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# Chlorinated polyethylene/layered silicate nanocomposites: Poly(ε-caprolactone)-based "masterbatch" approach

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## Abstract

Chlorinated polyethylene (CPE)/organophilic-montmorillonite (Cloisite®30B (CL30B)) nanocomposites have been prepared by melt intercalation using (poly(ε-caprolactone), (PCL)) as CPE/clay compatibilizer. Actually, a high clay content masterbatch-based on PCL was first produced and then dispersed by melt blending within CPE. CPE/CL30B nanocomposites was also prepared by direct blending of CPE with CL30B for sake of comparison. All the composites were characterized by wide-angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM). The thermal stability of the nanocomposites was analyzed by thermogravimetric analysis (TGA) while the mechanical properties were assessed by tensile testing. When using low molecular mass PCL chains as compatibilizer, the nanocomposites displayed a rather intercalated structure but their ultimate properties remained unchanged whereas with high molecular weight PCL chains, clay delamination was favoured and led to an increase of both thermal and mechanical properties of the resulting nanocomposites.

*Keywords:* Chlorinated polyethylene; Poly(ε-caprolactone); Organophilic-montmorillonite; Nanocomposites, clay; Melt intercalation, masterbatch; Compatibilizer

## 1. Introduction

Polymer/clay nanocomposites have attracted great interest because of their potential to improve polymer strength, stiffness and thermal properties [1–3], barrier resistance [4,5] and flame retardancy [6], at especially low filler content (3–5 wt%), compared to traditional polymer micron-sized composites (10–70 wt%).

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Smectite-type layered silicates, such as montmorillonite (MMT), are among the most commonly used for the preparation of nanocomposites, because of their very high active surface area and the high aspect ratio of their silicate nanolayers. $Na^+$-montmorillonite is a crystalline 2:1 layered mineral, which consists of regular stacks of aluminosilicate sheets with a framework composed of a central alumina octahedral layer sandwiched between two silica tetrahedral layers. The thickness of the constitutive lamellae is around 1 nm and lateral dimension may vary from 20 nm to around 1 μm depending on the silicate nature. Isomorphic substitution within the layers generates negative charges that are counterbalanced by sodium cations located in the interlayer spacings.

In order to improve the polymer/clay compatibility, cation exchange reaction between sodium cations and an alkylammonium salt is often required. The reinforcing action of organo-modified clays has been investigated for a large variety of polymer matrices including polyolefins [7–10], polyesters [11–14], etc...

The two strategies most usually used for the polymer/clay nanocomposites preparation are *in situ* intercalative polymerization [15] and melt intercalation of preformed polymers [16]. For the first approach, the organo-clay is swollen within the monomer, either in liquid state or in solution, followed by the *in situ* polymerization initiated either thermally or by addition of a suitable initiator or catalyst fixed within the interlayer spacing [15]. The second strategy consists in mixing the layered silicates with the molten polymer. Depending on the nanoscale dispersion of the aluminosilicate sheets, nanocomposites can exhibit two extreme morphologies, i.e., an intercalated structure or a delaminated structure also called exfoliated structure [1].

Chlorinated polyethylene (CPE), obtained by free-radical substitution of hydrogen atoms of polyethylene [17], is a polymer mainly used in thermoplastic processes to modify impact properties of rigid poly(vinyl chloride) for applications such as vinyl siding and window profiles, but also in film applications, automotive, cable jacket and industrial sheet because of its excellent resistance to ozone, UV radiation and oil [18]. However, the loss of hydrochloric acid, at temperature higher to 150 °C, represents CPE major drawback [19] that limits its use. The most common way to overcome such a drawback is to use it in presence of stabilizers (hindered phenols, talc, magnesium oxide, epoxidized soybean oil, ...).

