Structure and Thermal Behavior of Poly(L-lactic acid) Clay Nanocomposites: Effect of Preparation Method as a Function of the Nanofiller Modification Level

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ABSTRACT: The structural and thermal characteristics of poly(L-lactic acid)/layered-silicate hybrid materials that were produced via two different routes, namely by solvent casting and by melt mixing, were compared in association with the degree of clay modification. Investigation of the produced materials' structure revealed that, at low modification levels, melt blending is necessary in dispersing the amine-treated clay into the polymer matrix. At intermediate degrees of modification, both techniques are capable of swelling the silicate clay with the solution casting to be a more effective method. Thermal measurements showed that the clay modification level influences significantly the thermal stability of both solution and melt processed hybrids. Moreover, the material derived from melt mixing displayed a higher onset decomposition temperature. The glass transition temperature of the polymer was not significantly affected by the preparation method followed. However, the crystallization process was found to be strongly dependent on both the preparation method and the degree of clay modification. © 2011 Wiley Periodicals, Inc. J Appl Polym Sci 124: 2999–3006, 2012

Key words: nanocomposites; poly(lactic acid); biodegradable; extrusion; solution casting

INTRODUCTION

Nanoclay-filled polymeric systems offer many greatly improved properties over the pristine polymers, which cannot be matched by micron-sized particle reinforcements.[1,2] The key in achieving these enhanced properties is the high degree of clay dispersion into the polymer matrix that generates high aspect ratio particles with one dimension in the nanoscale.[3] In the case of hydrophobic polymers, the first step in achieving this clay dispersion is to make the hydrophilic smectite clay more organophilic. The interlayer is normally occupied by cations such as hydrated alkali metal and alkaline earth cations that balance the charge deficiency generated by isomorphous substitution between the layers (e.g., Al^{3+} for Si^{4+} or Mg^{2+} for Al^{3+}). An ion exchange reaction between these cations and the alkylammonium cations of the surfactant is used to produce the organoclay.[4] It has been reported that the surface energy of layered silicates and thus, their interaction with the organic solvents and the polymer matrices can be easily adjusted by proper selection of the interlayer cation. Furthermore, surfactant packing density within the interlayer is also very important in determining the transport of polymer chains into the galleries of the layered host.[5]

The polymer/layered-silicate hybrid materials have been mainly synthesized via two different routes, that is, solution casting[6] and melt compounding.[7] The thermodynamic aspect of nanocomposite formation in solution casting requires a negative variation in the Gibbs free energy. The entropy loss of the confined polymer chains is counterbalanced by an entropy gain related to the desorption of previously adsorbed solvent molecules. These molecules are dislodged from the interlayer and are substituted by the incoming polymer chains.[8] The level of clay dispersion in the organic solvent, as well as the solubility of the polymer are the primary parameters, which govern the insertion of the polymer into the clay galleries. Optimal sonication conditions may also contribute, when the selection of desirable solvent and organically modified clay are not adequate in producing a delaminated nanocomposite.[6]

However, in melt intercalation, the entropy loss related to the confinement of the molten macromolecules into the interlayer is compensated by the entropic gain associated with layer separation and the increase of conformational freedom of the tethered surfactant alkyl chains. Therefore, the interlayer structure, which depends on the surfactant molecular architecture and packing density, should be

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optimized to maximize the conformational freedom of the organic modifier's chains and facilitate polymer-clay interactions. However, for a successful hybrid formation an enthalpic contribution is required, which can arise from the presence of strong interactions between the polymer and the silicate surface.[9] Investigations on melt compounding revealed that the chemical compatibility between the polymer matrix and the clay (which depends on the chemistry of mineral treatment) plays the dominating role for the final morphology of the produced nanocomposites. Optimization of the processing parameters such as the applied shear stress, the residence time, and the mixing temperature can only decrease the size of the clay tactoids, when the chemical compatibility between the two components is not strong enough.[7,10,11]

