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Chlorinated polyethylene nanocomposites using PCL/clay nanohybrid masterbatches

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ABSTRACT

Exfoliated nanocomposites were prepared by dispersion of poly(ϵ -caprolactone) (PCL) grafted montmorillonite nanohybrids used as masterbatches in chlorinated polyethylene (CPE). The PCL-grafted clay nanohybrids with high inorganic content were synthesized by *in situ* intercalative polymerization of ϵ -caprolactone between silicate layers organo-modified by alkylammonium cations bearing two hydroxyl functions. The polymerization was initiated by tin alcoholate species derived from the exchange reaction of tin(II) bis(2-ethylhexanoate) with the hydroxyl groups borne by the ammonium cations that organo-modified the clay. These highly filled PCL nanocomposites (25 wt% in inorganics) were dispersed as masterbatches in commercial chlorinated polyethylene by melt blending. CPE-based nanocomposites containing 3–5 wt% of inorganics have been prepared. The formation of exfoliated nanocomposites was assessed both by wide-angle X-ray diffraction and transmission electron microscopy. The thermal and thermo-mechanical properties were studied as a function of the filler content, by differential scanning calorimetry and dynamic mechanical analysis, respectively. The mechanical properties were also assessed by tensile tests. The Young's modulus of CPE is increased by a decade when a PCL-grafted clay masterbatch is exfoliated to reach 5 wt% of clay in the resulting nanocomposite. The influence of PCL-grafting on the properties of these nanocomposites was investigated by comparison with materials obtained with ungrafted-PCL.

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1. Introduction

Polymer nanocomposites constitute a class of polymers reinforced with a small amount (typically less than 10% in weight) of particles with nanometric size. Over the past

years [1–4], the scientific community has largely focused on the polymer-clay nanocomposites owing to the improved properties that can be obtained with such nano-dimensional materials. Among other improvements, tensile, thermal and flame retardancy properties are increased [1–5] while gas transport properties can be significantly decreased [6,7]. For this purpose, layered silicate minerals, such as sodium montmorillonite (MMT) organo-modified by adequately chosen alkylammonium cations, are extensively used. Indeed, this crystalline 2:1 layered clay mineral is environmentally friendly, readily available in large quantities and its intercalation chemistry has been

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well studied [8]. The reinforcing action of these organo-modified clays has been investigated in a large variety of polymer matrices including polyolefins [9–12], polyesters [13–16], etc.

Depending on the nano-scale dispersion of the layered silicate, the whole spectrum of structure ranging from intercalated to exfoliated nanocomposites can be observed [1,17]. However, only delaminated structures lead to the complete and uniform dispersion of the individual silicate layers in a continuous polymer matrix and optimization of the mechanical and barrier properties.

Chlorinated polyethylene (CPE), obtained by free-radical substitution of hydrogen atoms of polyethylene by chlorine [18], is a polymer mainly used in thermoplastic processes, to modify the impact properties of rigid poly(vinyl chloride) (PVC) for applications such as vinyl siding and window profiles, but also in film and automotive applications, cable jackets and industrial sheets, because of its excellent resistance to ozone, UV radiation and oil [19]. However, the loss of hydrochloric acid, at temperatures higher than 150 °C, represents a major drawback [20] which limits the use of CPE. The most common way to overcome such drawback is to add stabilizers (hindered phenols, magnesium oxide, epoxidized soybean oil etc.). Furthermore, talc is commonly used as an anti-agglomeration additive in the case of suspension chlorination of PE [21].

The preparation of CPE/clay nanocomposites offers a novel approach to obtain new materials with improved mechanical and fire resistance properties, but only a few studies have been reported so far. Kim and White [22] prepared CPE/layered silicate nanocomposites with natural and organo-treated MMT by melt blending and discussed the mechanical properties enhancement with organoclays. These authors suggest that the CPE polymer chains largely intercalate the clay layers of their organoclay (Cloisite®30B). However, a close examination of the WAXD pattern points out a diffraction peak at $2\theta \approx 6^\circ$, characteristic for the degradation of the intercalated ammoniums, as described later on in other publications [23,24].