Preparation of CPE/clay nanocomposites offers a novel approach to obtain new materials with improved mechanical and fire resistance properties, but only few studies have been reported so far for CPE matrices in comparison with other polymer matrices. Kim and White [20] prepared CPE/layered silicate nanocomposites with natural and organo-treated MMT by melt blending and discussed the mechanical properties enhancement with organo-clays. On another side, the use of masterbatches where a high clay content is premixed/dispersed in a polymer known to behave as compatibilizer for the selected matrix has recently been reported for improving the nanocomposite structure and the related performances [21–23]. Precisely, poly(ε-caprolactone) (PCL) might be a good compatibilizing agent, owing to its known miscibility with CPE [24]. This paper presents the preparation of CPE/organo-clay nanocomposites via the PCL-based masterbatch approach to achieve high degree of clay dispersion and exfoliation within the CPE matrix. It focuses on the preparation of highly-filled (25 wt% inorganics) PCL/organo-clay masterbatch by melt blending, followed by its redispersion in a CPE commercial matrix. Morphological as well as thermal and mechanical properties of the resulting (nano)composites are studied as well.

## 2. Experimental part

### 2.1. Materials

CPE usually originates from the chlorination of linear high-density polyethylene suspension. CPE used in this study, was supplied by Dupont–Dow Elastomers (Tyrin®3652 with 36 wt% chlorine and stabilized by calcium stereate and talc). Its limited residual crystallinity and low glass transition induce elastomeric properties. The CPE was systematically further stabilized by 4 phr Lankroflex®E2307 (epoxidized soybean oil) supplied by Brenntag. Cloisite®30B (CL30B), an organo-modified montmorillonite with 21 wt% of methyl bis(2-hydroxyethyl) tallowalkyl ammonium cations was supplied by Southern Clay Products. Commercial grades of poly(ε-caprolactone) (CAPA®2402 ($M_n = 4000$ g mol$^{-1}$) and CAPA®6500 ($M_n = 50{,}000$ g mol$^{-1}$)) were obtained from Solvay Interox. In order to differentiate these two commercial PCL grade, we note PCL4000 and PCL50000 for CAPA®2402 and CAPA®6500, respectively.

### 2.2. Melt compounding and processing conditions

PCL/CL30B masterbatches and CPE/layered silicate nanocomposites were melt-mixed using a Brabender® internal mixer operating at 175 °C for 10 min with a rotation speed of 75 rpm. Recovered samples were then compression-molded for 2 min 30 s at 175 °C under 150 bar, followed by cold pressing at 15 °C under 150 bar for 5 min, to obtain 3 mm-thick samples.

### 2.3. Characterization

Wide-angle X-ray diffraction (WAXD) was used to identify the structures of polymer–clay nanocomposites. WAXD patterns were recorded between 1.65° and 30° with a Siemens D5000 diffractometer and Cu $K_\alpha$ radiation ($\lambda = 1.\ 5406$ Å).

TEM micrographs analyses were performed with a Philips CM100 apparatus using an acceleration voltage of 100 kV. Ultrathin sections of the composites (ca. 80 nm thick) were cut at −100 °C from 3 mm thick hot-pressed plates with a LEICA ultra-cryomicrotome equipped with a diamond knife.

Thermogravimetric analysis (TGA) was performed under air at a heating rate of 20 °C/min from room temperature to 700 °C by using a Hi-Res TGA 2950 device from TA Instruments.

Differential scanning calorimetry (DSC) was carried out using DSC Q 100 apparatus of TA Instruments under a nitrogen atmosphere; DSC data are reported for the second heating run from −80 to 150 °C at 10°/min.

The stress–strain curves of stabilized CPE and related (nano)composites filled with PCL/CL30B were recorded at 20 °C at a constant deformation rate of 50 mm/min with a Lloyd LR 10 K tensile tester using dumbbell-shaped specimens (ASTM 638 type V norm) obtained by die cutting of compression-molded 3 mm-thick plates. All tensile data were calculated from the average of five independent measurements; the relative errors committed on each data are reported as well.

