SBA-15 presence seems to be the reason for the stabilisation effect observed in the pyrolysis of these nanocomposites.

Thermal stability under air

The oxidative dynamic TGA analysis reveals also profound changes in the stability of the PP because of the presence of SBA-15 particles. Similarly to the case of the anaerobic degradation, the higher the content of SBA-15 is the more stable the nanocomposite becomes. Figure 6a includes TGA runs obtained at 2, 5, 10 and 20°C/min for the most stable specimen PP13 compared with those found in the reference PP. The corresponding derivatives are also represented in Figure 6b. Correlation is not as good as in case of the pyrolysis but the distinct PP/SBA nanocomposites display an increasing resistance against oxidation, which is proportional to the SBA-15 content, as depicted in Figure 7 for all of them at a specific rate.

This study is again mainly focussed at low conversion range, as the previous pyrolysis evaluation. Thus, the oxidation of either the initial or little modified PP takes place. Nevertheless, some comments on the process at high conversions will be included next, for the purpose of clarifying the peculiar behaviour in the weight loss trend, which is clearly visible in the PP13 specimen. In this nanocomposite, the TGA curves from 5°C/min onwards show a quick loss weight at the high temperature range. This apparent final weight loss step is clearly visible in Figure 6b, where the DTGA curves of PP13 and virgin PP are presented. Despite the low mass of film used, there can be, certainly, some phenomena inducing these discontinuities in the TGA curve, like a heterogeneous diffusion of air into the sample or some temporarily retention of volatiles, which could account for this sudden weight loss. This could be the case in the nanocomposite with the highest SBA-15 content, where particles may form a somewhat continuous shield at very advanced degradation, which would eventually be responsible for either the access of oxygen or the retention of volatiles. The plausibility of this hypothesis is supported by some results on the TGA analysis of polyolefin/silicate nanocomposites³³⁻³⁶. However, there is another factor that might account for this phenomenon in this particular case. The mesoporous nature of the SBA-15 particles offers an internal volume able to be occupied by certain amount of polymer during processing in the molten state. These “internal PP” may be thereby, more protected against the oxygen attack and then, it can degrade at higher temperatures.

Figure 6. (a) TGA and (b) DTGA curves in air for the PP (black) and PP13 (blue) films at 2 (solid thick lines), 5 (solid thin lines), 10 (dashed lines) and 20°C/min (dotted lines).

Figure 7. Normalised TGA curves in air for the different samples at 5°C/min. The colour code is inserted into the plot.

To address this issue, nanocomposites with a higher proportion of SBA-15 could lead to get more understanding. For that, two polymerisations of propylene in the presence of a metallocene catalyst supported on SBA-15 were performed. The in-situ polymerization may also favour the inclusion of PP chains inside the SBA-15 channels. The reaction conditions were chosen to ensure low activities of the catalyst and, consequently, to attain materials with high contents in SBA-15 particles. The two so-prepared samples are the ones labelled as PP43 and PP80 (see Table I). They clearly show quite small PP/SBA ratios, but different enough to distinguish between the weight loss response of the bulk PP and that one of the PP closely associated with the SBA-15 particles, i.e. included in the internal volume of SBA-15. The TGA curves of these specimens under air at 10°C/min are shown in Figure 8a, together with the oxidative TGA curve for the PP13 material and those ones corresponding to the PP homopolymer under both environments, air and nitrogen.

It is quite noticeable that both PP43 and PP80 nanomaterials show a net oxidative weight loss within a temperature range that, although far from the anaerobic pyrolysis temperature range, is clearly beyond the one for the neat PP and PP13 composite. In fact, this specific temperature range corresponds to the almost entire weight loss in the PP80 sample, where the PP/SBA weight ratio is 0.25, while it is responsible of a minor portion of PP in the PP43 specimen. This latest material shows a PP/SBA weight ratio of 1.32 and most PP is not associated with the mesoporous network of the SBA-15. These remarks are also illustrated in Figure 8b, which displays the corresponding DTGA curves. This plot makes evident the

bimodal distribution of the sample PP43, with a weight loss fraction still in the expected temperature range for the PP and PP13, and another weight loss at a higher temperature interval where the PP homopolymer degrades completely under the action of the oxygen.

