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Solution casting versus melt compounding: effect of fabrication route on the structure and thermal behavior of poly(L-lactic acid) clay nanocomposites

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Abstract Poly(L-lactic acid) (PLLA) nanocomposites containing various loadings of organo-modified montmorillonite were prepared via twin screw extrusion and solution casting in order to investigate the effect of processing route on the structure and the thermal properties of the fabricated nanohybrid materials. X-ray diffraction (XRD) testing indicated that a better dispersion of the modified inorganic filler can be achieved by solution intercalation. The interlayer distance of the mineral, and thus the type and structure of the nanohybrid formed, was found to be affected by the polymer content only in the case of the nanocomposites produced by the solution casting method. Thermogravimetric analysis (TGA) revealed that the hybrids prepared by melt compounding displayed increased thermal stability. Differential scanning calorimetry (DSC) showed that the fabrication route influences the crystallization process of the polymer.

Introduction

The dispersion of nanometer-sized silicate particles within a polymer matrix has long been an attractive topic of scientific research both in industry and academy due to its potential applications and the theoretical underlying of it, especially in the context of nanoscience. The nanoscopic phase distribution as well as synergism between the polymer and the filler result in nanohybrids exhibiting markedly improved properties, which are not observed in either component [1, 2]. These properties include increased Young's modulus and storage modulus, higher thermal stability and flame retardancy and more efficient gas barrier properties compared to pure polymers or conventional micro-composites [3–6]. Because of biomedical and ecological concerns, this approach of creating improved hybrid materials, applied to biodegradable and biocompatible synthetic aliphatic polyesters, has been receiving growing attention [7]. Indeed, the physicochemical response of these polymers can be significantly enhanced expanding their application field without sacrificing their biodegrability [8].

Poly(lactic acid) (PLA) is a highly versatile biopolymer derived from renewable plant sources, such as starch and sugar. PLA has been viewed as a promising material for biomedical applications, while its low toxicity along with its environmentally benign characteristics render it an ideal material for food packaging and for other consumer products [9]. Depending on the proportion of the optically active L- and D-enantiomers, a polymer of variable properties can be derived [10].

In order to capitalize on the improvements offered by the nanocomposites, a high dispersion level of the inorganic nanoparticles must usually be obtained [2]. Two of the main approaches used to fabricate polymer/layered silicate nanohybrids are solution casting and melt compounding. The first route involves the selection of an appropriate solvent capable of swelling the clay and dissolving the polymer. Using mechanical or ultrasonic stirring, the polymer chains intrude into the clay galleries and a homogenous three-component mixture is prepared. Hybrid material is obtained by solvent removal [11]. Solution casting is a very important method for polymers

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with low or no polarity and favors the preparation of thin membranes. Moreover, polymer and organic modifier degradation can be avoided due to the absence of elevated temperatures. However, from the industrial point of view, the use of organic solvents renders this technique environmentally unfriendly and economically unadvisable.

In melt intercalation, the polymer is heated above its softening point and the dispersion of the layered silicate particles into the polymer matrix is usually achieved by the synergism of chemistry with the applied shear [12]. This method is compatible with the current plastic's industry processing techniques. Furthermore, the absence of solvents makes melt intercalation environmentally sound. However, the high temperature required, the shear stresses applied, and the local overheating resulting from the shear can cause decrease of the polymer molecular weight, surfactant degradation, and possible reduction in the clay's aspect ratio [12, 13].

Poly(lactic acid) (PLA) nanocomposites have been successfully prepared via both solution casting [14–16] and melt intercalation [17–19]; and numerous benefits of the nanocomposites formed have been described. However, even though the processing route is one of the most important parameters in defining the dispersion of the organosilicate into the polymer matrix and, hence, the properties of the prepared composite, there is very little information in the literature relating the influence of the fabrication method with the characteristics of PLA nanocomposites.