## 3. Results and discussion

### 3.1. Miscibility of CPE with PCL

Interestingly, CPE and PCL polymers have been reported to be miscible [24]. However, the miscibility highly depends on the nature of the CPE used, the PCL molecular weight, and the blending conditions. Therefore, binary blends of Tyrin®3652 with PCL characterized by two different molecular weights (ca. 4000 and 50000 g mol$^{-1}$) have been prepared and characterized by DSC in order to evaluate their degree of miscibility. For all the studied blends (from 3 to 20 wt% PCL), only one $T_g$ is observed, which value is located in between $T_{gCPE}$ and $T_{gPCL}$ (Fig. 1 and Table 1). This result indicates a good miscibility between CPE and PCL. However, in the case of the low molecular weight (4000 g mol$^{-1}$) and high PCL content (20 wt%) a

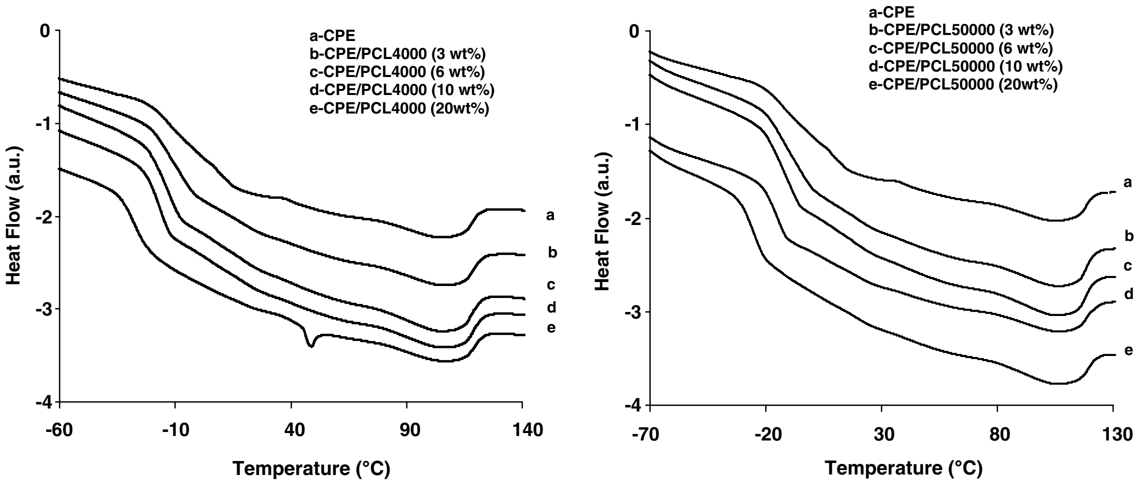

Fig. 1. DSC thermograms of CPE/PCL4000 and CPE/PCL50000 blends.

Table 1
Glass transition temperature ($T_g$) of CPE/PCL4000 and CPE/PCL50000 blends

| Composition | CPE/PCL4000<br>$T_g$ (°C) | CPE/PCL50000<br>$T_g$ (°C) |
|---|---|---|
| 100/0 | −5.5 | −5.5 |
| 97/3 | −12.1 | −11.1 |
| 94/6 | −14.9 | −13.1 |
| 90/10 | −17.8 | −16.0 |
| 80/20 | −27.8 | −26.1 |
| 0/100 | −62.7 | −61.3 |

tiny melting peak appears at 48 °C revealing the presence of immiscible PCL crystalline phase in the blend with CPE. These observations show that a high relative content in shorter PCL chains leads to partial miscibility of PCL and CPE. Accordingly, the CPE/PCL polymer blends considered in this study have been carried out within the miscibility window, i.e., 8.5 wt% of PCL.

### 3.2. CPE/PCL–organo-clay nanocomposites

CPE/PCL/CL30B nanocomposites have been produced by melt blending the PCL/CL30B masterbatches (25 wt% of inorganics) with Tyrin®3652. The blend composition was such that the final clay content was always kept at 3 wt%. As a reference, a CPE/clay (nano)composite was also prepared by melt blending Tyrin®3652 with CL30B (CPE/CL30B, 3 wt% in inorganics).

### 3.3. Morphological characterization

The morphological characterization of CPE/CL30B compositions by wide-angle X-ray diffraction (WAXD) and transmission electron microscopy (TEM) show an increase in the interlayer spacing of the organo-modified clay owing to the intercalation of (extended) polymer chains between the silicate layers. As a matter of fact, on the diffractogram (Fig. 2), the peak related to interlayer spacings is shifted from $2\theta = 4.8°$ for the neat Cloisite®30B to a lower angle of $2\theta = 2.1°$ for CPE/CL30B blend (see arrow), which is associated to a $d$ spacing of 4.2 nm. This intercalated structure is confirmed by TEM analysis (Fig. 3) at high magnification, where a well-ordered multilayer morphology with alternating polymeric (light clear regions) and inorganic layers (dark regions) can be observed.

