ABSTRACT. The present study focused on the mechanical and thermal properties of a Polyamide(PA6)/Kaolinite composite. Several kaolinites (showing different shape factor) with appropriate surface treatments (showing more or less affinity with the matrix) are incorporated in PA6 inducing a high level of disparity in the composite morphology. For each composite, kaolinites dispersion and distribution is obtained by a statistical analysis from MEB and optical micrographs. Mechanical and thermal tests (uniaxial tensile test, Charpy impact test, cone calorimeter test) are conducted on each composite. It was found that: first the higher is the interparticular distance, the lower are both the Young modulus and the resilience, second the higher is the kaolinites median diameters, the lower is the yield stress and the higher is peak of Heat Release (pHRR).

KEY WORDS: Fire retardancy, mechanical properties, morphological characterization
1. Introduction

Incorporation of nanomineral in polymer offers a promising way to improve both their thermal and mechanical properties. First of all, nanomineral particles such as organic montmorillonite (oMMT) are usually used to improve flame retardancy but their processability limits their level of incorporation [1]. Our research tries to promote another kind of disposable mineral particles: the kaolinites. Regarding its low shape factor, the main interest is its high potential of rate incorporation in polymer matrix. Secondly, the broadly potential use of this material necessitates investigation on mechanical composite performances. Even if native particles are submicronic, their level of dispersion in the matrix and their distribution is usually responsible of poor mechanical properties. A surface treatment is therefore advisable.

The present study focuses on the use of kaolinites (30% by mass fraction) to improve both mechanical and thermal behavior of PA6 material. At first the composites morphologies are characterized. Then mechanical (static/dynamic) and thermal tests (cone calorimeter) are performed. Relation between morphology and thermal/mechanical properties is then discussed.

2. Experimental

2.1. Material and preparation

The polyamide matrix (PA6) used in this study is supplied by Rhodia (trade mark Technyl® C206). PA6 pellets were dried in a vacuum oven at 80°C for a minimum of 8h prior to the compounding. A melt blending of PA6 with kaolinites was carried out on a co-rotating twin-screw extruder. The samples were injected in moulds to obtain specific specimens (ISO 527-2 (1A) for uniaxial tests, notched test bars for Charpy impact and square specimens for cone calorimeter tests.

Two kinds of lamellar kaolinite (supplied by Imerys) were selected for this study: a commercial one (K1): PARALUX® with a shape factor of 10 and an average primary particle size of 0.9 µm and a non-commercial one (K2) with a shape factor of 5 and an average primary particle size of 0.2 µm. Some of the fillers are used after surface modification: coupling agents (treatment A: (3-aminopropyl)triethoxysilane and treatment E: (3-glycidyloxypropyl)trimethoxysilane). Fillers are incorporated at 30% by mass fraction, which corresponds to a good compromise between processability and expected flame retardancy. Six different formulations named PAK1,PAK1A,PAK1E,PAK2,PAK2A,PAK2E were realized.

2.2. Characterization

Tensile test specimens were cryo-fractured and the central zone of the samples (perpendicular to the flow direction) was observed using a Quanta SEM instrument under an accelerating voltage of 5kV. The injection process induces a preferential orientation of the fillers; we suppose that dispersion of the particles
PA6-Kaolinites composites: relation microstructure-properties

observed in the section qualify the volume particle size distribution. SEM images of nanocomposites reveal the presence of large aggregates well distributed of kaolinites stacks, at a higher magnitude it appears that these stacks are quite multidispersed and some platelets are detached from the stacks. For each samples, particle size distribution is obtained by image analysis for 3 scales factors: 100, 1000 and 25000 to describe particles diameter (d) from 1 to 80µm. For each composite a distribution and a cumulated density in d are obtained. This cumulative distribution can be easily fitted by a log-normal law and consequently a couple of parameters (mean (M) and standard deviation (SD)) describe each formulation. This statistical analysis leads to the definition of median diameter (dm), interparticular distance (L), elementary diameter (del) and level of agglomeration (A) [2]:

$$d_m = e^M, \quad L = d_m \left( \frac{\pi}{6d_{el}} \right)^{1/3} e^{\frac{S}{2d_{el}}} - e^{\frac{S}{d_{el}}}$$

Uniaxial tensile tests were conducted up to the rupture with a crosshead speed is equal to 1 mm/min. The software used is TestXpert® and allows the recording of time, load (F) and elongation (ε). The nominal stress is defined by the following expression: $$\sigma = F / S_0$$ where S0 is the initial sample ISO 527-2 1A section (40mm²). Young’s modulus (E) value is given by the slope of the curve giving F vs. axial ε (0.05%<ε<0.25%). Out of this range of elongation, the nominal stress reached a maximum (the yield stress) corresponding to $$\sigma_{yield}$$ at the deformation εyield.

For the instrumented Charpy impacts testing the specimen is impacted by an instrumented drop tower impact device CEAST9300 series (m=3.14kg, h=130mm) at a velocity of 1.6m/s to obtain a global parameter, the resilience J.

The fire retardancy of PA6 composites was characterized by cone calorimetry tests (irradiance 50kW/m²). Several parameters are obtained: Time To Ignition (TTI), Peak of Heat Release Rate (pHRR), Total Heat Release (THR) which is formally the integral of the HRR curve with respect to the time, Total Heat Evolved (THE) and Mass Loss Rate (MLR).

