Thermooxidative degradation of injection-moulded sepiolite/polyamide 66 nanocomposites

A. Yebra-Rodríguez1,*, C. Fernández-Barranco1, M. D. La Rubia2, A. Yebra3, A. B. Rodríguez-Navarro4 and J. Jiménez-Millán1

1 Department of Geology and CEA Cierra, Associated Unit IACT (CSIC-UGR), Faculty of Experimental Sciences, University of Jaén, Campus Las Lagunillas s/n, 23071 Jaén, Spain
2 Department of Chemical, Environmental and Materials Engineering, Higher Polytechnic School, University of Jaén, Campus Las Lagunillas s/n, 23071 Jaén, Spain
3 Department of Optics, Faculty of Sciences, University of Granada, Campus Fuentenueva s/n, 18071 Granada, Spain
4 Department of Mineralogy and Petrology, Faculty of Sciences, Campus Fuentenueva s/n, 18071 Granada, Spain

[Received 15 November 2013; Accepted 20 November 2014; Associate Editor: R. Wogelius]

ABSTRACT

Clay/polymer nanocomposites (CPN) exhibit improved technical properties compared to their micro- and macro-counterparts. Nevertheless, thermal degradation of CPN may limit the applicability of these hybrid materials. In this paper accelerated ageing (110ºC and 150ºC) was performed in injection moulded pure polyamide 66 (PA66-S-0 samples) and polyamide 66 reinforced with 5 wt.% sepiolite (PA66-S-5 samples) CPN. Polymer degradation was monitored by the amount of newly formed carbonyl bonds. The carbonyl indices obtained indicate that degradation occurs to a greater extent as the temperature of the ageing process increases. Moreover, the degradation increases with time at the highest treatment temperature (150ºC). On the other hand, the occurrence of carbonaceous silicates in the nanocomposite samples at high temperatures yields greater thermal stability of sepiolite/PA66 nanocomposites compared to pure PA66. Furthermore, the sepiolite nanofibres maintain their position in the reticulated semicrystalline structure. In agreement with those results, differential scanning calorimetry and X-ray diffraction analyses show that the motion of the amide groups in the polymer chains are constrained by the well dispersed sepiolite.

KEYWORDS: sepiolite, nanocomposites, polyamide 66, thermal degradation.

Introduction

Clay/polymer nanocomposites (CPN) are hybrid materials in which a small amount of nanoclay is dispersed uniformly in the polymer matrix, providing improved technical properties compared to those of the neat components (Usuki et al., 2005). Clay minerals are naturally hydrophilic, therefore they are immiscible in hydrophobic polymers. Moreover, the cations in the interlayer hold the layers together, hindering (1) the penetration of polymer macromolecules and (2) the dispersion of the clay nanolayers in the polymer matrix. Compatibility between the clay minerals and the polymer is achieved through ion-exchange reactions by replacing the interlayer cation in the clay with organic surfactants, mainly quaternary salts (Araújo et al., 2007;
Uribe-Calderon et al., 2008). The organophilization process makes the clay hydrophobic and thus compatible with the polymer matrix.

Since the first CPN manufactured by Toyota (Usuki et al., 1993), these materials have gradually become more widely used in different industrial applications (Alena et al., 2013; Balakrishnan and Raghavan, 2003; de Sousa Rodrigues et al., 2013; Hong et al., 2005; Sancaktar and Kuznicki, 2011; Rhim et al., 2013). Although CPN materials can be affected by biological agents, ultrasound and different types of high-energy radiation, the main causes of degradation of nanocomposites are photooxidation and thermodegradation (Pandey et al., 2005). The degradation process causes irreversible structural changes (mainly in the polymer matrix) that affect the technical properties of the material (Ito and Nagai, 2010; Kiliaris et al., 2009).

