Poly(ε-caprolactone)/clay nanocomposites prepared by melt intercalation: mechanical, thermal and rheological properties

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Abstract

(Nano)composites of poly(ε-caprolactone) (PCL) were prepared by melt blending the polymer with natural Na^+ montmorillonite and montmorillonite modified by hydrogenated tallowalkyl (HTA)-based quaternary ammonium cations, such as dimethyl 2-ethylhexyl HTA ammonium and methyl bis(2-hydroxyethyl) HTA ammonium. Microcomposites or nanocomposites were prepared depending on whether neat or modified montmorillonites was used, as assessed by X-ray diffraction and transmission electron microscopy. Mechanical and thermal properties were studied as a function of the filler content by tensile testing, Izod impact testing, thermogravimetric analysis and differential scanning calorimetry. The rheological behaviour at 80 °C was also analysed in relation to the structure and content of the layered silicate. Effect of exfoliated silicates on the mechanical properties, thermal stability and flame resistance of PCL was considered. Stiffness and thermal stability improved with the filler loading until a content of 5 wt%. Further loading resulted in the levelling off and possibly in a decrease of these properties. A marked charring effect was observed upon exposure to a flame.

Keywords: Nanocomposites; Poly(ε-caprolactone); Melt intercalation

1. Introduction

Nanocomposites have emerged as a very efficient strategy to upgrade properties of synthetic polymers to the point where performances exceed largely the ones of conventional composites. One additional advantage is that relatively small amounts of layered silicates, typically 3–5 wt%, are required as result of the nanometric scale dispersion of the filler in the matrix [1-2]. Among other improvements, tensile properties are increased, permeability to oxygen and other gases is decreased and thermal stability and flame retardancy are enhanced.

Montmorillonite is a clay most commonly used in polymer nanocomposites preparation. It is a crystalline 2:1 layered clay mineral with a central alumina octahedral sheet sandwiched between two silica tetrahedral sheets. When these nanoparticles are dispersed in a polymer, they are either intercalated by macromolecules or exfoliated. Therefore, intercalated structures show regularly alternating layered silicates and polymer chains in contrast to exfoliated structures in which the individual clay layers are delaminated and dispersed in the polymer matrix. The best performances are commonly observed for the exfoliated nanocomposites. The two extreme situations can however, coexist in the same material.

Three main techniques can be used to prepare polymer/clay nanocomposites [3]: melt intercalation, exfoliation–adsorption and in situ intercalative polymerisation. In the first two techniques, the preformed polymer is mixed with the clay either in the molten state or in solution. In the third approach, clay is dispersed in the monomer which is then polymerised. In this study, layered silicate nanocomposites have been prepared by melt intercalation, as previously reported for a variety of polymers, including poly(styrene) [4], nylon-6 [5], ethylene vinyl-acetate copolymers [6], poly(propylene) [7], poly(etherimide) [8], poly(styrene-*b*-butadiene) [9], poly(ethylene oxide) [10],… The polymer–silicate compatibility is promoted by an ion-exchange reaction of the silicate interlayer sodium cations with alkyl ammonium cations.

Because of rapidly increasing environmental concerns, biodegradable and biocompatible synthetic polymers are receiving a growing attention such as aliphatic polyesters based on lactones and lactides. Performances of these polymers, e.g. poly(ε-caprolactone) (PCL), can be greatly enhanced by nanodispersion of layered silicates. In

this respect, melt intercalation is an environmentally friendly preparation technique because no solvent is required.

According to Giannelis et al. [11], PCL-based nanocomposites can be prepared by in situ intercalative polymerisation of ε-caprolactone in the presence of a protonated ω-amino-acid exchanged montmorillonite. These authors [12] also reported on the direct preparation of PCL nanocomposites by heating Cr^{3+}-fluorohectorite in the presence of ε-caprolactone. Recently, some of us published preliminary results on melt intercalation of montmorillonites by poly(ε-caprolactone) [13]. Several modified montmorillonites bearing either non-functional long alkyl chains or chains terminated by carboxylic acid or hydroxyl groups were melt blended with PCL. This study highlighted the key role of both the structure of the ammonium used to modify the layered silicates and the dispersion technique.