Several researchers have examined the effect of solution and melt intercalation on the dispersion of layered silicate particles into a polymer matrix.[12–21] Their observations differ, which is probably due to the different systems examined, and consequently, due to the variant compatibility between the organically modified mineral and the polymer matrix. Nevertheless, only one of these works[15] refers to the effect of the preparation technique on the properties of poly(lactic acid) (PLA) nanocomposites. In that work, nanocomposites were prepared using various loadings of organomodified clay and the characteristics of the prepared materials were explored. However, that work did not examine the influence of the clay modification level, which is a very crucial parameter regarding the dispersion of clay into the matrix

The aim of this work was to extend our current understanding regarding the influence of the preparation method on the structural and thermal characteristics of polymer/clay nanocomposites. For this reason, the impact of the processing route on the properties of the hybrids is related with the degree of clay modification. To the best of our knowledge, this is the first time that this approach is attempted.

Poly(L-lactic acid) (PLLA), one of the most important biopolymers,[22] was selected as a polymer matrix. PLLA is a biodegradable aliphatic polyester derived from renewable resources and is extensively used in tissue engineering for treating patients suffering from damaged or lost organ or tissue.[23] Hybrids consisting of PLLA and montmorillonite (MMT) modified to a different degree, using various contents of hexadecylammonium cation, were prepared via melt mixing and solution casting. The inorganic content in every hybrid was kept constant. The effect of the fabrication route on the structural and thermal characteristics of the prepared materials was investigated in association with the filler modification level.

EXPERIMENTAL

Materials

PLLA (M_n = 81,000, 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 (TX). Hexadecylamine (HDA), chloroform ($CHCl_3$), and concentrated HCl were purchased from Sigma-Aldrich. All materials were used without any further purification.

Preparation of organically modified clay

NaMMT was modified through an ion-exchange reaction with hexadecylammonium salt loadings ranging from 30 to 300% the CEC of the inorganic material.[24] The morphological, thermal, and colloidal characteristics of the organophilic clay (C_{16}MMT) were studied previously.[24] The exact amount of inorganic part in each of the modified clays was determined by thermogravimetric analysis.

Preparation of composite material

Nanocomposites were prepared using two different approaches; melting blending and solution casting. The inorganic content in every composite prepared was 3 wt %.

Melting intercalation was conducted in a twin screw microextruder-compounder (MiniLab, ThermoHaake). A screw speed of 200 rpm was used, while the barrel temperature was 190°C. The compounding time was 10 min. Constant nitrogen flow was employed during nanocomposite preparation to prevent thermal decomposition of the matrix.

In solution casting, chloroform was selected as a solvent for swelling the clay and dissolving the polymer. A detailed description of the process followed can be found in a previous work.[2]

Characterization

The structure of the prepared hybrids was investigated by X-ray diffraction (XRD) using a Rich. Seifert 3003 TT diffractometer with Ni-filtered CuKα radiation (λ = 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 investigated by a Scimadzu 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 to release their thermal
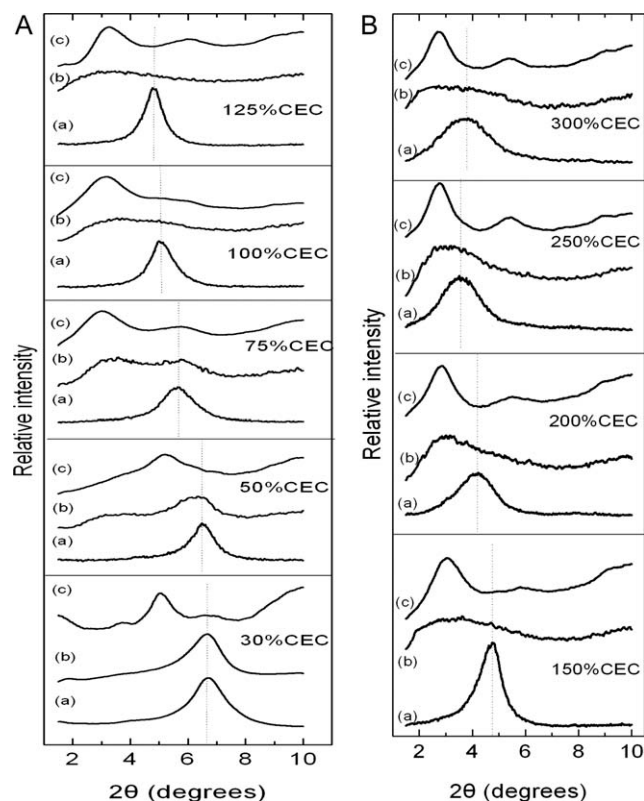
Figure 1 X-ray diffraction patterns of (a) the modified clay and the hybrids prepared by (b) the solution casting and (c) the melt intercalation technique. The added montmorillonite was modified to a different level, with respect to the percent clay's cation exchange capacity (CEC), by hexadecylammonium cation.