The intent of this work was to evaluate the effect of the processing route on the structural and thermal properties of poly(L-lactic acid) nanocomposites prepared by solution casting and melt intercalation methods. The morphology of the nanohybrid materials produced was explored by X-ray diffraction (XRD), while thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were used to investigate their thermal characteristics.

Materials and methods

Materials

Poly(L-lactic acid) (PLLA) ($M_n = 81000$, $M_w/M_n = 1.9$ and 0% content in D-lactide stereoisomer) was supplied by Galactic S.A. (Belgium). Sodium montmorillonite (NaMMT) with a cation exchange capacity (CEC) = 92.6 meq/100 g was obtained from Southern Clay Products (Texas, USA). Hexadecylamine (HDA), chloroform ($CHCl_3$), and concentrated HCl were purchased from Sigma–Aldrich. All materials were used without any further purification.

Organically modified montmorillonite (C_{16}MMT) was prepared through an ion-exchange reaction between NaMMT and hexadecylammonium salt concentration equivalent to 1.4 times the clay CEC [20].

Preparation of nanocomposite materials

Two different processes were employed for the preparation of the nanocomposites; solution and melt intercalation. In the first case, the organomodified-montmorillonite was initially dispersed in chloroform and the clay suspension was sonicated for 1/2 h with a Heat Systems-Ultrasonics sonicator, model W-375. The polymer was dissolved in chloroform and was sonicated for 1/2 h, as well. The solution was added to the clay suspension and the final mixture was further sonicated for another 1 h. The mixture was then cast onto Petri dishes and the solvent was slowly evaporated. Eventually, hybrid films with organoclay loadings of 1, 3, 5, and 9 wt% were obtained and were subsequently dried in vacuum at 50 °C for 24 h.

Melt intercalation was performed using a co-rotating twin screw micro-extruder/compounder (MiniLab, ThermoHaake). A screw speed of 200 rpm was used, while the barrel temperature was at 190 °C. The compounding time was 10 min. Constant nitrogen flow was used during nanocomposite preparation in order to prevent thermal decomposition of the PLLA matrix. This technique also resulted in four different hybrids with silicate contents of 1, 3, 5, and 9 wt%. For characterization purposes, film specimens were prepared by compression molding with small compressive stresses (identical in all cases).

Characterization

The effect of the fabrication route on the clay dispersion level into the polymer matrix was investigated by X-ray diffraction (XRD) using a Siemens D 500 diffractometer with Ni-filtered CuKα radiation ($\lambda = 0.154$ nm). The 2θ scanning range was varied from 1.5° to 10° with a step of 0.01 and a measuring time of 15 s per step.

The thermal properties of the produced composites were explored by a Shimadzu DSC-50 differential scanning calorimeter (DSC). Temperature scans were performed at a heating rate of 10 °C/min under constant nitrogen flow of 20 cm^3/min. The samples were heated to 200 °C and remained at that temperature for 5 min in order to release their thermal history and, afterward, they were quenched to −5 °C. The determination of the glass transition temperature (T_g), crystallization temperature (T_c), and melting point (T_m) took place during the second run.

The thermal stability of the hybrids were studied by thermogravimetric analysis (TGA) on a Shimadzu TGA-50 analyzer operating from ambient temperature to 750 °C, at a heating rate of 10 °C/min under flowing nitrogen (20 cm^3/min) and static air.

Results and discussion

Structure of nanocomposites

Figure 1 demonstrates the results of XRD analysis of the hybrid materials obtained by the two different preparation methods. Comparing the structure of these materials, it is evident that a higher degree of C_{16}MMT dispersion can be achieved by the solution process. These solution cast hybrids exhibit broader peaks probably due to a partial disorder of the parallel stacking of the clay layers (platelets) caused by extensive polymer insertion into the interlayer space. Moreover, the lack of peak detection for clay loadings lower than 5 wt% may be attributed to the delamination of the clay platelets. On the other hand, hybrids fabricated from the melt displayed an intercalated structure. The intensity of the peak related to the *d*-spacing value of the clay gradually increases with the mineral content rise due to the increase of the diffracted X-rays by the additional intercalated organoclay.