Figure 8. (a) TGA and (b) DTGA curves, performed under air at 10°C/min, for the PP homopolymer and PP13, PP43 and PP80 nanocomposites and for the pristine PP under N₂. Each curve is identified in the plots.

It is evident that degradation of the highly stable PP fraction does not take place in absence of oxygen, since it occurs well under the temperature at which PP losses weight in nitrogen. Nevertheless, it is far from being a normal oxidation and must be associated most probably with the polymer contained in the internal SBA-15 volume, whose accessibility to oxygen is greatly reduced.

Consistent with this conclusion, the quick weight loss observed in the PP13 sample at high temperature, but still into the PP homopolymer range, is not primarily due to the PP inside the SBA-15 particles. It is likely ascribed to the fast volatilization of final polymer residues, which are either temporarily protected from oxidation because of the high content of SBA-15, which plays as a barrier against air, or because such inorganic barrier delays the emission of volatiles, or for both reasons³³⁻³⁶. Anyway, the partial overlapping of the high temperature weight loss of PP13 with the low temperature weight loss of PP80 allows suspecting some PP degradation within SBA-15 particles. Some DSC results for nanocomposites based on ultra-high molecular weight polyethylene and SBA-15 particles and on polyethylene and decorated MCM-41 have pointed out the existence of confined polymer within the mesoporous channels^{43,44}.

Coming back to differences in stability in the initial stages of the PP oxidation and their SBA-15 nanocomposites, it is well-known that the oxidative weight loss of polyolefins takes place after an induction period, which finishes by a characteristic oxygen uptake process, as shown in Figure 9. The stability of the samples can be assessed by means of the induction length that, in dynamic TGA experiments, is also defined by the temperature at which the PP starts the oxygen uptake (T_{ind}). This is indicated in Figure 9a for the TGA curves obtained at 5°C/min. Moreover, the temperature at which the oxygen uptake reaches a maximum (T_{max}) can be also chosen as another alternative criterion of stability. These two temperatures have been found to increase with the content of SBA-15, according to the trends shown in Figure 9b at every heating rate.

Even though the mechanism of PP oxidation has nothing to do with that one of the pyrolysis, this result discloses an effect of the SBA-15 pretty much similar under both conditions. Such a similarity suggests in fact, that particles influence positively on the PP stability by means of a specific parameter in both cases, in particular the aforementioned change in viscosity of the molten material. It seems also certain that potential restrictions of SBA-15 particles to air diffusion may have some role in the observed increase of the induction period and, hence, in the enhancement of the stabilisation⁴⁵. This so-called labyrinth effect should be significant, especially at high SBA-15 contents or at high degradation stages.

Figure 9. (a) Induction period window for the PP homopolymer and their SBA-15 nanocomposites by TGA under air at 5°C/min. (b) Dependence of T_{ind} (black points) and T_{max} (blue points) for the oxygen uptake in the PP and SBA-15 materials at the different contents and heating rates.

It is important to check, and following the same methodology than that applied for the TGA measurements under nitrogen, that the PP oxidation mechanism remains unaltered because of the presence of SBA-15. The variation of the apparent E_a with conversion has been also studied by applying the Friedman's method. As seen in Figure 10, both the values and the trends of the oxidation E_a are similar for all the specimens up to weight losses of around 30%, and it seems to range into the typical value for the oxidation of the virgin PP. The apparent decrease of E_a for SBA-15 contents lower than 13 wt.% could be, however, real and might obey the above-mentioned influence of the Lewis character of the SBA-15. The magnitude of such effect would not drive the final response of the nanocomposites in the

molten state, where oxidation is really delayed. On the contrary, the thermal performance of the nanocomposites under air might be deteriorated in the solid state, if there are indeed low E_a processes controlling the response against oxygen attack over the effect of air diffusion into the bulk. This issue is of great practical importance and deserves a further study.