history and, subsequently, were quenched to −5°C. The thermal parameters of the materials, glass transition temperature (T_g), crystallization temperature (T_c), and melting point (T_m), were determined during the second run.

Thermogravimetric analysis (TGA) of the hybrids was performed on a Shimadzu TGA-50 Analyzer with a heating ramp of 10°C/min up to 750°C, for both, under flowing nitrogen (20 cm^3/min) and static air. TGA measurements were also conducted in isothermal conditions, at 260°C, under air presence.

RESULTS AND DISCUSSION

Structure of the hybrids

XRD patterns of the hybrids prepared by the two methods are illustrated in Figure 1. At surfactant levels equivalent to 30% the clay CEC, the mineral's characteristic peak of the hybrid prepared by the solvent casting technique was not shifted towards lower 2θ values indicating that intragallery penetration of the polymer chains was not feasible. Increasing the alkylammonium cation concentration, this

solvent-cast hybrid displays two 001 reflections due to an inhomogeneous dispersion of the clay particles into the matrix. The peak at lower 2θ values is owing to the intercalation of PLLA into mineral interlayer. The intensity of this peak gradually enhances with the increase of the alkylammonium content up to 1.25 times the clay CEC, while the intensity of the initial peak shown at higher 2θ values gradually decreases. This means that, with the increase of the surfactant loading, a bigger quantity of the inorganic material has swollen due to the polymer intrusion into the mineral's galleries.

It has been reported[25] that a substantial part of the driving force for polymer intercalation from solution is the entropy gained by desorption of solvent molecules from the clay galleries. Studies on the effect of the modification level on the hexadecylammonium-treated clay colloidal behavior showed that surfactant concentration higher than the mineral CEC was necessary for the dispersion of the organoclay into CHCl$_3$.[24] For this reason, proper separation of the silicate layers into the PLLA matrix was not achieved for surfactant concentration level lower than the mineral CEC.

In the case where melt mixing was applied, increased d_{001} values were observed even at low clay modification levels (50% the clay CEC), implying that PLLA chains were capable of diffusing into the montmorillonite galleries swelling the clay structure. Direct melt intercalation of polymers in organosilicates is primarily driven by enthalpic polymer-host interactions.[25] Thus, the level of polymer insertion into the clay galleries depends mostly on the affinity between the two components. Dispersion of clay at surfactant loadings below CEC was also mentioned by Zhao et al.,[26] who studied the effect of clay modification level on the structure of maleated polypropylene nanocomposites prepared by melt compounding.

At surfactant coverage of 1.25–1.5 times the clay CEC both solution and melt intercalation methods led to a C$_{16}$MMT dispersion at the nanoscale level in the PLLA matrix. The effectiveness of both processing methods indicates that, when there is good interaction between the polymer and the reinforcing agent, the need of an optimized processing path is decreased. However, solution cast hybrids demonstrate a wider peak, which is shifted at smaller angles as compared to the characteristic peak of the melt intercalated ones. The broad peaks are probably owing to the superposition of reflections corresponding to various interlayer distances and a possible presence of a silicate-layers portion in the exfoliated state.