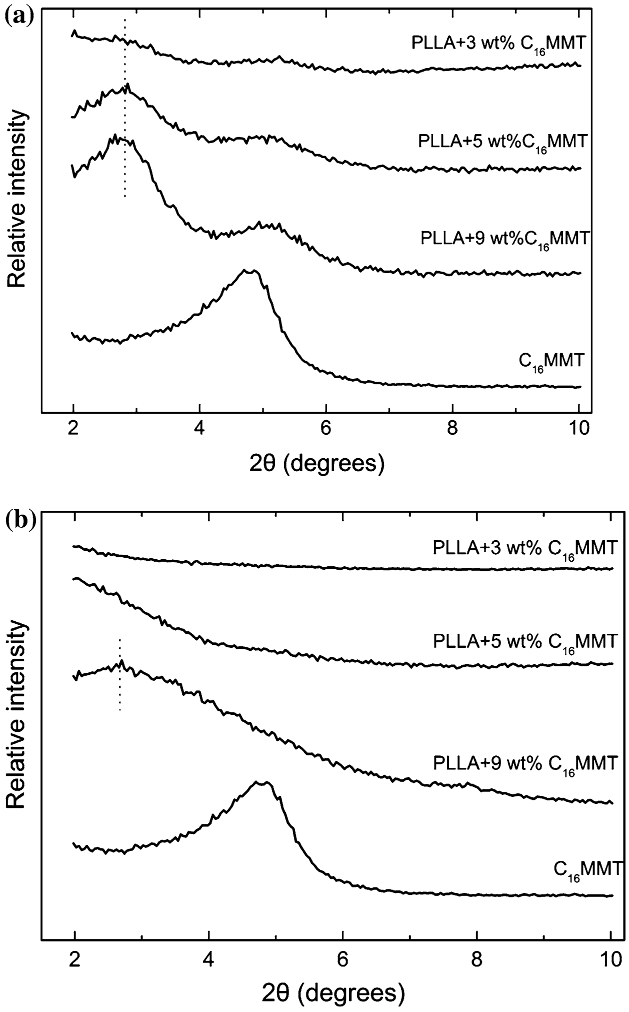

Fig. 1 X-ray diffraction patterns of PLLA nanohybrids prepared by **a** melt mixing and **b** solution casting technique

Valsecchi et al. [21] studied the effect of the aforementioned preparation methods on the properties of fluoroelastomer/organomodified-montmorillonite nanocomposites. They found that better organoclay dispersion can be attained by solution casting. The same process was found to be necessary in dispersing organically modified clay in styrenic polymers [22]. On the contrary, Finnigan et al. [23] mentioned that high shear stresses involved with melt blending may lead to a higher miscibility between polyurethane and nanoclays. However, solvent casting was found to be the preferable route as it avoids the polymer and surfactant degradation associated with melt processing. Similarly, Filippi et al. [24] reported that the processing route was essential for the fabrication of ethylene–acrylic acid copolymers/organoclay nanocomposites, since only melt compounding was successful. They also observed that the structure of the prepared hybrids was not related to the clay loading, the application of the shear forces during thermal treatment and the dimensions of the added organoclay.

Another important issue emerging from Fig. 1 is related to the dependence of the interlayer spacing of the hybrids on the components content. Thus, the basal spacing of the composites prepared by solution was found to be strongly dependent on the clay content, since it decreases with an increase of the content. As Fig. 1b denotes, for clay loadings less than 5 wt%, the parallel stacking of the platelets is destroyed and this corresponds to a *d*-spacing that can be considered as infinite. When the clay loading exceeds 5 wt%, in most of the clay particles the parallel stacking is maintained and the particles simply swell by the insertion of the polymer chains inside the galleries.