Polyamides are among the thermoplastics used most commonly in engineering applications. Polyamide chains organize in well defined two-dimensional H-bonded sheets forming three-dimensional structures (lamellae) linked through van der Waals interactions. The most common commercial aliphatic polyamides are polyamide 6 (PA6) and polyamide 66 (PA66) of which the designations refer to the number of carbon atoms of the monomers involved in the polymerization mechanism. PA6 generally has one amine and one carboxylic acid group at the end of each chain. The amide bonds lie in the same direction and the number of methylene groups between them is invariably five. PA66 chains can contain amines only, acid groups only or both acid and amine groups at their ends. The direction of the amide bond reverses alternately and, thus, the polymer chains contain six and four methylene groups between the amide bonds. The different organization of the molecules results in a higher melting point, glass-transition temperature and tensile modulus for PA66, among other properties (Dasgupta et al., 1996). Although different polymorphic phases can be found depending on the crystallization conditions, α and γ have been identified as the main polymorphs (Bunn and Garner, 1947; Starkweather, 1989). Both structures result from a different arrangement of the H bonds between the O in the carbonyl group of one chain and the H attached to the N in the next chain. The α structure is in fully extended zig-zag conformation while the amide groups of the γ structure are rotated.

The number of industrial applications of PA66 has been growing since they were first considered to be new and exciting industrial materials in the late 1930s. The degradation of polyamides has been studied widely (Shamey and Sinha, 2003 and references therein). Degradation starts when the articles are produced and continues through its lifetime, reducing its value, therefore increasing the production costs. PA66 is widely used as a matrix in clay-reinforced nanocomposites, hence the thermal degradation in the presence of ambient oxygen has been studied extensively by many authors throughout the last decade (Davis et al., 2003; Ito and Nagai, 2010; Jain and Vijayan, 2002; Jang and Wilkie, 2005; Zhao et al., 2012, among others). Polyamides react with ambient oxygen when exposed to high temperatures, resulting in the cleavage of the polymer chains (Cerruti and Carfagna, 2010; Dong and Gijsman, 2010; Ghosh et al., 2000). The degradation begins with the loss of an H atom of the methylene group adjacent to the amide group (−CONH$_2$−). The resulting free radicals react with the atmospheric O and new carbonyl groups (C=O) are formed. Further degradation implies a greater amount of carbonyl groups, including hydroperoxides, aldehydes or carboxylic acids, through the cleavage of NC or CC bonds. In the case of CPN, the clay nanoparticles act as a barrier to the diffusion of O and volatile degradation products. However, the clay also triggers the decomposition of the polymer matrix due to the presence of water in its structure or the quaternary salts in the organoclay (Kiliaris et al., 2009). Thermo-gravimetric analyses performed by Xie et al. (2001) showed that the organic surfactants of the organoclays decompose at temperatures <180°C under non-oxidative atmosphere. Other authors (VandertHart et al., 2001a,b) pointed out that the high temperatures reached during the processing of CPN affect the organoclay stability and thus negatively influence the polymer matrix. Moreover, Fornes et al. (2003), in their study on different organoclays in a PA6 matrix, indicated that the observed degradation (colour variation in the material) depends mainly on the clay and the chemicals used during the organophilization process. However, some authors have shown that the addition of montmorillonite (Mt) restricts the thermooxidative degradation of Mt/PA6 nanocomposites and increases its durability (Jang and Wilkie, 2005).

The design of clay/polymer nanocomposites takes into account the mechanical properties and applicability of the materials. The elastic modulus
is often the most important mechanical property in plastics. This mechanical property is highly dependent on the extent of exfoliation of the clay (and thus the clay percent in the samples) in the polymer matrix (Ruiz-Hitzky and Van Meerbeek, 2006 and references therein). According to the literature, an improvement in mechanical properties without sacrificing those of the neat polymer is achieved by adding ~5 wt.% of clay filler in the matrix (Choudalakis and Gotsis, 2009 and references therein; Rao and Pochan, 2007). These nanocomposites meet market needs: improved mechanical properties at a reasonable cost. Understanding the thermal stability of CPN is essential for industrial applications. In particular, the ability to predict the evolution and response of CPN under high temperatures and their degradation mechanisms is essential. CPN manufactured with PA66 has a wider application field than those manufactured with PA6 due to the dramatic increase in heat resistance compared to other materials (Liu and Wu, 2002). The aim of this present work was to assess the thermal degradation of sepiolite/PA66 nanocomposites similar to those CPNs already used in industrial processes. For that purpose plates were made by injection moulding (to simulate industrial processes) of pure PA66 (PA66-S-0) and PA66 reinforced with 5 wt.% sepiolite (PA66-S-5).