Further increase of the amphiphilic cation concentration (200–300% the clay CEC) restricted the polymer insertion into the silicate galleries of the
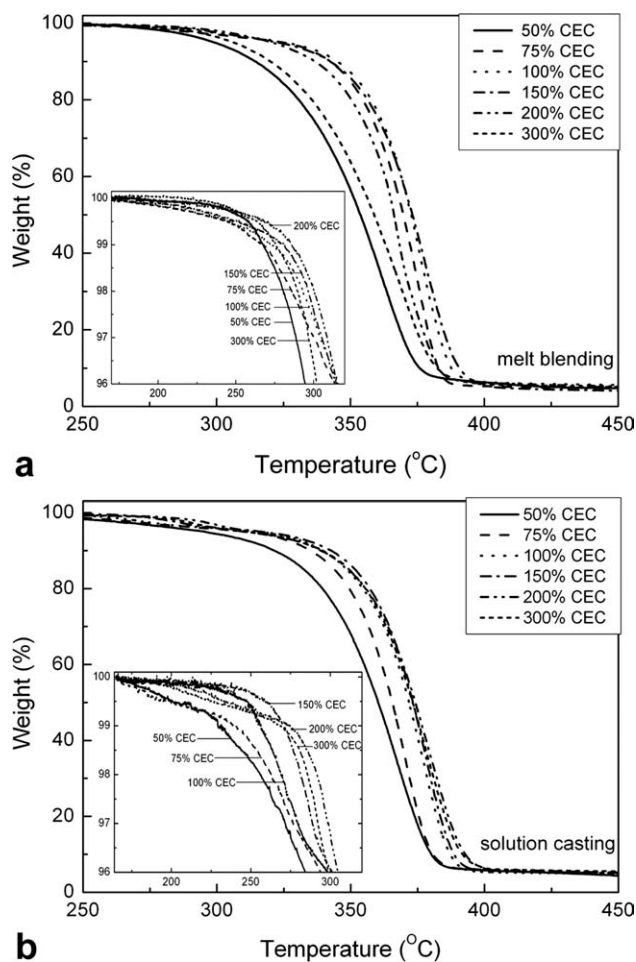
Figure 2 Thermogravimetric analysis curves of PLLA hybrids prepared by (a) melt blending and (b) solution casting, in inert atmosphere. The added MMT was modified to a different level with respect to the percent clay's cation exchange capacity (CEC), by hexadecylammonium cation.

Thermal behavior of the hybrids

Figure 2 shows the TGA curves of the hybrids obtained by the two preparation methods, in inert atmosphere. The inorganic part in every sample examined was constant and equal to 3 wt %. Figure 3(a) was derived from Figure 2 and presents the effect of the preparation route on the onset decomposition temperature in inert (N_2) atmosphere (estimated at 2 wt % loss) of the hybrids as a function of the clay modification level. Similar measurements were also performed in oxidative conditions, under air presence. In this case, the influence of the surfactant concentration on the temperature of the decomposition initiation for both nanocomposite types is illustrated in Figure 3(b).

Inspection of Figures 3(a,b) reveals that the thermal stability of both nanohybrids enhances with an
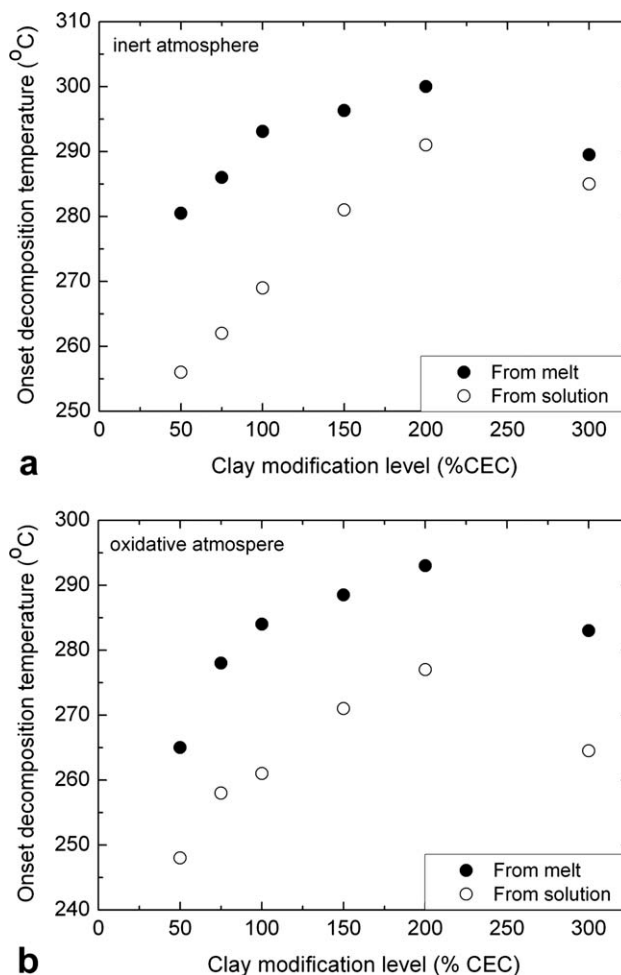