This paper deals with the characterisation of PCL-based nanocomposites prepared by melt intercalation of PCL into montmorillonite organo-modified by alkyl chains end-capped by a hydroxyl group or not, i.e. methyl bis(2-hydroxyethyl) (hydrogenated tallowalkyl) ammonium and dimethyl 2-ethylhexyl (hydrogenated tallowalkyl) ammonium, respectively. For the sake of comparison, PCL microcomposites filled with natural sodium montmorillonite have been prepared under the same experimental conditions. Mechanical, thermal and rheological properties of the PCL-based nano- and microcomposites have been studied as a function of the clay content.

2. Experimental part

2.1. Materials

Commercial grade poly(ε-caprolactone) (CAPA®650) was supplied by Solvay Chemicals sector-SBU. The number average molar mass was 49,000 with a polydispersity of 1.4, as determined by size exclusion chromatography. The clay minerals were supplied by Southern Clay Products (Texas USA). The cation-exchange capacity (CEC) of unmodified montmorillonite-Na (Cloisite®Na) (MMT–Na) was 90 mequiv./100 g. The two organo-modified montmorillonites were Cloisite®25A (MMT–Alk; modified by dimethyl 2-ethylhexyl (HTA) ammonium cation) and Cloisite®30B (MMT–(OH)$_2$; modified by methyl bis(2-hydroxyethyl) (HTA) ammonium cation where HTA stands for hydrogenated tallowalkyl). Content of organics was 26 and 21 wt% for Cloisite®25A and Cloisite®30B, respectively, as determined by thermogravimetric analysis (TGA).

2.2. Composite preparation

The PCL-layered silicate composites were prepared by mechanical kneading with an Agila two-roll mill at 130 °C for 10 min. The collected molten materials were compression-molded into 3 mm-thick plates by hot-pressing at 100 °C under 150 bar for 10s, then under 30 bar for 10 additional seconds, followed by cold pressing at 15 °C under 30 bar for 5 min. Composites containing 1, 3, 5 and 10 wt% of montmorillonite were prepared. The inorganic content of each composite was analysed by TGA under air flow and calculated from the residue left at 600 °C.

2.3. Characterisation

Clay dispersion was analysed by X-ray diffraction (XRD) and transmission electron microscopy (TEM). XRD patterns were recorded by a Siemens D5000 diffractometer equipped with an X-ray generator (λ=0.15406 nm) between 1.5 and 30° by step of 0.04°. Sheets were hot-pressed at 100 °C for this purpose. TEM observations were performed with a Philips CM100 apparatus using an acceleration voltage of 100 kV. Ultrathin sections of nanocomposites (ca. 80 nm) were prepared by ultramicrotomy at −130 °C of the 3 mm-thick hot-pressed plates (Reichert-Jung Ultracut 3E, FC4E ultra-cryomicrotome equipped with a diamond knife).

TGA was performed under air (74 cm^3/min) at a heating rate of 20 K/min from room temperature up to 600 °C by using a Hi-Res TGA 2950 from TA Instruments. Thermal behaviour was analysed by differential scanning calorimetry (DSC) (DSC 2920 from TA Instruments) at a heating rate of 10 K/min under nitrogen from −120 to 140 °C.

Tensile testing was performed at 20 °C at a constant rate of 50 mm/min with a Lloyd LR 10K tensile tester and dumbbell-shaped specimens (ASTM 638 type V norm). Notched-Izod impact tests were carried out at 20 °C
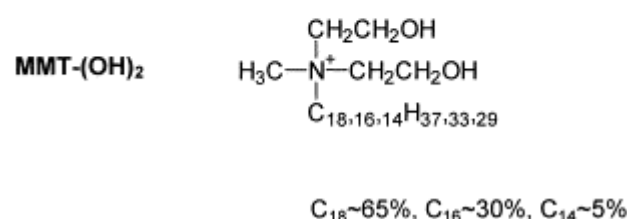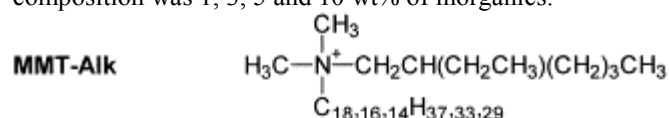
with a pendulum-type impact tester Ray-Ran 2500. Samples were prepared according to the ASTM D256 B norm. Tensile and impact data were the average of five independent measurements.