Treatment temperatures were chosen in the range of industrial applications according to standard procedure ISO 4892-1 (2014), below the Brill transition temperature ($T_B$). Temperatures above $T_B$ would change the crystal structure of PA66 and thus the organization of both the organic and inorganic phases in the nanocomposite (Vasanthan et al., 1998). Moreover, Bernstein et al. (2005) reported that the oxidation mechanism remains the same over the temperature range 37–138°C ($\pm$2°C). Accelerated ageing was performed at 110°C and 150°C for periods of 7, 14, 21, 28 and 35 days. Polymer degradation was monitored by colour alteration and by the formation of new carbonyl bonds. Additionally, changes in the structure of CPN due to thermal treatments were characterized by X-ray diffraction (XRD) and differential scanning calorimetry (DSC) analyses.

**Materials and methods**

Polyamide 66 (PA66-S-0 samples) and sepiolite/polyamide 66 nanocomposites with 5 wt.% clay loading (PA66-S-5 samples) were manufactured as described by Yebr-Rodriguez et al. (2009a), using pure polyamide 66 (Dinalon®, Grupo Repol, Spain) and organophilized sepiolite with dimethyl di(hydrotallow) ammonium chloride (Tolsa S.A., Spain) as a reinforcement agent. The pellets were injected (BABYPLAST 6/10, CRONOPLAST) into moulds 80 mm × 50 mm in size and 1 mm thick (according to the UNE-EN ISO 527-2 (2012) standard procedure) to simulate industrial processing. Injection moulding was performed at 250 MPa injection pressure, 280°C in the cylinder of the extruder and 40°C tool temperature. Transmission electron microscopy (TEM) was used to trace exfoliation of the sepiolite in the PA66 matrix, in a TEM JEOL JEM-1010 operating at 80 kV with a camera (Gatan model 782). For this purpose, the samples were cut (70–100 nm) with an ultramicrotome Leica UC7 equipped with a diamond blade and stained with OsO4 to improve the contrast between the organic and inorganic phases in the nanocomposite samples. Thermal ageing was carried out at 110°C and 150°C in a CARBOLITE® TLK38 oven with air flow from the external environment for periods of 7, 14, 21, 28 and 35 days, after 72 h pretreatment at 60°C.

Carbonyl indices (CI) were calculated to assess the degree of polymer degradation as described by Dong and Gijsman (2010). For that purpose a FT-IR Bruker Tensor 27 was used in ATR mode over the range 400 to 4000 cm$^{-1}$ at a spectral resolution of 4 cm$^{-1}$. The maximum absorbance in the carbonyl region (1710–1760 cm$^{-1}$) was compared with a baseline spectrum of the polymer unaffected by the degradation.

The yellowness index (YI) was used to evaluate the degradation of nanocomposites. This index was calculated from spectral data that describe the change in colour of a test sample from white or clear towards yellow and has been used widely to measure the degradation degree of polymers and composites, among other materials (Ammala et al., 2002; Karmalm et al., 2009; Reis and Caneparolo, 2012). According to the ASTM method E313-96 (ASTM, 1996) the YI is calculated as follows:

$$YI = 100(C_XX - C_ZZ)/Y$$

where $X$, $Y$ and $Z$ are the CIE tristimulus values of the sample. The YI was calculated for illuminant/observer combination D65/10°. In those conditions the values of $C_X$ and $C_Z$ are 1.3013 and 1.1498, respectively. Colour measurements were made using a non-contact SpectraScan PR-704 spectroradiometer (Photo Research, Chatsworth,
USA) with a 4% measurement accuracy and standard deviation of repeat measurements over a 15 min period of <0.1% (Pérez et al., 2000). This device measures colour in a way that matches the geometry of the visual assessments and has been used previously in this research field (Ghinea et al., 2010; Yebra-Rodríguez et al., 2011). Samples were measured in a colour-assessment cabinet (CAC 60, Verivide Limited, Leicester, UK) against a grey (L* = 80.6, a* = −0.5 and b* = −2.3) 50 mm × 50 mm ceramic tile background (Ceram, Staffordshire, UK) with a light source simulating the spectral relative irradiance of CIE standard illuminant D65. The illuminating and viewing configuration was CIE d/0º and the 1964 10º Supplementary Standard Observer was used to calculate colour. Short-term repeated measurements without replacement were performed and each sample was measured three times.