Figure 3 Effect of hybrids' preparation technique and clay modification level on the onset decomposition temperature (estimated at 2% of weight loss) in (a) inert and (b) oxidative atmosphere. The added montmorillonite was modified to a different level, with respect to the percent clay's cation exchange capacity (CEC), by hexadecylammonium cation.

solution intercalated hybrids. Lan et al.[27] reported that large population density of surfactant limits intragallery penetration of polymer contrary to low population density, which provides more interlayer space to accommodate polymer chains. On the contrary, hybrids prepared by melt processing displayed a higher level of clay dispersion. This may be due to the high temperature applied during nanocomposite preparation, which causes a slight reduction of the alkylammonium concentration.

In brief, at clay modification levels lower than 100 and higher than 200% the clay CEC, the melt intercalation process favors insertion of the polymer chains into the interlayer spacing, whereas, at intermediate levels of clay modification, better dispersion of the clay particles can be achieved by solution casting. Moreover, the melt-blended hybrids display a more ordered structure as the characteristic XRD peaks are sharper than the corresponding ones of the solution cast material.
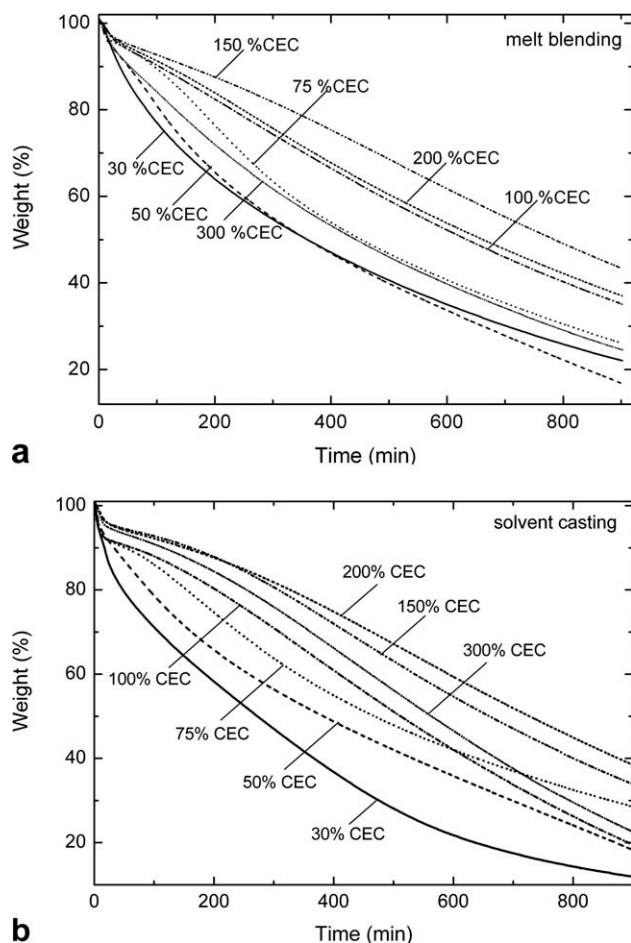
Figure 4 Effect of preparation method on the mass loss of the hybrids prepared via (a) melt blending and (b) solution casting, in oxidant atmosphere and isothermal conditions (260°C). The added montmorillonite was modified to a different extent, with respect to the percent clay's cation exchange capacity (CEC), by hexadecylammonium cation.