One millimetre-thick samples with a diameter of 25 mm were pressed for 10 min at 100 °C and analysed by a Rheometric Scientific (ARES), strain-controlled rheometer equipped with parallel plates. Each sample was analysed at 80 °C in a frequency range from 16 to 10^{-2} Hz (deformation: 1%).

3. Results and discussion

3.1. Preparation of the PCL/clay nanocomposites

Composites were prepared by melt blending. PCL and a known amount of montmorillonite were mechanically kneaded on a two-roll mill at 130 °C. Various amounts of natural montmorillonite (MMT–Na) and montmorillonites modified by dimethyl 2-ethylhexyl (HTA) ammonium (MMT–Alk) and by methyl bis(2-hydroxyethyl) (HTA) ammonium (MMT–$(OH)_2$), respectively, were dispersed in PCL, such that the final composition was 1, 3, 5 and 10 wt% of inorganics.

MMT-Alk

$$H_3C-\overset{\overset{\displaystyle CH_3}{|}}{\underset{\underset{\displaystyle C_{18,16,14}H_{37,33,29}}{|}}{N^+}}-CH_2CH(CH_2CH_3)(CH_2)_3CH_3$$

MMT-$(OH)_2$

$$H_3C-\overset{\overset{\displaystyle CH_2CH_2OH}{|}}{\underset{\underset{\displaystyle C_{18,16,14}H_{37,33,29}}{|}}{N^+}}-CH_2CH_2OH$$

$C_{18} \sim 65\%$, $C_{16} \sim 30\%$, $C_{14} \sim 5\%$

3.2. Analysis of the clay dispersion

Composites were analysed by XRD and TEM in order to estimate the extent of the filler dispersion. As previously reported [13], microcomposite results from the melt dispersion of natural sodium montmorillonite (MMT–Na) into PCL. Indeed, the interlayer spacing of MMT remains unchanged and micron-size particles are randomly dispersed in the polyester matrix.

Fig. 1 shows XRD patterns recorded for the MMT–Alk organoclay and PCL-based composites filled with 1, 3, 5 and 10 wt% MMT–Alk (relative to inorganics). The interlayer spacing of the MMT–Alk organoclay is ca. 18.6 Å. After melt blending with PCL, a broad peak is observed at 27–28 Å which indicates that PCL chains are intercalated between the clay layers. The clay dispersion was also observed by TEM (Fig. 2). In addition to small stacks of intercalated montmorillonites, exfoliated sheets are also observed, consistently with formation of an intercalated/exfoliated structure [2].

At high filler content (10 wt% MMT–Alk), two diffraction peaks are observed in the low 2θ angle region at 3.1° (d_{001}) corresponding to the interlayer spacing of 27.7 Å and a secondary registry (d_{002}) at 6.6 Å, which suggests some ordering of the intercalated structure. The intensity of the basal diffraction peak d_{001} increases with the clay content. Diffraction characteristic peaks of semi-crystalline PCL are observed at 4.25, 4.13 and 3.84 Å. Their intensity decreases when the clay content is increased. A decrease in the PCL crystallinity has previously been reported for PCL-based nanocomposites prepared by in situ intercalative polymerisation [14].

Fig. 3 shows XRD patterns for the organo-modified montmorillonite MMT–$(OH)_2$ and PCL composites containing 1, 3, 5 and 10 wt% of this clay. Consistently with TEM observations (not shown here), the PCL composites again show an intercalated/exfoliated structure together with a decrease in the PCL crystallinity upon increasing addition of clay. In this case, the interlayer spacing increases from 18.5 Å for the organo-modified clay up to 30–31 Å when PCL chains are intercalated.
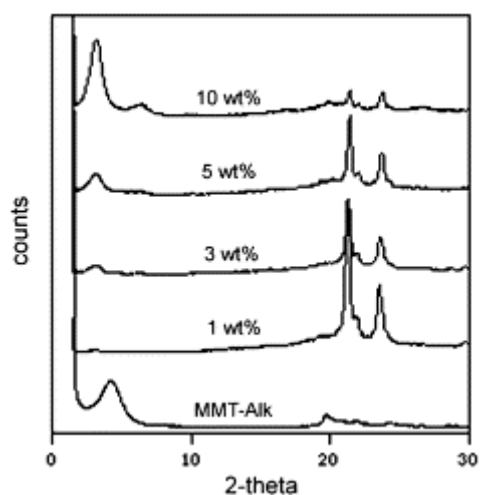
Fig. 1. XRD patterns for montmorillonite modified by dimethyl 2-ethylhexyl (HTA) ammonium cation (MMT–Alk) and for PCL nanocomposites containing 1, 3, 5 and 10 wt% MMT–Alk.
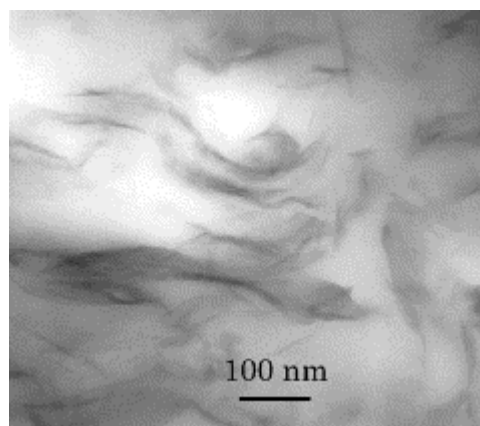