Figure 10. Dependence of apparent E_a of oxidation with the weight loss for the distinct materials. The samples are identified by the colour code inserted into the plot.

Together with the distinctive E_a value, the series of oxygenated species generated during the process provides the fingerprint of an unaltered oxidation pathway. The oxidation of the PP and the PP13 nanocomposite has been analysed by tracking the carbonyl index, through FTIR spectroscopy at 160°C. Figure 11a shows the evolution with time of the carbonyl species in the window of stretching mode, for both samples. It can be seen that the distribution of carbonyl-containing species does not change from a qualitatively point of view. Therefore, the oxidation mechanism of PP works similarly in the presence of SBA-15.

A quantitative difference is, however, remarkable if the carbonyl index at 1712 cm^{-1} is determined. Thus, figure 11b shows that it takes longer to start the oxidation for PP13 than for PP. This comparison of isothermal kinetics at 160°C is consistent with the order in stability found for the PP and their nanocomposites under dynamic conditions and points, likely, to the factor to be considered as the driving one in the oxidation rate of the molten nanocomposites. The improvement of the thermal stability, under both dynamic and isothermal conditions, as increasing SBA-15 content seems to indicate that, the rising values in molten viscosity of these materials slow down the oxygen diffusion into the bulk. As a matter of fact, the

oxidation of the molten PP has been reported to be diffusion controlled⁴⁶ and viscosity is the most important parameter on the accessibility of oxygen into the bulk.

Figure 11. (a) Dependence on time of the FTIR stretching-mode carbonyl species at 160°C for PP and PP13 samples. Degradation times are identified in the graph by the colour code inserted in. (b) Isothermal kinetics of the carbonyl index at 160°C for PP (black line) and PP13 (blue line) samples.

CONCLUSIONS

A superior thermal stability is found in the PP/SBA-15 nanocomposites, both under nitrogen and air atmospheres, compared with that observed in pristine PP. In spite of degradation mechanisms underlying each environment are completely different, they do not

change because of the presence of SBA-15 particles. Nevertheless, an effective delay in the build-up of the distinctive species is observed under both conditions.

Notwithstanding the different degradation mechanism, the main reason for such a positive impact seems to be similar. An increasing content of SBA-15 makes the viscosity of the molten material to increase. As a result, PP chain dynamics is gradually constrained and the temperature at which anaerobic chain scission occurs rises up and, by doing so, the activation energy associated with the process is also raised.

Under oxidative conditions, the increasing viscosity promoted by the presence of SBA is thought to hinder the diffusion of air into the bulk and, thus, to delay the oxidation of PP chains. Concurrently with this parameter, a positive impact of the SBA presence itself should be also taken into account, especially at high SBA contents, because of the forced diffusion of air through distorted pathways within the molten PP matrix.

The stabilisation effect seems to prevail in these materials over the reported action of other specific detrimental parameters, like the Lewis acid character of the SBA-15 surface, which would exert a destabilising effect.

Finally, the PP chains located within the internal SBA-15 channels are oxidised at higher temperatures than those outside the mesoporous particles. Nevertheless, their effect on the thermal stability against oxidation of the ultimate material is not very important since they constitute a minor fraction of the whole polymeric material. Only in the case of the two nanocomposites prepared by in-situ polymerisation their relative significance becomes more noticeable.

ACKNOWLEDGEMENTS

The financial support from project MAT2016-79869-C2-1-P (AEI/FEDER, UE) is greatly acknowledged. Ms. R Barranco-García also thanks her pre-doctoral funding (BES-2014-070972) associated with the MINECO (MAT2013-47972-C2-1-P) project. EMV and JR also express their gratitude to the Consejo Nacional de Investigaciones Científicas y Técnicas de la República Argentina (CONICET) and Universidad Nacional del Sur (UNS, Argentina) for supporting this study.