the degree of clay modification did not affect the onset decomposition temperature of the material.[30]

Comparing the thermal behavior of the two nano-composite types, it is obvious that melt intercalated materials display an increased temperature of the thermal decomposition initiation compared to the solution cast ones. This may be attributed to the structure of the hybrids derived from melt. As presented in the XRD characterization graphs, these hybrids demonstrate a more ordered structure opposed to those prepared by solution, which exhibit a more homogeneous distribution of the clay particles. However, it has been reported that the intercalated nanohybrids are more thermally stable than the delaminated.[28,31,32]

Thermal stability studies were also conducted in isothermal conditions, at 260°C, and oxidative atmosphere. The decomposition rate of the hybrid is presented at Figure 4, while the time required for 40% mass loss is given in Figure 5 for both nano-composite types. As shown in these figures, an increment of the surfactant loading up to 150% CEC greatly retards the degradation of the matrix. This is probably due to the enhancement of the mineral's dispersibility, which is observed, when the alkylammonium concentration increases from 30 to 150% CEC. It should be mentioned, that the melt compounded material exhibits slightly greater improvement of its thermal stability at surfactant loadings 100–150% CEC.

However, when the alkylammonium quantity exceeds 150% CEC, these hybrids undergo a dramatic attenuation of their thermal stability increasing the mass loss rate. High levels of surfactant excess, when thermal treatment is involved during nano-composite preparation, can promote hydrolysis of
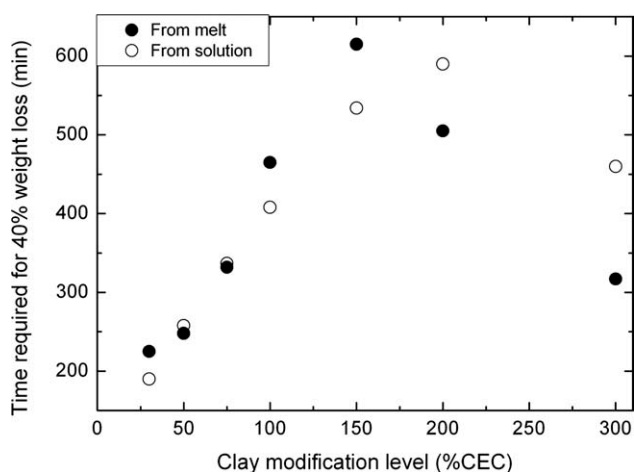
increase of the montmorillonite modification level. Rise of the surfactant concentration improves the miscibility between the two components and strengthens their interaction increasing the onset decomposition temperature of the material. The intimate contact between the clay layers and the polymer favors the formation of a carbonaceous-silicate char structure on the surface of the nanocomposite during burning, which acts as an insulator and a mass transport barrier retarding the decomposition rate of the polymer matrix.[28]

Nevertheless, surfactant coverage higher than 200% CEC causes a deterioration of the hybrids thermal stability. Investigation of the influence of the surfactant loading on the properties of polyethylene/clay nanocomposites showed that the material displays the best firing properties at surfactant concentration equivalent to 1.5 times the mineral CEC.[29] In addition, studies on the thermal stability of polypropylene/layered silicate nanocomposites showed that