However, hybrids prepared by melt mixing exhibited a constant gallery size regardless of the clay concentration. Similar observations were also reported by other researchers, who studied the preparation of poly(ethylene oxide)/Na-montmorillonite nanocomposites by the aforementioned techniques [25].

Thermal characteristics of nanocomposites

Figures 2 and 3 demonstrate the results of TGA analysis for the prepared nanocomposites in inert and oxidative conditions, respectively. The influence of the processing method on the temperature of the material decomposition initiation (estimated at 2 wt% loss) is presented in Fig. 4, which has been constructed with data taken from Figs. 2 and 3. Inspection of these figures reveals that both solution-cast and melt-intercalated nanocomposites show an enhanced thermal stability either in inert or in oxidative atmosphere. In addition, the melt-intercalated nanohybrids

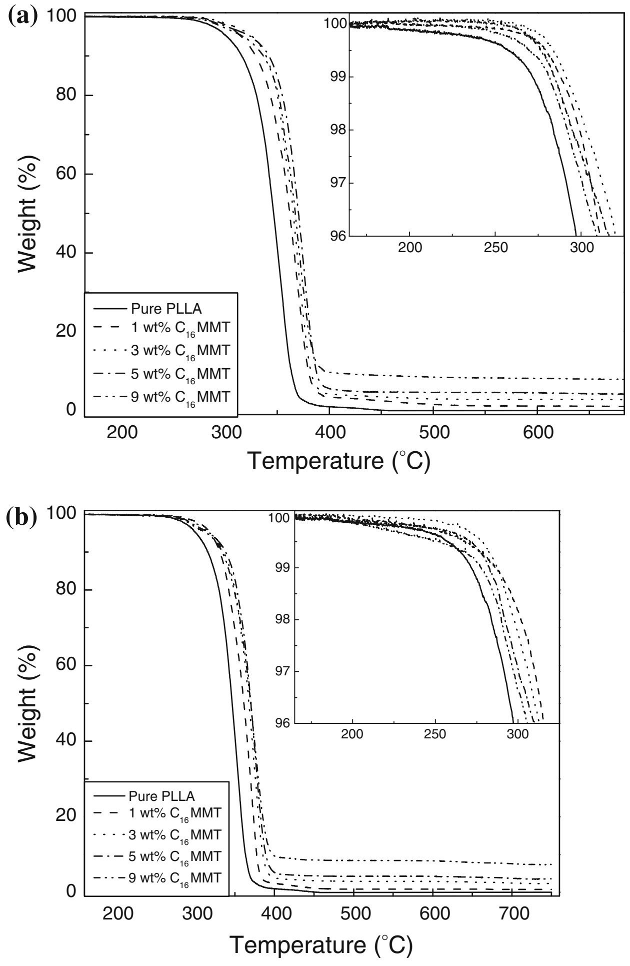

Fig. 2 TGA curves for PLLA nanohybrids prepared by **a** melt mixing and **b** solution casting technique, in inert atmosphere