These results show that direct melt intercalation only leads to intercalated nanocomposites.

The CPE/PCL/CL30B nanocomposites, thus obtained in presence of PCL, have been also analyzed by WAXD and TEM in order to assess the compatibilizing effect of the PCL on the extent of the clay dispersion in the CPE matrix. Fig. 2 shows

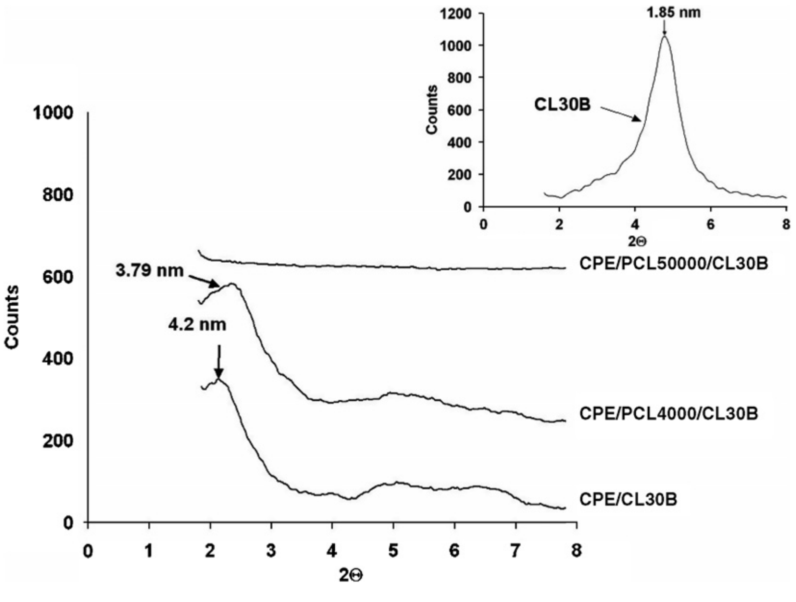

Fig. 2. XRD patterns for CL30B, CPE/CL30B, CPE/PCL4000/CL30B and CPE/PCL50000/CL30B nanocomposites (3 wt% in inorganics; representing 8.5 wt% PCL).

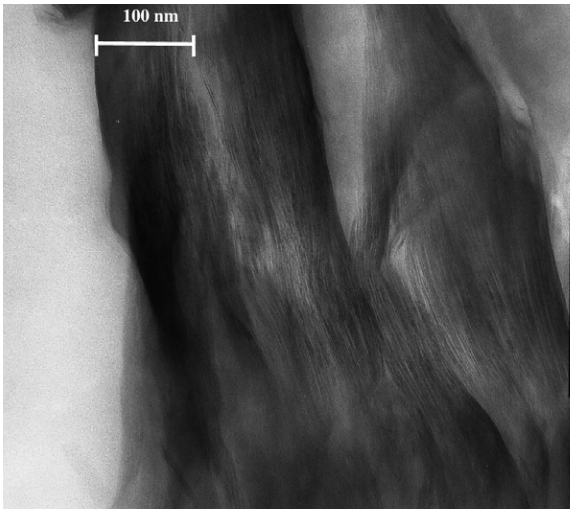

Fig. 3. TEM images of the CPE/CL30B (3 wt% in inorganics) at high magnification.

the WAXD patterns for the nanocomposites containing 3 wt% of CL30B initially dispersed in from the masterbatches prepared with the two commercial grades of PCL.