The DSC analyses were carried out under a nitrogen flow in a DSC 822e (Mettler Toledo), over a temperature range of 25–300ºC at a heating rate of 5ºC/min. The samples (~10 mg) were dried by vacuum heating at 60ºC for 48 h prior to the DSC analysis. Crystallinity indices (Wc) were calculated from the ratio between the enthalpy of melting (DHm, obtained for each sample from the area in the DSC curve between onset and endset temperatures) and that of a fully crystalline PA66 sample (196 J/g, Lee and Phillips, 2007), according to the formula:

\[
W_c (%) = \frac{\Delta H_m}{(196 J/g)} \times 100
\]

The XRD was performed in a single-crystal diffractometer SC-XRD Smart APEX D-8 Bruker (Karlsruhe, Germany), with the samples aligned perpendicular to the incident X-ray beam and parallel to the CCD area detector. A transmission diffraction pattern was recorded for each sample and each stage of the thermal treatment, using MoKα radiation and the experimental conditions as follows: 50 kV acceleration voltage, 30 mA filament current, 0.5 mm collimator diameter, 30 s exposure time and 60 mm distance to detector. The two-dimensional X-ray diffraction (2DXRD) patterns were analyzed using the XRD2DScan software (Rodriguez-Navarro, 2006).

Results and discussion

The extent of exfoliation of the sepiolite in the PA66 matrix was observed in the TEM image shown in Fig. 1, where a satisfactory dispersion of the clay is shown. The degree of polymer degradation estimated from the CI was calculated for each set of samples and treatments and is shown in Fig. 2. In general, the CI values of nanocomposites (PA66-S-5) are slightly less than those of pure polyamide (PA66-S-0) after treatment at 110ºC. The CI values of both sets of samples increase slightly with treatment time, and start to stabilize after 28 days of treatment. The CI values are larger for both sets of samples after the ageing temperature of 150ºC, which means that the degradation occurs to a greater extent as the temperature increases (i.e. higher degree of broken chains in the polymer structure). Moreover, PA66-S-0 samples show larger CI values than PA-66-S-5 samples throughout the entire ageing process at 110ºC. According to the literature, the increase in CI is due to two different processes: (1) the formation of new carbonyl groups from the uptake of environmental oxygen by the carbon adjacent to the amide groups of PA66; and (2) the cleavage of the polymer chains between the carbon atom and the amide group of PA66, thus resulting in the formation of additional carbonyl bonds (Gijsman et al., 1995). The presence of sepiolite hinders the polymer chain cleavage of N–C or C–C bonds, even at extended treatment time. Thermal stabilization of the polymer in the nanocomposites is achieved through deactivation of the macroradicals formed during high-temperature processing. At 110ºC,
the degradation process occurs only by the uptake of O into the polymer chain (i.e. in the C atoms). The sepiolite prevents cleavage of the polymer, therefore the stabilization is achieved in a shorter time than in PA66 nanocomposites reinforced with other materials (e.g. salts; Cerruti and Carfagna, 2010). According to our previous work (Fernández-Barranco et al., 2014), the sepiolite and the PA66 matrix form a reticulated semicrystalline structure where the clay fibres are bonded to the PA66 lamellae through strong H bonding between Si–OH groups located at the edge of the sepiolite crystals and the amide groups of the polymer matrix (Fig. 3). Sepiolite is rich in reactive silane coupling agents (Si–OH groups) due to the discontinuity of the TOT layers (tetrahedral-octahedral-tetrahedral sheets) (Ahlrichs et al., 1975; Jones and Galán, 1988). The Si–OH groups are grafted to the polymer chains after the organophilization of the clay fibres, and the attached groups are eliminated only after heating at high temperatures (Ruiz-Hitzky and van Meerbeek, 2006). At 150°C ageing the degradation begins in the links between the sepiolite and the PA66 chains, hence the CI value of the nanocomposite samples is larger than in those corresponding to the neat polymer.