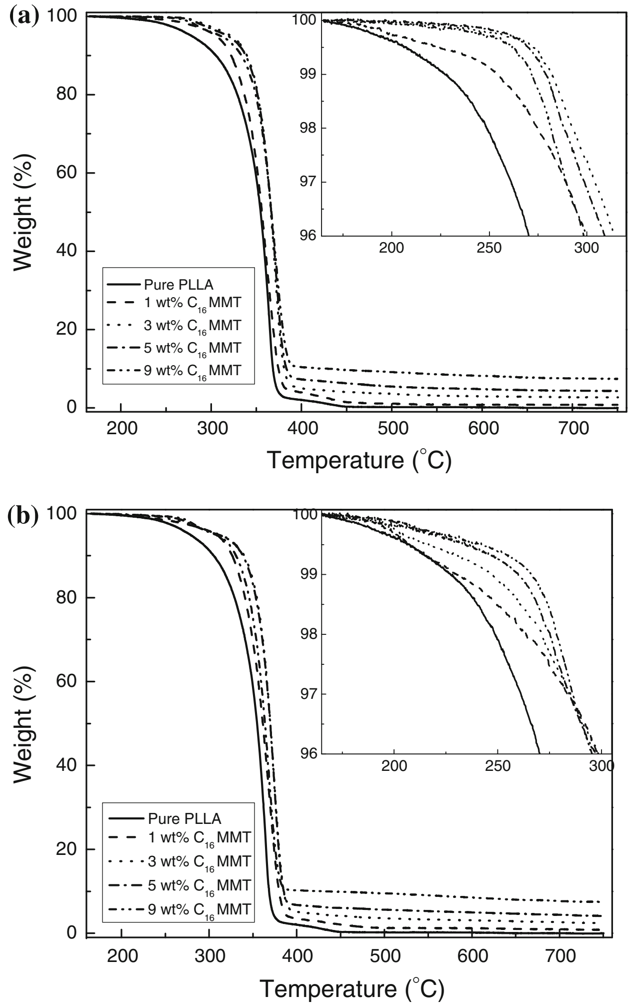

Fig. 3 TGA curves for PLLA nanohybrids prepared by **a** melt mixing and **b** solution casting technique, in oxidative atmosphere

exhibit a higher thermal stability compared to the solution cast ones. This may be due to the structure of the prepared materials. XRD analysis indicated that the melt-compounded nanohybrids exhibit mainly intercalated structure, while the composites formed by solution casting have a high percent of exfoliated silicate platelets. However, it has already been highlighted [26, 27] that intercalated nanocomposites display enhanced thermal stability compared to exfoliated ones. The dispersed ultrafine inorganic nanoparticles promote the formation of a carbonaceous-silicate char layer on the surface of the polymer, which acts as an insulator and mass transport barrier impeding the decomposition rate of the matrix [28]. This charring process is probably favored by an increased number of intercalated lamellar stacks that improve the thermal stability of the matrix. Furthermore, the formation of the protective char layer may be assisted by the temperature treatment involved during hybrids preparation.

In inert atmosphere, the effect of filler loading on the decomposition initiation temperature was similar for both nanocomposite types. As illustrated in Fig. 4a the onset decomposition temperature of both nanocomposites types goes through a maximum and subsequently decreases. This maximum is observed at organoclay loadings 1 wt% for the solution cast material and 3 wt% for the hybrids prepared by extrusion.

On the contrary, the clay concentration had a different impact on the thermal properties of these samples, under the presence of air (Fig. 4b). An increase of the mineral's concentration led to an increment of the onset decomposition temperature for the hybrids prepared by solution. It seems that this increment is less intense at high C_{16}MMT contents. However, the temperature of the decomposition initiation of the melt-intercalated hybrids reaches a maximum at clay loadings equal to 3 wt% and then gradually decreases. This may be attributed to the increase of the

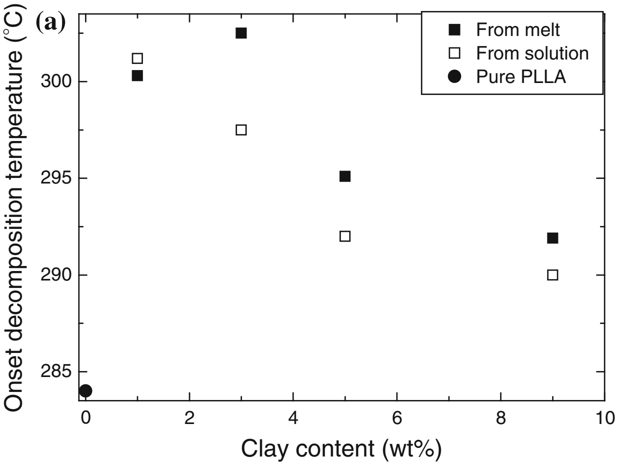
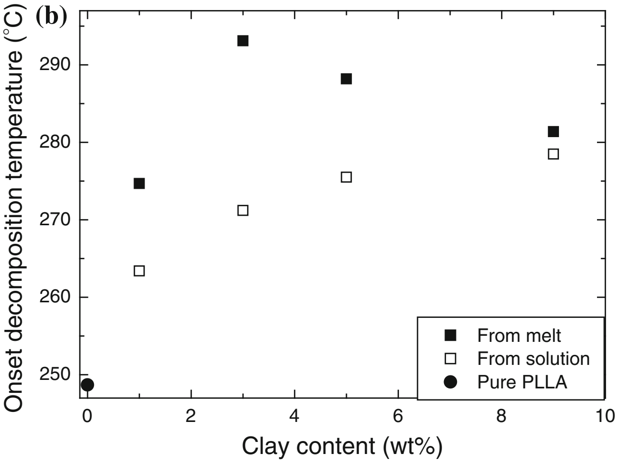