3. Results and discussion

The morphologies and mechanical/thermal properties of all the PA6 composites have been resumed in Tables 1 and 2. First of all particles are highly agglomerate in the composite: extrusion process protocol is not successful from this point of view. Sure enough, the smaller particles produce the bigger agglomerates. Excepted for the K1A particles, the surface treatment induces a reduction of the agglomerate size (dm).
Kaolinite filler incorporation leads to an enhancement of elastic properties. It’s seems that surface treatment doesn’t impact so much global material elasticity. In fact, as reported in the literature, the young modulus is evaluated at a low level of strain inducing a little perturbation of the interface area [3]. Considering results of table 2, there is no obvious relation between median diameter and Young modulus.

Usually, yield stress increases and yield strain decreases with the incorporation of well dispersed rigid particles. The reason reported in the literature is the good adhesion between fillers and matrix (which is responsible for the stress increasing) and the lower volume matrix restriction which is enable to deform (which is responsible for the strain decreasing). Some authors involve particle size and shape to explain the stress increasing [4]. The key parameter for the yield stress seems to be for our study the median diameter $d_m$ (Fig. 2a): $\sigma_{\text{yield}}$ depends linearly on the median diameter. Concerning the yield strain the same trend is observed for each kind of kaolinites: $\varepsilon_{\text{yield}}$ depends linearly on the level of aggregation (A) (Fig. 2b).
**PA6-Kaolinites composites: relation microstructure-properties**

Bibliography results reveal the incontestable relation between breakage and interfacial quality between fillers and matrix. It seems that rupture is first of all conditioned by the bigger particles [5]. There are even authors defining a morphological criterion in relation with the fragile/ductile composites breakdown [2]. According to these authors, a morphological analysis is performed from the lowest magnification (∼100) in order to qualify only bigger agglomerates dispersion. These results are summarized in Table 3 with the associated mode of failure.

**Table 3 : Morphological characteristics of the PA6 composites with the 100× magnification**

<table>
<thead>
<tr>
<th>Name</th>
<th>M(µm)</th>
<th>S_D</th>
<th>d_m(µm)</th>
<th>L(µm)</th>
<th>J(J)</th>
<th>Failure mode</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.9</td>
<td>-</td>
</tr>
<tr>
<td>PAK1</td>
<td>3.16</td>
<td>1.99</td>
<td>23.5</td>
<td>12.3</td>
<td>1723</td>
<td>ductile</td>
</tr>
<tr>
<td>PAK1A</td>
<td>3.13</td>
<td>1.94</td>
<td>22.9</td>
<td>7.2</td>
<td>1344</td>
<td>fragile</td>
</tr>
<tr>
<td>PAK1E</td>
<td>2.88</td>
<td>1.96</td>
<td>17.8</td>
<td>10.1</td>
<td>1149</td>
<td>fragile</td>
</tr>
<tr>
<td>PAK2</td>
<td>3.48</td>
<td>1.99</td>
<td>32.7</td>
<td>7.1</td>
<td>2588</td>
<td>ductile</td>
</tr>
<tr>
<td>PAK2A</td>
<td>2.66</td>
<td>1.81</td>
<td>14.3</td>
<td>8.</td>
<td>492</td>
<td>fragile</td>
</tr>
<tr>
<td>PAK2E</td>
<td>3.00</td>
<td>1.95</td>
<td>20.1</td>
<td>12.5</td>
<td>1303</td>
<td>fragile</td>
</tr>
</tbody>
</table>

We find a great correlation first between resilience and interparticular distance through a sigmoid function (Fig. 3a). This graph confirms the existence of a critical interparticular value related the ductile-brittle material transition.

The combustion process is greatly described by the evolution of HRR vs time. Regardless of their shape factor, the kaolinites (and even more the treated one) reduce the pHRR significantly. Moreover it seems that pHRR evolution behaves as median diameter (from ×100 magnification) (see Fig. 3b). The better is the dispersion of the bigger agglomerates, the lower is the pHRR. Some authors found qualitatively the same kind of results on PP/MMT composites even if there exists no theoretical background to describe the link between the pHRR reduction and particle dispersion [6]. Regarding the THR values reported in Table 2, lower values are obtained introducing kaolinites. This is a direct consequence of organic fillers (so...
non-combustible) incorporation. Finally, HEC of all composites does not change significantly indicating that the main action of kaolinite is in the condensed phase. A notable difference between composites is the TTI which never exceeds 2 mn; no correlation with the morphology has been found.

![Graph showing the relationship between resilience and interparticular distance](image1)
![Graph showing the relationship between pHRR and median diameter](image2)

**Figure 3**: (a) Resilience vs interparticular distance (b) pHRR vs median diameter

4. Conclusion

In this paper the influence of the microstructure on both flammability and mechanical properties is investigated. The mechanical testing reveals the strong relationship yield stress/strain, resilience and microstructure. The yield stress is clearly decreasing when the median diameter increases and the yield strain follows the same trend with the level of agglomeration. Dynamical and flammability testing however are sensitive to the biggest agglomerates: the resilience decreases when the interparticular distance increases and below a critical value (around 1500µm) the composites become fragile; the pHRR is reduced when a better dispersion of the biggest agglomerates is reached.

**REFERENCES**