The diffractogram of CPE/PCL4000/CL30B nanocomposite highlights an increase of the interlayer spacing from 1.85 to 3.79 nm, which attests for the formation of an intercalated structure. In the case of CPE/PCL50000/CL30B nanocomposite, no diffraction peak at low $2\theta$ angle is observed anymore (Fig. 2). This observation seems to indicate that high molar mass PCL chains favour clay delamination in the polymer matrix. Comparative TEM analyses of CPE/CL30B, CPE/PCL4000/CL30B and CPE/PCL50000/CL30B are shown in Fig. 4a–c, respectively. Before discussing on these images, we have to note, here, the presence of some stabilizers (calcium stereate (round object) and talc (see arrow)). It will be necessary to take in account the presence of this talc stabilizer for TEM (nano)composites interpretation. So, based on these representative TEM images, the presence of smaller tactoids (stacks of layers) relatively well dispersed throughout the CPE matrix as well as a significant amount of exfoliated nanoplatelets can be observed for CPE/PCL50000/CL30B (Fig. 4c). Although the layered structure of CL30B in such domains is most probably disordered, the silicates are not completely exfoliated into randomly distributed individual sheets as supported by WAXD analysis. These results thus show that the "physical" method for the masterbatch preparation does not allow reaching complete exfoliation of the silicate sheets within CPE matrix. However, the use of high molar mass of PCL leads to a larger destructuration of these layers, which is not observed for the lower molecular masses.

### 3.4. Thermogravimetric analysis

The thermal degradation behaviour of CPE, CPE/CL30B and CPE/PCL/CL30B (nano)composites has been studied by thermogravimetric analysis (TGA) with a heating rate of 20 °C/min under air flow. As neat PVC [25], the thermo-degradation of neat CPE and its nanocomposites takes place in two main steps (Fig. 5). The first step, attributed to the volatilization of hydrogen chloride molecules (HCl), is observed between 250 and 375 °C and leads to the formation of carbon–carbon double bonds along the polymer backbone. In a second step

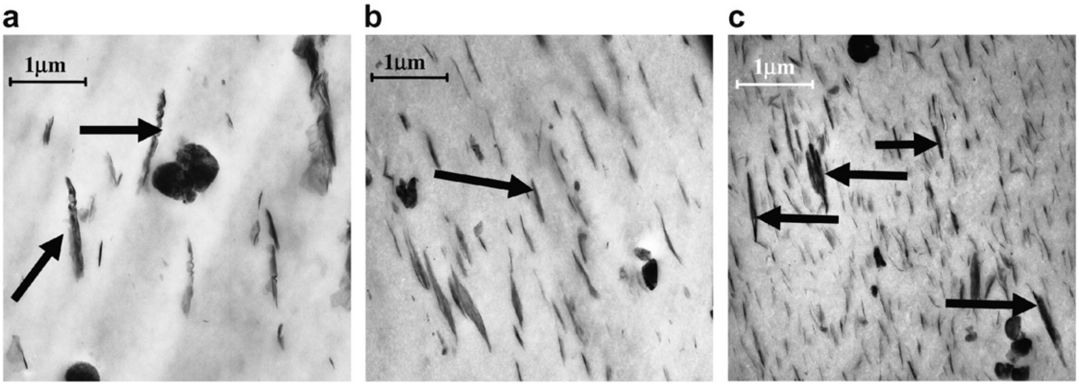

Fig. 4. TEM images at low magnification of: (a) CPE/CL30B; (b) CPE/PCL4000/CL30B; (c) CPE/PCL50000/CL30B (3 wt% in inorganics; representing 8.5 wt% PCL in (b) and (c). The round black objects visible throughout both samples represent the calcium stereate stabilizer and some long objects represent talc stabilizer (see arrows).