Fig. 4 Effect of preparation method on the temperature of thermal decomposition initiation (estimated at 2% of weight loss) of PLLA nanocomposites in **a** inert and **b** oxidative atmosphere

surfactant concentration which can promote hydrolysis of PLLA chains at elevated temperatures that have been used, when melt compounding is applied. This reduction of polymer's molecular weight can encourage thermal decomposition of the matrix [19, 29].

Investigations on clay based acrylonitrile–butadiene–styrene as well as on polystyrene nanocomposites prepared by solution and melt intercalation showed that their thermal stability was not affected by the preparation method [30, 31].

Thermal characteristics of the hybrids were investigated by DSC and the results are presented in Fig. 5. The exothermic peak shown between 95 and 120 °C is due to the crystallization of the polymer, while the melting point is represented by an endothermic peak at around 170 °C. The influence of the preparation method on the crystallization temperature (T_c) and the melting point (T_m) is depicted in Fig. 6. It is obvious that in both cases the inorganic material's presence led to a depression of T_c. However, this depression was more intense for the solution cast hybrids.

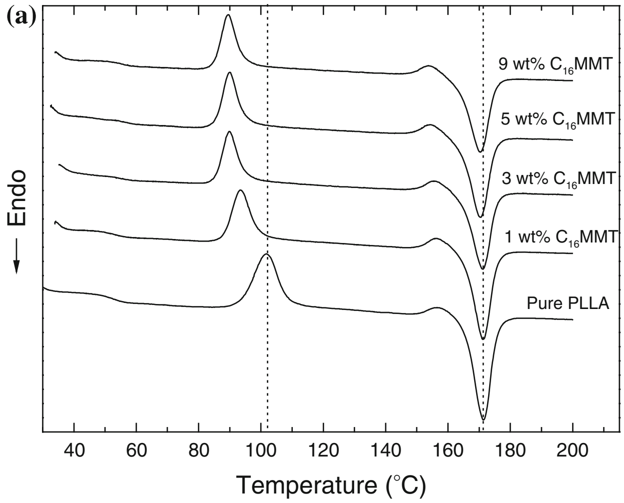
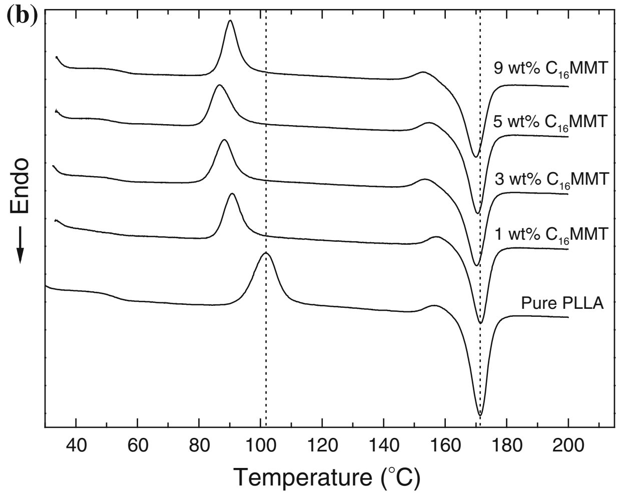