REFERENCES

- ¹ Ajayan PM, Schadler LS, Braun P, Nanocomposite Science and Technology, Wiley-VCH, Weinheim, 2004.
- ² Beck JS, Vartuli JC, Roth WJ, Leonowicz ME, Kresge CT, Schmitt KD, Chu CT-W, Olson DH, Sheppard EW, McCullen SB, Higgins JB, Schlenkert JL. A new family of mesoporous molecular sieves prepared with liquid crystal templates. *J Am Chem Soc* 1992;114:10834-43.
- ³ Roth WJ, Vartuli JC. Synthesis of mesoporous molecular sieves. *Stud Surf Sci Catal* 2005;157:91-110.
- ⁴ Zhao DY, Feng JL, Huo Q., Melosh N, Fredrickson GH, Chmelka BF, Stucky GD. Triblock Copolymer Syntheses of Mesoporous Silica with Periodic 50 to 300 Angstrom Pores. *Science* 1998;279: 548-52.
- ⁵ Marcilla A, Beltrán M, Conesa JA. Catalyst addition in polyethylene pyrolysis Thermogravimetric study. *J Anal Appl Pyrol* 2001;58-59:117-26.
- ⁶ Marcilla A, Gómez A, García AN, Olaya MM. Kinetic study of the catalytic decomposition of different commercial polyethylenes over an MCM-41 catalyst. *J Anal Appl Pyrol* 2002;64:85-101.
- ⁷ Marcilla A, Gómez A, Reyes-Labart JA, Giner A. Catalytic pyrolysis of polypropylene using MCM-41: kinetic model. *Polym Deg Stab* 2003;80:233-40.
- ⁸ Aguado J, Sotelo JL, Serrano DP, Calles JA, Escola JM. Catalytic Conversion of Polyolefins into Liquid Fuels over MCM-41: Comparison with ZSM-5 and Amorphous SiO₂-Al₂O₃. *Energy Fuels* 1997;11:1225-31.
- ⁹ Park HJ, Yim JH, Jeon JK, Kim JM, Yoo KS, Park YK. Pyrolysis of polypropylene over mesoporous MCM-48 material. *J Phys Chem Solids* 2008;69:1125-28.
- ¹⁰ Obali Z, Sezgi NA, Dogu T. The synthesis and characterization of aluminum loaded SBA-type materials as catalyst for polypropylene degradation reaction. *Chem Eng J* 2011;176-177:202-10.
- ¹¹ Obali Z, Sezgi NA, Dogu T. Catalytic degradation of polypropylene over alumina loaded mesoporous catalysts. *Chem Eng J* 2012;207-208:421-25.
- ¹² Campos JM, Lourenço JP, Cramail H, Ribeiro MR. Nanostructured silica materials in olefin polymerisation: From catalytic behavior to polymer characteristics. *Prog Polym Sci* 2012;37:1764-1804.
- ¹³ Xu H, Guo CY. Polymerisation in the confinement of molecular sieves: facile preparation of high performance polyethylene. *Eu Polym J* 2015;65:15-32.
- ¹⁴ Cerrada ML, Pérez E, Lourenço JP, Campos JM, Ribeiro MR. Hybrid HDPE/MCM-41 nanocomposites: Crystalline structure and viscoelastic behavior. *Micropor Mesopor Mat* 2010;130:215-23.