The degradation of nanocomposites was also monitored by the changes in their optical properties (yellowness index; YI). Yellowness results from degradation of the materials by light, chemical exposure and processing (Ammala et al., 2002; Karmalm et al., 2009; Reis and Canevarolo, 2012). The evolution of the YI calculated for each set of samples is shown in Table 1 and Fig. 4. In general, YI increases with ageing time and treatment temperature. On the other hand, nanocomposite samples show larger
YI values due to the slight original yellow colouration due to Fe present in the clay particles. However, the evolution of the YI with ageing time is similar in PA66-S-0 and PA66-S-5. Yellowing in aliphatic polyamides after thermal treatment has been explained through accumulation of pyrrole type products or formation of C=C bonds with carbonyl groups (Levchik et al., 1999). As colour formation is associated with the polymer degradation, longer exposure time leads to larger YI values. As expected, the thermal ageing at 150ºC produces further yellowing of the samples at the early stages of the degradation process. After 7 days, the sepiolite inhibits the reactions leading to the yellowing of the samples. Similar results have been observed in Mt/PA66 nanocomposites (Qin et al., 2003), where the clay shields the sub-products generated during the degradation. Under air atmosphere, the occurrence of carbonaceous silicates in the nanocomposite yields greater thermal stability of sepiolite/PA66 nanocomposites compared to pure PA66. The coat-like char retards the penetration of oxygen and delays significantly the rate of degradation of the nanocomposite with increasing exposure time (i.e. 28 and 35 days) and, at the same time, decreases the yellowness of the samples.

The DSC analyses (Fig. 5) show a broadening of the melting peak in aged samples, indicating pre-melting decompositions. The broadening is more pronounced in the PA66-S-0 samples than in the nanocomposites, and again more pronounced at 150ºC ageing temperature as the PA66 chains

<table>
<thead>
<tr>
<th>Sample</th>
<th>Time (days)</th>
<th>Temperature, 110ºC</th>
<th>Temperature, 150ºC</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>YI±σ</td>
<td>YI±σ</td>
</tr>
<tr>
<td>PA66-S-0</td>
<td>0</td>
<td>21.49±0.04</td>
<td>19.84±0.03</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>58.39±0.03</td>
<td>125.17±0.09</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>66.31±0.03</td>
<td>133.92±0.19</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>68.96±0.04</td>
<td>144.01±0.06</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>65.13±0.03</td>
<td>127.24±0.08</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>72.54±0.04</td>
<td>110.54±0.12</td>
</tr>
<tr>
<td>PA66-S-5</td>
<td>0</td>
<td>52.37±0.04</td>
<td>54.55±0.05</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>73.12±0.05</td>
<td>125.65±0.14</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>84.24±0.06</td>
<td>116.29±0.16</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>87.49±0.06</td>
<td>120.32±0.07</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>81.93±0.06</td>
<td>88.93±0.08</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>90.92±0.06</td>
<td>75.06±0.12</td>
</tr>
</tbody>
</table>

Fig. 4. Yellowness indices of PA66-S-0 and PA66-S-5 after thermal ageing at 110ºC (upper) and 150ºC (lower).
FIG. 5. DSC thermograms of neat polymer (PA66-S-0 samples) and nanocomposites (PA66-S-5) after thermal ageing at 110°C and 150°C. The curves have been arbitrarily shifted vertically for clarity.
break further. Moreover, the melting temperature \( T_m \) moves to lower temperatures as less heat is required to complete melting when the polymer chains are broken.

The DSC curves of unaged samples display a small exothermic peak at \( \sim 240^\circ \text{C} \). Similar pre-melting transitions have been reported by Yebras-Rodrı´guez et al. (2009b) in Mt/PA6 nanocomposites. According to other authors (Murthy, 2006; Vasanthan et al., 1998) polyamides have a memory, i.e. a fraction of the H bonds remains in the melt. Under these conditions, PA66 might recrystallize small already-melted crystals. This peak attenuates in the aged samples (at 110 and 150ºC), particularly in PA66-S-0 samples. Moreover, at 150ºC ageing temperature, the pre-melting recrystallizations take place at temperatures closer to the \( T_m \). Considering the arrangement of the phases in the nanocomposite (Fernández-Barranco et al., 2014), the sepiolite nanofibres are placed perpendicular to the PA66 lamellae through H bonds without modifying the polymer chains, breaking H bonds between adjacent lamellae, but creating new ones. Therefore, the presence of sepiolite increases the memory effect of the PA66 crystals through the H bonds between the sepiolite rods and the polymer lamellae.