In order to improve the nanocomposite structure (exfoliation) and its related performances, it has been suggested to use masterbatches where a high clay content is pre-mixed/dispersed in a polymer known to behave as a compatibilizer for the selected matrix [25,26]. Owing to its known miscibility with CPE [27], poly(ϵ -caprolactone) (PCL) can be considered as a good compatibilizing agent.

Highly destructured and even exfoliated nanocomposites based on PCL can be prepared by *in situ* polymerization of ϵ -caprolactone (CL) in the presence of montmorillonite modified by alkylammonium cations containing a carboxylic acid [28] or hydroxyl end-group(s) [29,30]. Therefore, largely exfoliated CPE/clay nanocomposites might be prepared by combining the *in situ* intercalative polymerization of CL within the organoclay to prepare highly destructured masterbatches, followed by melt processing of this masterbatch with the CPE matrix.

Such a masterbatch strategy has been used with PVC nanocomposites by Lepoittevin et al. [17] with interesting results. Grafted-PCL masterbatches with high clay content (32 wt%) were obtained *by in situ* intercalative polymeriza-

tion of CL in the presence of $\text{Bu}_2\text{Sn}(\text{MeO})_2$ catalyst, then dispersed in a commercial PVC matrix to prepare largely exfoliated PVC/clay nanocomposites with improved mechanical properties. The conditions necessary to control all the molecular parameters of the grafted polyester chains, i.e., control over the grafting efficiency, grafting density, length of the grafted polyester chains, have been extensively studied by Lepoittevin et al. [14,15].

Based on those studies, we propose a two-step preparation of CPE-based nanocomposites. In a first step, the organomodified silicate layers are delaminated by the catalyzed polymerization of CL directly initiated from hydroxyl groups borne by the exchanged ammonium cations, in order to prepare masterbatches with a filler content of about 25 wt%. Then, the resulting polyester-grafted organoclay masterbatches are dispersed in a commercial CPE matrix by melt blending for reaching 3 and 5 wt% of clay (and thus 8.4 and 13.7 wt% of PCL, respectively). The morphological, thermal and mechanical properties of the resulting materials have been investigated. To assess the role of PCL-grafting and of the different components of the nanocomposites (CPE, clay, and PCL) on the materials properties, composites of lower complexity were also prepared and analyzed: CPE/PCL blends, CPE/clay blends, and CPE nanocomposites obtained from a non-grafted-PCL/clay masterbatch.

2. Experimental part

2.1. Materials

ϵ -Caprolactone (CL, Fluka) was dried over CaH_2 and distilled under reduced pressure prior to use. Tin (II) bis(2-ethylhexanoate), also known as tin(octoate) ($\text{Sn}(\text{Oct})_2$), was purchased from Fluka, diluted with dried toluene and stored under nitrogen atmosphere.

Commercial CPE, Tyrin®3611P (36 wt% chlorine), obtained from a chlorination process of linear high-density polyethylene, was supplied by Dupont-Dow Elastomers. The supplier notes the presence of talc in the CPE matrix (<7 wt%). CAPA®2402, a PCL oligomer ($M_n = 4000 \text{ g mol}^{-1}$) was obtained from Solvay Interlox. Cloisite®30B (CL30B), a montmorillonite organomodified by 23.4 wt% of methyl bis(2-hydroxyethyl)tallowalkyl ammonium cations was supplied by Southern Clay Products.

2.2. Preparation of poly(ϵ -caprolactone)/clay masterbatches

Poly(ϵ -caprolactone) (PCL) has been grafted on the organoclay surface by ring-opening polymerization of ϵ -caprolactone (CL) in the presence of $\text{Sn}(\text{Oct})_2$ according to a 'coordination-insertion' mechanism in appropriate conditions [14].

Before polymerization, the organo-modified montmorillonite (CL30B) (5.25 g) was dried under vacuum (10^{-2} mm Hg) at 70 °C overnight in a glass reactor equipped with a magnetic stirrer. A toluene solution of $\text{Sn}(\text{Oct})_2$ (7 mL, $3.5 \cdot 10^{-4} \text{ mol}$) was then added to the clay under nitrogen flow. A given amount of ϵ -caprolactone (11 mL, 0.09 mol) was finally added such that the $[\text{monomer}]_0/[\text{Sn}]_0$ molar ratio was 283 and the polymerization

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