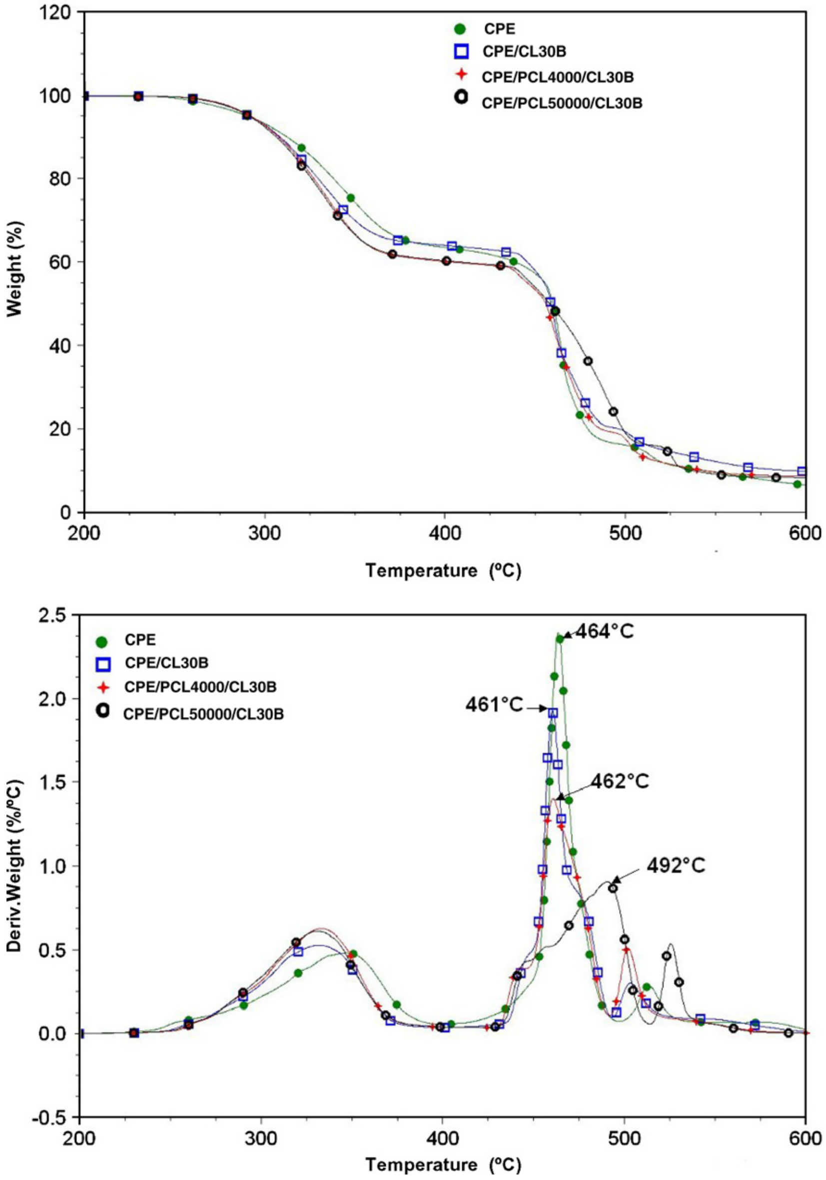

Fig. 5. Thermogravimetric analysis of neat CPE, CPE/CL30B, CPE/PCL4000/CL30B and CPE/PCL50000/CL30B nanocomposites under air flow at 20 °C/min (3 wt% of inorganics; representing 8.5 wt% of PCL).

(between 460 and 500 °C), the unsaturated chains are oxidized and volatilized through statistic chain breaking.

For CPE nanocomposites based on CL30B, the presence of clay tends to promote the dehydrochlorination at lower temperature. Thermal decomposition of the quaternary ammonium salt according to Hofmann degradation mechanism leading to the formation of an amine can explain such behaviour [26]. The resulting amine can initiate the dehydrochlorination of CPE at a lower temperature. With regard to the second degradation, CL30B does not seem to influence significantly the degradation of the hydrocarbon backbone. In conclusion, the addition of CL30B to the CPE matrix does not improve thermal stability but activates the loss of HCl.

Fig. 5 also shows the thermograms for the nanocomposites that contain 3 wt% of inorganic material as introduced via the PCL/CL30B masterbatches. The first thermo-degradation of masterbatch-based CPE nanocomposites occurs at about the same temperature as neat CPE or CPE/CL30B