Figure 5 Effect of hybrid's preparation route on the time required for 40% volatilization of the material. The added montmorillonite was modified to a different level, with respect to the percent clay's cation exchange capacity (CEC), by hexadecylammonium cation.
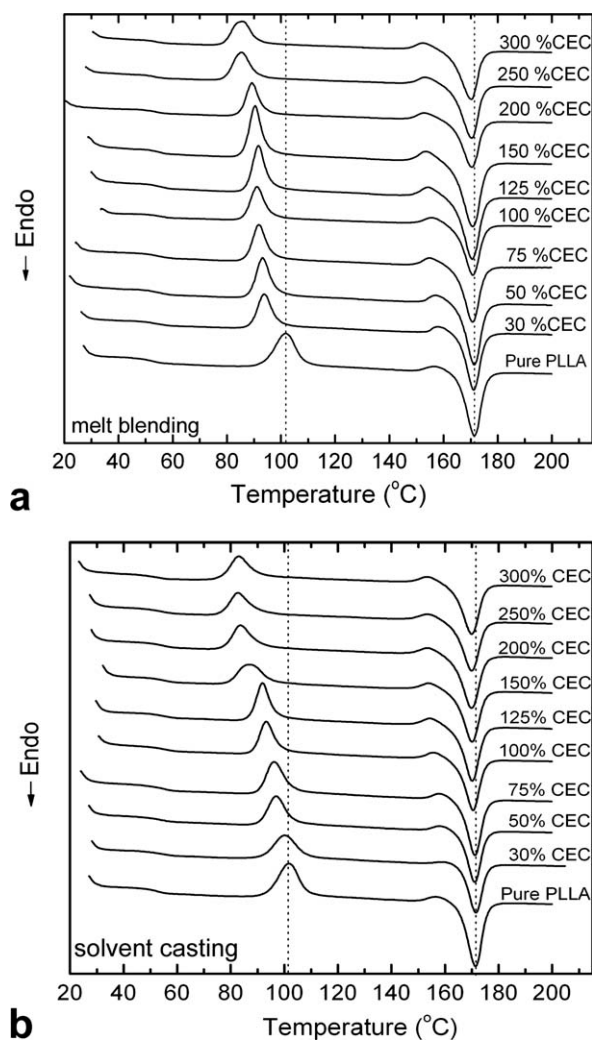
Figure 6 DSC heating thermographs of quenched PLLA hybrids obtained from (a) melt blending and (b) solution casting. The added MMT was modified to a different extent, with respect to the percent clay's cation exchange capacity (CEC) by hexadecylammonium cation.

the polymer chains.[33,34] This reduction in PLLA molecular weight can be the reason of the decreased thermal stability that the melt intercalated nanohybrids display at high surfactant concentrations (higher than 150% CEC).

Figure 6 illustrates the DSC heating curves of the quenched nanocomposites. In all samples, a step-like shape of the curves can be observed in the temperature range of 50–55°C, which represents the glass transition temperature (T_g) of the polymer. The exothermic peak in the range 80–105°C corresponds to the temperature of polymer crystallization (T_c), while the endothermic peak around 170°C is due to polymer melt. The effect of the preparation route on T_g, T_c, and T_m is presented in Table I.

As shown in this table, the trend in T_g values is similar for the two nanocomposites methods preparation indicating that T_g is not significantly affected by the preparation method followed. Initially, an increment of the alkylammonium concentration improves the dispersibility of the mineral into the polymer matrix leading to an increase of the polymer's T_g. The relaxation kinetics of the macromolecular chains confined between the silicate layers is restricted, while the good affinity between the two components partially immobilizes polymer chains attached to the clay layers. However, high levels of surfactant excess (200–300% CEC) promote the mobility of polymer chains due to a plasticizing effect causing a slight depression of the polymer's T_g.[5] This plasticizing effect was lower for the material derived from melt, because the elevated temperatures required during hybrids preparation probably gave rise to the decomposition of a surfactant's portion.

On the contrary, T_c was found to be strongly dependent on the way the hybrid was prepared. Thus, at low filler modification levels (30–100% CEC), melt

TABLE I
Effect of Clay Modification Level on the Thermal Characteristics (T_g, T_c, and T_m) of PLLA Nanocomposites Prepared by Melt Intercalation and Solution Casting