The melting process is complete at 266ºC, corresponding to the typical \( T_m \) of the \( \alpha \) polymorph of the PA66. The smooth shoulder at \( \sim 255^\circ \text{C} \) is ascribed to the melting of the \( \gamma \) polymorph, which remains in the aged samples. The sepiolite nanofibres do not trigger the nucleation of \( \alpha \) or \( \gamma \) PA66 crystals at temperatures below the Brill transition temperature \( (T_B, 160^\circ \text{C for PA66; Brill, 1942}) \). As would be expected, the clay maintains its position in the reticulated semicrystalline structure, which leads to the stabilizing effect already observed in the CI.

Crystallinity indices \( (W_c) \) were calculated from DSC analysis (Table 2) and are plotted in Fig. 6. \( W_c \) values are smaller for the samples aged at 150ºC than for those aged at 110ºC, irrespective of the exposure time. The crystallinity index of PA66-S-5 shows an increase of 8.9% from 31.1 to 40.0% in the early stage of ageing at 110ºC as a result of the annealing (Hindeleh and Johnson, 1978). After longer exposure time (21 days), the value of \( W_c \) decreases below the crystallinity of the unaged sample, with a minimum value after 28 days of exposure. Similar results have been obtained for Mt/PA66 nanocomposites (Kartalis et al., 2001; Kiliaris et al., 2009; Warwicker, 1970). As shown by those authors, a

<table>
<thead>
<tr>
<th>Sample</th>
<th>Ageing time (days)</th>
<th>( T_{onset} ) (ºC)</th>
<th>( W_c ) (%)</th>
<th>( T_{onset} ) (ºC)</th>
<th>( W_c ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA66-S-0</td>
<td>0</td>
<td>257.8ºC</td>
<td>39.6ºC</td>
<td>257.8ºC</td>
<td>39.6ºC</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>258.9ºC</td>
<td>39.7ºC</td>
<td>258.9ºC</td>
<td>39.7ºC</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>257.9ºC</td>
<td>39.6ºC</td>
<td>257.9ºC</td>
<td>39.6ºC</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>255.9ºC</td>
<td>38.9ºC</td>
<td>255.9ºC</td>
<td>38.9ºC</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>254.9ºC</td>
<td>38.3ºC</td>
<td>254.9ºC</td>
<td>38.3ºC</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>253.7ºC</td>
<td>37.8ºC</td>
<td>253.7ºC</td>
<td>37.8ºC</td>
</tr>
<tr>
<td>PA66-S-5</td>
<td>0</td>
<td>260.4ºC</td>
<td>31.1ºC</td>
<td>260.4ºC</td>
<td>31.1ºC</td>
</tr>
<tr>
<td></td>
<td>7</td>
<td>259.4ºC</td>
<td>30.1ºC</td>
<td>259.4ºC</td>
<td>30.1ºC</td>
</tr>
<tr>
<td></td>
<td>14</td>
<td>257.4ºC</td>
<td>29.1ºC</td>
<td>257.4ºC</td>
<td>29.1ºC</td>
</tr>
<tr>
<td></td>
<td>21</td>
<td>256.4ºC</td>
<td>28.1ºC</td>
<td>256.4ºC</td>
<td>28.1ºC</td>
</tr>
<tr>
<td></td>
<td>28</td>
<td>254.1ºC</td>
<td>27.1ºC</td>
<td>254.1ºC</td>
<td>27.1ºC</td>
</tr>
<tr>
<td></td>
<td>35</td>
<td>252.7ºC</td>
<td>26.1ºC</td>
<td>252.7ºC</td>
<td>26.1ºC</td>
</tr>
</tbody>
</table>