-
- ¹⁵ Campos JM, Lourenço JP, Pérez E, Cerrada ML, Ribeiro MR. Self-reinforced hybrid polyethylene/MCM-41 nanocomposites: In-situ polymerisation and effect of MCM-41 content on rigidity. *J Nanosci Nanotech* 2009;9:3966-74
- ¹⁶ Ferreira AE, Cerrada ML, Pérez E, Lorenzo V, Vallés E, Ressia J, Cramail H, Lourenço JP, Ribeiro MR. UHMWPE/HDPE in-reactor blends, prepared by in situ polymerization: Synthetic aspects and characterization. *eXPRESS Polymer Letters* 2017;11:344–61.
- ¹⁷ González DM, Quijada R, Yazdani-Pedram M, Lourenço JP, Ribeiro MR. Preparation of polypropylene-based nanocomposites using nanosized MCM-41 as support and in situ polymerization. *Polym Int* 2016;65:320–326.
- ¹⁸ Kaminsky W, Strübel C, Lechert H, Genske D, Woo SI. Syndiotactic polypropylene with MCM-41 supported metallocene $[\text{Me}_2\text{C}(\text{Cp})(\text{Flu})]\text{ZrCl}_2$. *Macromol Rapid Commun* 2000;21:909–12.
- ¹⁹ Marques MV, da Silva OFC, Coutinho ACSLS, de Araujo AS. Ethylene polymerization catalyzed by metallocene supported on mesoporous materials. *Polym Bull* 2008;61:415–23.
- ²⁰ Fereidoon A, Memarian S, Albooyeh A, Tarahomi S. Influence of mesoporous silica and hydroxyapatite nanoparticles on the mechanical and morphological properties of polypropylene. *Mat Design* 2014;57:201–10.
- ²¹ Wang N, Fang Q, Shao Y, Zhang J. Microstructure and properties of polypropylene composites filled with co-incorporation of MCM-41(with template) and OMMT nanoparticles prepared by melt-compounding. *Mat Sci Eng A* 2009;512:32–38.
- ²² Friedman H. Kinetics of thermal degradation of char-forming plastic from thermogravimetry. Application to a phenolic plastic. *J Polym Sci C* 1964; 6:183-195.
- ²³ Gómez-Elvira JM, Benavente R, Martínez MC. Unravelling the contribution of chain microstructure in the mechanism of the syndiotactic polypropylene pyrolysis. *Polym Deg Stab* 2013;98:1150-163.
- ²⁴ He P, Xiao Y, Zhang P, Xing Ch, Zhu N, Zhu X, Yan D. Thermal degradation of syndiotactic polypropylene and the influence of stereoregularity on the thermal degradation behaviour by in situ FTIR spectroscopy. *Polym Deg Stab* 2005;88:473-79.
- ²⁵ Martínez MC, Benavente R, Gómez-Elvira JM. Molecular weight dependence and stereoselective chain cleavage during the early stages of the isotactic polypropylene pyrolysis. *Polym Deg Stab* 2017;143:26-34.
- ²⁶ García-Peñas A, Cerrada ML, Gómez-Elvira JM, Pérez E. Microstructure and thermal stability in metallocene iPP-materials: 1-pentene and 1-hexene copolymers. *Polym Deg Stab* 2016;124:77-86.
- ²⁷ Sawaguchi T, Ikemura T, Seno M. Preparation of α,ω -Diisopropenyloligopropylene by thermal degradation of isotactic polypropylene. *Macromolecules* 1995;28:7973-78.
- ²⁸ Tsuchiya Y, Sumi K. Thermal decomposition products of polypropylene. Part A *Polym. Chem.* 1969;7:1599-607.