Modification level of the added clay (normalized to the %CEC)	Glass transition temperature (°C)		Crystallization temperature (°C)		Melting point (°C)	
	From melt	From solution	From melt	From solution	From melt	From solution
30	53.8 ± 0.3	53.2 ± 0.4	93.8 ± 0.5	100.5 ± 1	171.2 ± 0.2	171.5 ± 0.2
50	54.1 ± 0.5	53.7 ± 0.4	93.2 ± 0.8	97.2 ± 0.8	171.2 ± 0.1	171.2 ± 0.2
75	54.4 ± 0.3	53.9 ± 0.3	92 ± 0.5	96.2 ± 0.7	170.8 ± 0.3	171.2 ± 0.2
100	55.1 ± 0.3	55.5 ± 0.3	91.5 ± 05	93.2 ± 0.7	170.7 ± 0.2	170.5 ± 0.1
125	55.2 ± 0.3	55.4 ± 0.3	91.5 ± 0.7	91.9 ± 0.6	170.5 ± 0.2	170.3 ± 0.3
150	55.5 ± 0.4	55.3 ± 0.3	90.5 ± 0.7	86.9 ± 0.8	170.6 ± 0.3	170.2 ± 0.2
200	53.2 ± 0.4	54.3 ± 0.5	89.2 ± 0.8	83.6 ± 0.7	170.4 ± 0.2	169.9 ± 0.3
250	53.1 ± 0.5	53.3 ± 0.4	85.4 ± 0.5	82.6 ± 0.5	170.3 ± 0.2	169.9 ± 0.1
300	53.3 ± 0.4	51.6 ± 0.4	85.2 ± 0.7	83.1 ± 0.5	170.2 ± 0.1	169.9 ± 0.2
Pure PLLA	52.5 ± 0.3		102 ± 0.6		171.4 ± 0.2	

The inorganic part in every hybrid was 3 wt %.

compounded hybrids presented a higher degree of clay dispersion compared to the solution cast ones; however, the dispersed inorganic particles act as nucleating agents.[2] Consequently, an increased number of nucleation centers was formed in the extruded material facilitating polymer crystallization and causing a significant decrease of T_c. However, at surfactant concentrations higher than the clay CEC (i.e., 100% CEC), hybrids prepared from solution exhibited a better miscibility between the two components and showed a lower T_c. The dispersed inorganic particles as well as the surfactant excess aggregates serve as additional nucleation sites depressing the temperature of polymer crystallization. This depression is more intense in the hybrids prepared from solution, as the high temperature applied during melt mixing caused degradation of the surfactant excess quantity.

Further increase of the surfactant concentration led to the formation of more aggregates from the surfactant excess especially in the case, where solution casting was employed. Thus, when the clay loading exceeds 250% CEC, these aggregates along with the dispersed nanoclays can retard the crystallization process serving as a physical hindrance obstructing the PLLA molecules from taking part in the flow process, increasing the polymer T_c.[5] Finally, the preparation technique had no apparent effect on the melting point of the hybrids.

CONCLUSIONS

PLLA/organoclay nanocomposites were synthesized via solution and melt intercalation and the effect of the preparation route on the structural and thermal characteristics of the resultant materials was investigated in association with the degree of clay modification.

XRD testing indicated that at low surfactant concentration only melt mixing led to proper dispersion of the nanoclays into the polymer matrix. At intermediate clay modification levels, there was good affinity between the polymer and the inorganic material and hence, both processing paths succeeded in swelling the organoclay due to polymer insertion. However, the miscibility of the two components was higher, when solution casting was applied.

TGA characterization revealed that increase of the alkylammonium concentration up 200% of the clay CEC improves successively the thermal stability of both nanocomposite types. Especially, hybrids derived from melt displayed a particularly high onset decomposition temperature.

Investigation of the nanocomposites thermal properties by DSC showed that, T_g was affected by the surfactant concentration used, in both preparation routes. Moreover, the preparation methodology was found to be very important for the crystallization process of the material.

In conclusion, PLLA/MMT nanocomposites can be preferably prepared by melt intercalation. This method, apart from being environmentally friendly and compatible to current industrial techniques, is capable of dispersing the clay even at very low surfactant concentrations such as 50% CEC. Furthermore, nanocomposites prepared in the melt under shear were found to exhibit higher thermal degradation temperatures. However, alkylammonium loading should not exceed 200% the mineral CEC, otherwise, a reduction of the polymer molecular weight is promoted and consequently a deterioration of the composite's thermal properties occurs. Solvent casting can be also used if the surfactant level will be in the range 100–200% CEC, so that a proper dispersion of MMT particles can be achieved.

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