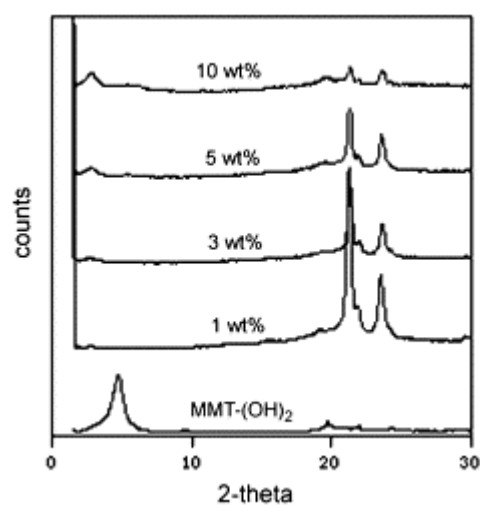*Fig. 2. TEM image for the PCL nanocomposite containing 3 wt% MMT–Alk.*

Fig. 3. XRD patterns for montmorillonite modified by methyl bis(2-hydroxyethyl) (HTA) ammonium cation (MMT–$(OH)_2$) and for PCL nanocomposites containing 1, 3, 5 and 10 wt% MMT–$(OH)_2$.

3.3. Thermal properties

Thermal properties of the poly(ϵ-caprolactone) composites were studied by DSC and by TGA. DSC measurements indicate that the filler has no effect on the glass transition temperature (T_g) of PCL which is observed at ca. −60 °C for all the samples. Similarly, the melting temperature (T_m) of the composites is very close to that one of neat PCL (ca. 57 °C). Nevertheless, the melting enthalpy, ΔH_m, is adversely affected by clay addition as typically reported in Table 1 for nanocomposites containing MMT–$(OH)_2$. The degree of crystallinity is accordingly decreased from 52.4% for neat PCL to 35.5% for the nanocomposite sample with 10 wt% of filler. These data are in qualitative agreement with the previously discussed XRD observations.

Table 1. Calorimetric data for nanocomposites prepared with MMT–$(OH)_2$

Samples	Filler content (wt%)	ΔH_m (J/g)[a]	Degree of crystallinity[b]
Commercial PCL	0	71.2	52.4
PCLC1	1	64.8	47.2
PCLC2	3	58.6	41.5
PCLC3	5	55.7	38.4
PCLC4	10	40.6	35.5

Thermal degradation was followed by TGA under an air flow at a heating rate of 20 K/min. Fig. 4 shows that the nanocomposites degrade at a higher temperature than neat PCL. This beneficial effect can be explained by a decrease in the diffusion of oxygen and volatile products throughout the composite material.
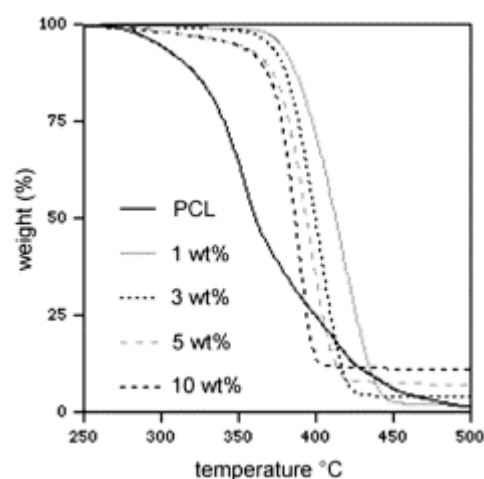

Fig. 4. Temperature dependence of the weight loss under an air flow for unfilled PCL and PCL nanocomposites containing 1, 3, 5 and 10 wt% (relative to inorganics) of MMT–Alk (heating rate: 20 K/min).