-
- ²⁹ Kiang JKY, Uden PC, Chien JCW. Polymer reactions. Part VII: thermal pyrolysis of polypropylene. *Polym Deg Stab.* 1980;2:113-27.
- ³⁰ Amorini MTSP, Comel C, Vermande P. Pyrolysis of polypropylene. I. Identification of compounds and degradation reactions. *J. Anal. Appl. Pyrolysis* 1982;4:73-81.
- ³¹ Thompson MR, Tzoganakis C, Rempel GL. Evaluation of vinylidene group content in degraded polypropylene. *J Polym Sci Part A Polym Chem* 1997;35:3083-86.
- ³² Flett MSC. Characteristic frequencies of chemical groups in the infra-red. In: Elsevier monographs. vol. 35, Elsevier, London, 1963.
- ³³ García N, Hoyos M, Guzmán J, Tiemblo P. Comparing the effect of nanofillers as thermal stabilizers in low density polyethylene. *Polym deg Stab* 2009;94:39-48.
- ³⁴ Leszczynska A, Njuguna J, Pielichowski K, Banerjee JR. Polymer/montmorillonite nanocomposites with improved thermal properties Part I. Factors influencing thermal stability and mechanisms of thermal stability improvement. *Thermochimica Acta* 2007;453:75-96.
- ³⁵ Qiu L, Chen W, Qu B. Morphology and thermal stabilization mechanism of LLDPE/MMT and LLDPE/LDH nanocomposites. *Polymer* 2006;47:922-30.
- ³⁶ Al-Malaika S, Sheena H, Fischer D, Masarati E. Influence of processing and clay type on nanostructure and stability of polypropylene clay nanocomposites. *Polym Deg Stab* 2013;98:2400-10.
- ³⁷ Taliba SFA, Azmib WH, Zakaria I, Mohamed W, Mamata AMI, Ismaila H, Daud WRW. Thermophysical properties of silicon dioxide (SiO₂) in ethylene glycol/water mixture for proton exchange membrane fuel cell cooling application. *Energy Procedia* 2015;79:366 –71.
- ³⁸ Mahajan SS, Subbarayan G, Sammakia BG. Estimating thermal conductivity of amorphous silica nanoparticles and nanowires using molecular dynamics simulations. *Phys. Rev. E* 76, 056701, <https://journals.aps.org/pre/abstract/10.1103/PhysRevE.76.056701>
- ³⁹ Standau T, Pospiech D, Pötschke P, Kretzschmar B, Vogel R, Häubler L, Harre K, Koutsoumpis S, Pissis P, Logakis E. Preparation and properties of thermally conductive polypropylene composites. *Journal of Plastic Technology* 2016;12:466-96.
- ⁴⁰ Lee WS, Yu J. Comparative study of thermally conductive fillers in underfill for electronic components. *Diamond Relat Mater* 2005;14:1647-53.
- ⁴¹ Serrano DP, Aguado J, Escola M. Catalytic Cracking of a Polyolefin Mixture over Different Acid Solid Catalysts. *Ind Eng Chem Res* 2000;39:1177-84.
- ⁴² Wang N, Fang Q, Chen E, Zhang J, Shao Y. Structure, crystallization behavior, and thermal stability of PP/MCM-41 nanocomposite. *Polym Eng Sci* 2009;12:2459-66.
- ⁴³ A.E. Ferreira, M.L. Cerrada, E. Pérez, V. Lorenzo, H. Cramail, J.P. Lourenço, M.R. Ribeiro. UHMWPE/SBA-15 nanocomposites synthesized by in situ polymerization. *Micropor. Mesopor. Mat.* 232, 13-25 (2016).

-
- ⁴⁴ M.L. Cerrada, A. Bento, E. Pérez, V. Lorenzo, J.P. Lourenço, M.R. Ribeiro. Hybrid Materials Based on Polyethylene and MCM-41 Particles Functionalized with Silanes: Catalytic Aspects of In Situ Polymerization, Crystalline Features and Mechanical Properties. *Micropor. Mesopor. Mat.* 232, 86-96 (2016).
- ⁴⁵ Sumino KI, Taniike T, Terano M, George G.A. Thermal and photooxidative degradation behaviors of poly(propylene)/SiO₂ nanocomposites with various polymer morphologies. *Macromol React Eng* 2008;2:135-41.
- ⁴⁶ Achimsky L, Audouin L, Verdu J, Rychlá L, Rychlý J. The effect of oxygen pressure on the rate of polypropylene oxidation determined by chemiluminescence. *Eur Polym J* 1999;35:557-63.