Table 2. Crystallinity indices \( (W_c, \%) \) and melting temperature \( (T_m) \) of PA66-S-0 and PA66-S-5 samples after thermal ageing at 110ºC and 150ºC, and the thermal data used to calculate \( W_c \).
post-crystallization of the polymer takes place for up to 21 days exposure time due to the reordering of the amorphous PA66 molecules after the chain cleavage during annealing (i.e. higher lattice order without affecting crystallite size). However, \( W_c \) decreases progressively during the degradation (again with a minimum after 28 days exposure time) when ageing takes place at 150ºC. Similar behaviour was observed in PA66-S-5. At 150ºC, the \( W_c \) value of the nanocomposite samples increases slightly in the first stage of the degradation. After 21 days, the crystallinity decreases below the values obtained for the sample before the degradation process, with a minimum after 28 days exposure. From the results above, it appears that the samples reach a critical point in the degradation process after 28 days. Yoon et al. (2002) observed that the addition of Mt to PA6 reduced the thermal expansion coefficient of the polymer in the flow and transverse directions of injected samples. The motion of the polymer chains is constrained by the well dispersed clay particles, thus the CPN samples need greater energy (induced by temperature) to attain the crystallinity changes produced in the neat polymer samples (Lu et al., 2003). However, PA66-S-0 and PA66-S-5 show similar tendencies after 14 days of ageing at 150ºC and beyond. Murthy (2006) reported that a large fraction of the amide groups of polyamides are still H bonded in the melt due to low entropy of fusion. Therefore, the motion of the amide groups is restricted at temperatures below \( T_B \), irrespective of the presence of clay particles.

The XRD patterns (Fig. 7) display peaks corresponding to the (001) PA66 \( \gamma \) reflection (\( \gamma \) peak at \( \sim 10.2^\circ 20 \)), (100) PA66 \( \alpha \) reflection (\( \alpha_1 \) peak at \( \sim 8.7^\circ 20 \)) and the (010)+(110) PA66 \( \alpha \) reflection (\( \alpha_2 \) peak at \( \sim 11.7^\circ 20 \)). The \( \alpha_1 \) and \( \alpha_2 \) peaks are attributed to the distance between adjacent polyamide chains bonded by H bonds and to the distance between lamellae, respectively (Liu and Wu, 2002; Vasanthan, 1998). The \( \alpha_1 \) reflection sharpens and increases in resolution in the clay-reinforced samples as the sepiolite fibres trigger a higher degree of order between adjacent lamellae in the nanocomposites (Fernández-Barranco et al., 2014). The \( \gamma \) and \( \alpha_2 \) peaks shift slightly to smaller 2\( \theta \) values at 110ºC degradation temperature (up to \( 9.99^\circ 20 \) and \( 9.85^\circ 20 \) after 35 days of exposure for PA66-S-0 and PA66-S-5 \( \gamma \) peaks, respectively; up to \( 11.3^\circ 20 \) and \( 11.2^\circ 20 \) after 35 days of exposure for PA66-S-0 and PA66-S-5 \( \alpha_2 \) peaks, respectively), meaning an anisotropic thermal expansion of the PA66 unit cell in the polymer chain direction (\( \gamma \) peak) and in the direction where the van der Waals interactions are located (\( \alpha_2 \) peak) (Kazaryan, 1987). Some authors (Murthy, 2006 and references within) have shown that the crystalline density of certain aliphatic polyamides decreases drastically in the temperature range from room temperature up to \( \sim 195^\circ C \) (above \( T_B \)). This reduction in crystal density (\( \sim 14\% \)) can be explained by the volume requirements of the methylene groups’ librational motions within the crystals. However, methylene motions occur in a cylindrical region around the polymer chain axis at \( T_B \) and above and do not require any lattice expansion. Instead, the \( \gamma \) reflection of the PA66-S-5 at 150ºC ageing temperature shifts slightly towards larger 2\( \theta \) values (up to \( 10.35^\circ 20 \)), which implies a shortening in the axis of the polymer chain. According to Itoh (1976), heat treatments of pure PA66 at 200ºC provoke the immobilization of the amide groups due to H bonds, while maintaining the H-bonded sheets’ structure. The presence of the sepiolite in the nanocomposite samples prevents the motion of the amide groups in the chains, resulting in a similar immobilization effect.

**Concluding remarks**

The degradation of PA66 crystals in injection moulded neat PA66 and sepiolite/PA66
nanocomposites was studied after thermal ageing at 110°C and 150°C. Carbonyl indices show that the degradation increases throughout the entire process at 150°C. However, the CI values start to stabilize after 28 days of treatment after ageing at 110°C. The sepiolite hinders the polymer-chain cleavage, even after increased exposure time. Therefore, the stabilization is achieved after a shorter time than in PA66 nanocomposites reinforced with other materials. Moreover, the sepiolite inhibits the reactions leading to the yellowing of the samples due to the occurrence of carbonaceous silicates in the nanocomposite samples at high temperatures, which is an important property when optical clarity is needed. Crystallinity indices are smaller for the