Moreover, the temperature at which the weight loss is 50% is shifted by 60 °C towards higher temperature upon the addition of as low as 1 wt% of clay. Higher amount of clay is however, unfavourable as exemplified by a temperature shift of only 30 °C when the content of organo-modified clay is 10 wt%.

The burning behaviour of the nanocomposites was visually observed. PCL nanocomposites burn without forming liquid droplets when they are exposed to a flame. Charring actually occurs with deposition of solid residue on the surface, which should provide the nanocomposites with fire retardant properties. This expectation is under current investigation by limiting oxygen index (LOI) and cone calorimetry testings.

3.4. Mechanical properties

The effect of clay content on the mechanical properties of PCL nanocomposites has been studied by tensile testing as reported in Table 2, Table 3 and Table 4.

Table 2. Tensile properties of neat poly(ε-caprolactone) and composites containing 1, 3, 5 and 10 wt% of natural montmorillonite MMT–Na

Samples	Filler content (wt%)	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
Commercial PCL	0	216±5	746 ±43	37 ±2
PCLC5	1	201±9	715 ±61	35 ±3
PCLC6	3	197±9	714.5±44	35 ±3
PCLC7	5	207±7	666 ±29	32.5±2
PCLC8	10	238±15	569 ±26	28 ±1

Table 3. Tensile properties of poly(ε-caprolactone) nanocomposites containing 1, 3, 5 and 10 wt% of organo-modified montmorillonite MMT–Alk

Samples	Filler content (wt%)	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
PCLC9	1	262±13	659±27	33±1
PCLC10	3	282±9	528±58	26±3
PCLC11	5	307±18	598±43	28±1
PCLC12	10	371±15	9 ±1	18±1

Table 4. Tensile properties of poly(ε-caprolactone) nanocomposites containing 1, 3, 5 and 10 wt% of organo-modified montmorillonite MMT–(OH)$_2$

Samples	Filler content (wt%)	Young's modulus (MPa)	Elongation at break (%)	Tensile strength (MPa)
PCLC1	1	259±11	705±47	36±2
PCLC2	3	272±16	563±62	25±4
PCLC3	5	313±23	560±46	24±3
PCLC4	10	399±23	7 ±1	17±0.5

The Young's modulus of the PCL nanocomposites is higher compared to neat PCL, as result of the intercalated/exfoliated structure. For instance, the Young's modulus is significantly increased from 216 MPa for pure PCL to more than 390 MPa for the composite that contains 10 wt% of MMT–(OH)$_2$. In contrast, the Young's modulus of the microcomposites formed by the non-modified montmorillonite (MMT–Na) is basically independent of the clay content at least within the investigated range (Fig. 5).
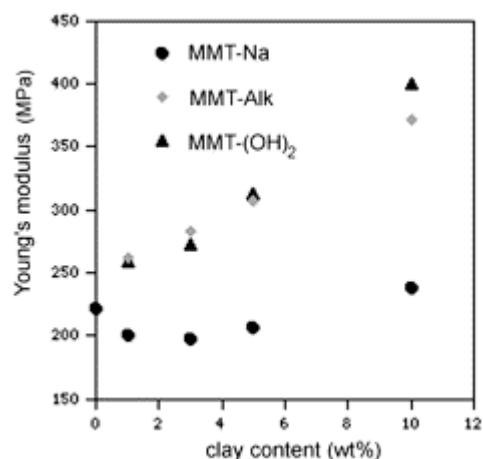

Fig. 5. Dependence of Young's modulus on the clay content for PCL modified by MMT–Na, MMT–Alk and MMT–(OH)$_2$.