Fig. 5 DSC heating thermographs of quenched specimens of PLLA nanohybrids prepared by **a** melt mixing and **b** solution casting

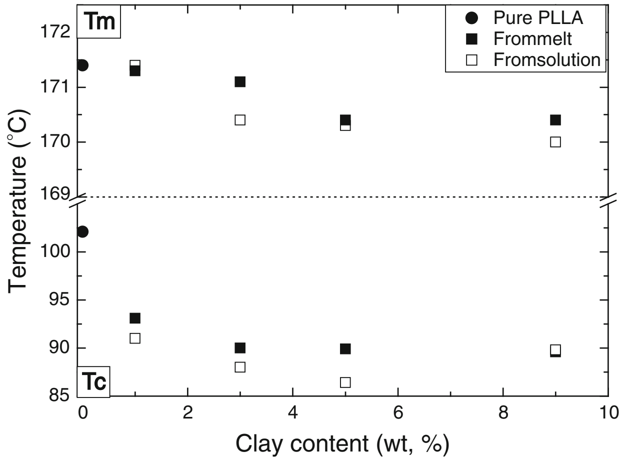

Fig. 6 Effect of the processing method on the crystallization temperature (T_c) and the melting point (T_m) of the nanocomposite materials

The clay platelets provide large surface area and serve as nucleating sites favoring the crystallization process during heating [17]. The crystallization process is also aided by the possible presence of surfactant aggregates that act as additional nucleating agents and can be formed as the surfactant in excess may leach or migrate from the organoclay to the polymer matrix; (the higher the organoclay concentration the higher the surfactant excess) [16]. When temperature treatment is involved during hybrid preparation, a part of the alkylammonium excess degrades. In this case, due to the reduced surfactant concentration and the lower dispersibility of the inorganic material (as the XRD results indicate) a smaller number of nucleation sites are formed. Hence, the T_c of the nanocomposites produced by melt compounding is higher than the corresponding one for the solvent-cast nanocomposite of the same clay loading as Fig. 6 shows.

However, for C_{16}MMT loading greater than 5 wt% an increase in T_c is observed only for the hybrids prepared from solution. It seems that for organoclay concentrations higher than a critical value, the plethora of particles (mineral and excess surfactant aggregates) retard the overall crystallization kinetics by hindering the mobility of PLLA chains [16, 32]. On the contrary, the decreased number of nucleation centers, when melt compounding is used, is capable of incorporating the surrounding polymer even when the clay content is as high as 9 wt%.

It is worth noting that clay incorporation caused a low decrease of the hybrids melting point. Furthermore, the glass transition temperature of the polymer, which is represented by a step-like shape of the curves in the temperature range 50–55 °C, was not significantly affected by the organoclay addition in both preparation techniques.

Conclusions

A comparison between solution casting and melt intercalation in terms of the structural and the thermal characteristics of PLLA layered silicate nanocomposites was attempted.

XRD studies revealed that both processing routes can be successfully employed for the dispersion of the organomodified inorganic material into the polymer matrix. However, a better delamination of the organoclay particles was achieved via solution casting. In this method, it was also observed that the gallery size of the mineral was increased in proportion to the polymer content, while in melt intercalation the interlayer distance in the swollen clay particles was not dependent on the concentration of the polymer.

Introduction of nanoclays was found to significantly improve the thermal stability of the polymer in both cases. Hybrids derived from polymer melt displayed higher onset decomposition temperature and hence, particularly improved thermal stability compared to the ones obtained by solution. DSC analysis showed that the crystallization temperature during heating for the hybrids processed by melt compounding was higher than the corresponding temperature of the solution cast nanocomposites. Surfactant excess degradation and considerably fewer exfoliated clay particles, which both occur during nanocomposite preparation via melt compounding, led to the creation of fewer nucleation sites which induce crystallization. Consequently, polymer crystallization is promoted, when solution intercalation is used.

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