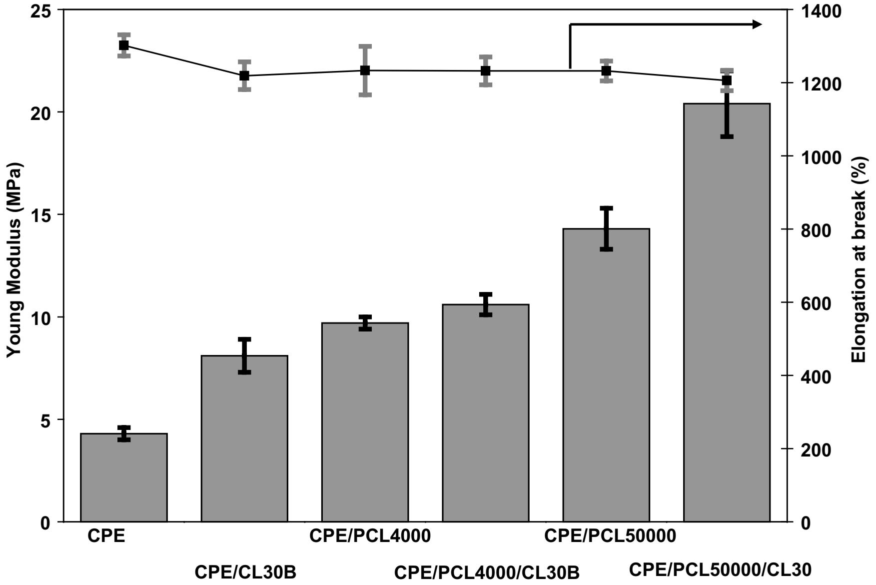

Fig. 6. Tensile properties of CPE, CPE/CL30B, CPE/PCL4000, CPE/PCL4000/CL30B, CPE/PCL50000, CPE/PCL50000/CL30B (nano)composites prepared by direct melt intercalation (3 wt% of inorganics; representing 8.5 wt% of PCL).

nanocomposites. Nevertheless, the weight loss for this degradation is more important with respect to both CPE matrix and CPE/CL30B nanocomposites. This observation can be explained by the simple fact that PCL chains undergo a thermal degradation process (ester pyrolysis) [27] in the same temperature range as the HCl loss of CPE. However, the most interesting information issued from the thermograms is the shift of the second degradation by ca. 30 °C towards higher temperature when the higher molecular mass PCL (PCL50000) is used in the masterbatche. The origin of such a shift is attributed to well dispersed clay layers, which hinder diffusion of volatile decomposition products as well as oxygen penetration within the nanocomposites upon thermal degradation.

### 3.5. Mechanical properties

Fig. 6 reports the mechanical properties for neat CPE, CPE/PCL binary blends, CPE/CL30B and CPE/PCL/CL30B nanocomposites, which have been determined by tensile testing. From the values of elongation at break, ca. 1200% CPE and related compositions proves to undergo large deformations typical of a ductile polymer.

The addition of a tiny amount of CL30B (3 wt% in inorganics), which has a much higher Young's modulus than the CPE matrix practically leads to twofold increase of the material stiffness. Such reinforcement is also observed by addition of the same amount of inorganic material introduced via the PCL/CL30B masterbatches. However, a higher Young's modulus is recorded when high molar mass of PCL (PCL50000) is used as compatibilizer (a threefold increase of the Young's modulus is recorded). In contrast, the elongation at break of the different compositions is not significantly influenced by the addition of CL30B or PCL/CL30B masterbatches. It does mean that, CPE remains ductile with an elongation at break higher than 1100%. It comes out from all these analyses that the addition of highly-filled PCL/CL30B masterbatches allows for reaching a particularly attractive set of properties, i.e., significant improvement of the material rigidity while preserving high ductility.

## 4. Conclusions

CPE/CL30B and CPE/PCL/CL30B nanocomposites have been successfully prepared by direct melt intercalation. From XRD and TEM results, intercalated structures are obtained for both nanocomposites preparation (i.e., direct melt blending of either CPE/CL30B or CPE/PCL4000/CL30B masterbatch). However, a larger extent in clay destructuration and delamination is observed for the nanocomposite based on CPE/PCL50000/CL30B (thus with higher molecular weight PCL compatibilizer), correlated with a large improvement of mechanical properties and thermal properties.

Even if this approach does not lead to strictly exfoliated nanocomposites, another complementary approach based on the production of PCL-g-clay where the polyester chains are surface-grafted on the organo-modified clay layers proved to provide much better nanocomposite structures. Such PCL grafting can be carried out by *in situ* intercalative ring-opening polymerization of ε-caprolactone as initiated by hydroxyl functions anchored onto the ammonium cations [28,29]. This investigation will be the subject of another forthcoming paper.

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