PCL is a ductile polymer able to sustain large deformations (700% elongation at break). Addition of nanofillers decreases only slightly the elongation at break as shown in Table 3 and Table 4 for filler contents of 1, 3 and 5 wt%. PCL remains ductile with an elongation at break higher than 550%. Higher content of silicates (10 wt%) has however a detrimental effect as confirmed by an ultimate elongation lower than 10% for the two types of organo-modified MMT. At high clay content, aggregates of non-intercalated silicates might embrittle the PCL matrix. Similar observations were reported elsewhere for nanocomposites of thermoplastics such as poly(methyl methacrylate) (PMMA) [15], poly(styrene) (PS) [16] and poly(propylene) (PP) [17]. For instance, the elongation at break of PP decreases from 150 down to 7.5% upon dispersion of 5 wt% of organo-modified clay. The stress

at break, which is the ultimate strength that the material can sustain before breaking, decreases with increasing clay content although it remains high enough.

These different observations show that PCL nanocomposites combine high stiffness and good ductility at least up to a clay loading of 5 wt%. Above this threshold, a drastic loss in ultimate tensile properties is observed.

Table 5 shows the Izod impact strength values for PCL composites prepared with MMT–Na, MMT–Alk or MMT–(OH)$_2$ as a function of clay content. The Izod impact strength systematically decreases with increasing clay content. It drops from 48 J/m for unfilled PCL to 33 and 13 J/m when 1 and 10 wt% of the MMT–(OH)$_2$ nanoclay, respectively, are incorporated. It is worth noting that Zhu et al. [18] observed that the notched impact strength of nylon-6/clay nanocomposites prepared by melt intercalation did not change significantly (ca. 28 J/m) for organo-clay contents ranging from 0 to 17 wt%.

Table 5. Izod-impact properties of composites containing MMT–Na, MMT–Alk and MMT–(OH)$_2$ clays

Filler content (wt%)	Izod impact strength (J/m)		
	MMT–Na	MMT–Alk	MMT–(OH)$_2$
1	33±5	28 ±6	33±3
3	22±2	22 ±2	18±3
5	19±1	15 ±1	13±1
10	15±1	16 ±3	13±2

3.5. Rheological properties

Storage (G') and loss (G'') moduli of unfilled PCL and PCL filled with 3 wt% of MMT–Na, MMT–Alk or MMT–(OH)$_2$ were measured at 80 °C in the frequency range from 16 to 10^{-2} Hz (Fig. 6).
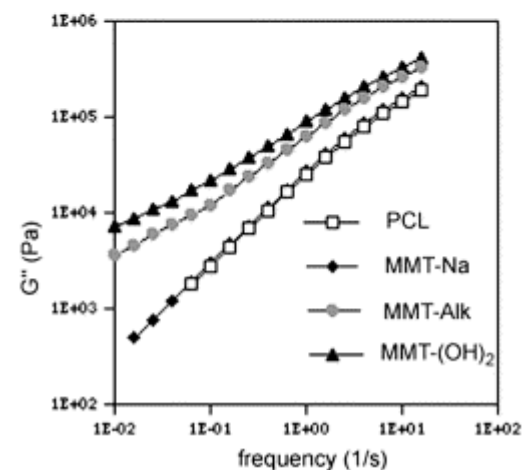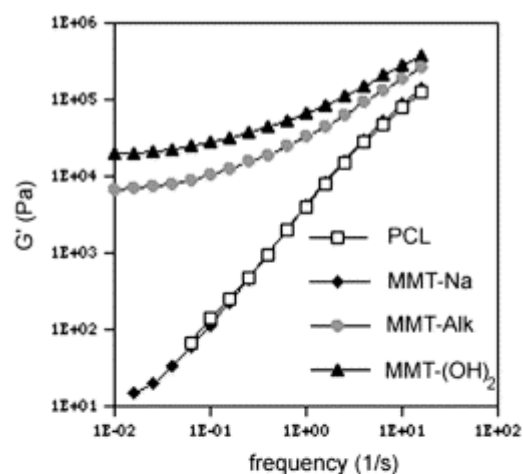
Fig. 6. Storage (G') and loss (G'') moduli for unfilled PCL and PCL modified by 3 wt% of MMT–Na, MMT–Alk, MMT–(OH)$_2$, at 80 °C.

According to Fig. 6, the rheological behaviour of the PCL filled with 3 wt% of MMT–Alk and MMT–(OH)$_2$ is significantly different compared to unfilled PCL and PCL/MMT–Na microcomposites, for which the power law observed at low frequencies agrees with expectation for thermoplastics, i.e. $G' \sim \omega^2$ and $G'' \sim \omega$. The frequency dependence of G' and G'' is however perturbed by organo-modified MMT. The effect is dramatic in case of G' which drops from 2 to 0.14 and 0.24 for MMT–(OH)$_2$ and MMT–Alk, respectively.