Fig. 7. XRD patterns of PA66-S-0 and PA66-S-5 samples after thermal ageing at 110°C and 150°C. Intensity of the peaks in arbitrary units.
samples aged at 150°C than those aged at 110°C, irrespective of the exposure time. The crystallinity of PA66-S-5 samples increases in the early stage of ageing due to a reordering of the amorphous PA66 molecules after the polymer-chain cleavage during annealing. The sepiolite nanofibres do not trigger the nucleation of α or γ PA66 crystals at temperatures below the Brill transition temperature and maintain their position in the reticulated semicrystalline structure. The nanofibres also prevent the movement of the amide groups in the chains. The results obtained indicate greater thermal stability of sepiolite/PA66 nanocomposites compared to pure PA66, at temperatures below the Brill transition temperatures.

Acknowledgements

This research was supported by Research Group RNM-325 (CICE, Junta de Andalucía, Spain) and Research Project CGL2011-25906 (Ministry of Economy and Competitiveness, Spain). The authors thank “Centro de Instrumentación Científico Técnica” (University of Jaén, Spain), “Centro de Instrumentación Científica” (University of Granada, Spain) and the technicians for data collection.

References

Kartiolas, C.N., Papaspyrides, C.D., Pfaendner, R.,
Karmalm, P., Hjertberg, T., Jansson, A. and Dahl, R.
Jones, B.F. and Gala´n, E. (1988) Sepiolite and
Hong, C.H., Lee, Y.B., Bae, J.W., Jho, J.Y., Nam, B.U.
Hindeleh, A.M. and Johnson, D.J. (1978) Crystallinity
ISO 4892-1 (2014) Methods of exposure to laboratory
Differences and similarities in the thermooxidative
degradation of polyamide 46 and 66. Polymer
Degradation and Stability, 49, 121–125.
Hindeleh, A.M. and Johnson, D.J. (1978) Crystallinity
and crystallite size measurement in polyamide and
polyester fibres. Polymer, 19, 27–32.
Hong, C.H., Lee, Y.B., Bae, J.W., Jho, J.Y., Nam, B.U.
properties after heat aging.
Hoffmann, K. and Herbst, H. (2001) Recycled and
Polymer Degradation and Stability
(2009) Thermal stability of poly(vinyl chloride) with
19

Thermal decomposition of aliphatic nylons.
Polymer International, 48, 532–557.
nanocomposites via melt intercalation.
Macromolecular Materials and Engineering, 287,
180–186.
Lu, Y., Zhang, G., Feng, M., Zhang, Y., Yang, M. and
Murthy, N.S. (2006) Hydrogen bonding, mobility, and
structural transitions in aliphatic polyamides.
Journal of Polymer Science: Part B: Polymer
Physics, 44, 1763–1782.
Pandey, J.K., Reddy, R., Kumar, A.P. and Singh R.P.
(2005) An overview on the degradability of polymer
nanocomposites. Polymer Degradation and Stability,
88, 234–250.
Pérez, M.M., Melgosa, M., El Moraghi, A. and Hita, E.
(2000) Usefulness of cathode ray tube color displays
in chromaticity–discrimination experiments. Applied
Optics, 22, 4021–4030.
Qin, H., Su, Q., Zhang, S., Zhao, B. and Yang, M.
Polymer, 44, 7533–7538.
clay nanocomposites. Macromolecules, 40,
290–296.
the structure of polypropylene/montmorillonite
nanocomposite by in-line light extinction and color
measurements during multiple extrusions. Polymer
Engineering & Science, 52, 1784–1794.
Rhim, J.W., Park, H.M. and Ha, C.S. (2013) Bio-
Rodriguez-Navarro, A. (2006) XRD2DScan: new soft-
ware for polycrystalline materials characterization
using two-dimensional X-ray diffraction. Journal of
Applied Crystallography, 39, 905–909.
mineral- and organoclay-polymer nanocomposite.
Pp. 583–621 in: Developments in Clay Science, 1
(F. Bergaya, B.K.G. Theng and G. Lagaly, editors).
Elsevier, Amsterdam.
adhesives: mechanical behavior with nanoclay.
International Journal of Adhesion and Adhesives,
31, 286–300.
degradation of nylon 6.6 as a result of exposure to
environmental conditions. Review of Progress in
Coloration and Related Topics, 33, 93–107.