How dependence of G' and G'' on frequency changes with the filler content is shown in Fig. 7 for the MMT–(OH)$_2$ clay. As soon as the clay content exceeds 1 wt%, not only the classical power laws for the frequency dependence of G' and G'' are deeply modified, particularly in case of G' but the moduli increase dramatically at low frequency. This behaviour is characteristic of a pseudo-solid-like response of the material. The same observation was reported for nanocomposites of, e.g. poly(propylene) [19], poly(styrene-*b*-polyisoprene) [20] and polyamide-12 [21]. Rheological properties of PCL nanocomposites were first reported by Krishnamoorti [22] and Giannelis [23] in case of delaminated structures generated by in situ polymerisation. With an organo-clay content ranging from 1 to 10 wt%, G' and G'' values displayed by these nanocomposites increased with the clay content as observed in this work. However, some deviations from the expected dependence were reported and explained by the formation of lower molecular weight PCL chains at higher clay content. In this study, all the composites were prepared from the same preformed PCL ($M_n \sim 50,000$) such that no deviation is observed.
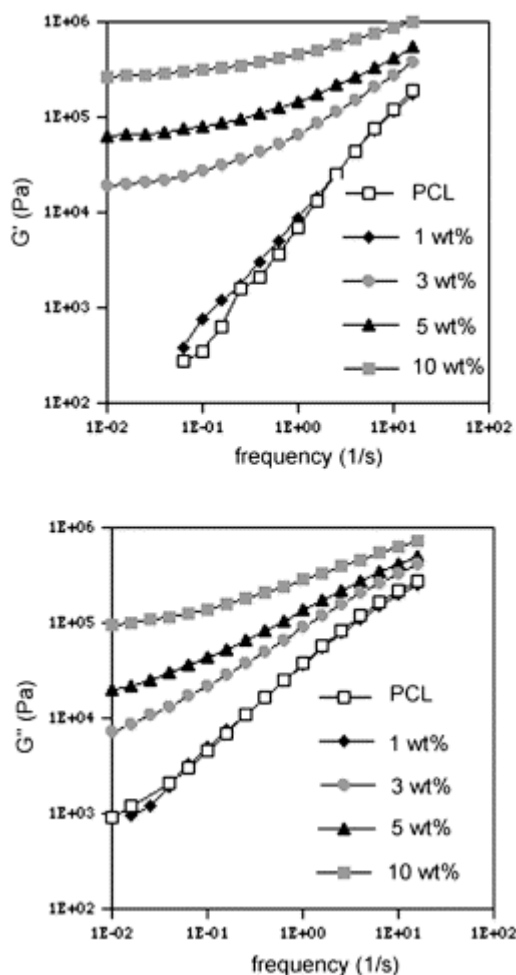

Fig. 7. Storage (G') and loss (G'') moduli for unfilled PCL and PCL nanocomposites containing 1, 3, 5 and 10 wt% of MMT–(OH)$_2$, at 80 °C.

4. Conclusions

PCL nanocomposites were prepared by melt blending at 130 °C using a conventional two-roll mill. Montmorillonite organo-modified by dimethyl 2-ethylhexyl (hydrogenated tallowalkyl) ammonium and methyl bis(2-hydroxyethyl) (hydrogenated tallowalkyl) ammonium, respectively, was used. An intercalated/exfoliated structure was observed by both XRD and TEM analyses. In contrast, natural sodium montmorillonite formed conventional composite, with micron-sized particles dispersed in PCL. Tensile properties of the nanocomposites, particularly stiffness, increased continuously with the filler content, at least until a content of 5 wt%, beyond which the mechanical properties levelled off and/or decreased. A significant improvement in thermal stability of PCL was noted especially at very low clay content (1 wt%). A solid-like rheological response was observed for PCL modified by 3 wt% and more of organo-modified MMT. Storage and loss moduli in the terminal region were substantially increased for all the studied nanocomposites compared with unfilled PCL and or PCL-based microcomposites. Further investigation of the flame retardancy behaviour and gas barrier properties of the PCL nanocomposites will be reported in a forthcoming paper.

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