Homocomposites of Polylactide (PLA) with Induced Interfacial Stereocomplex Crystallites

Veluska Arias, Karin Odelius, Anders Höglund, and Ann-Christine Albertsson*

Department of Fibre and Polymer Technology, KTH Royal Institute of Technology, SE-100 44 Stockholm, Sweden

Supporting Information

ABSTRACT: The demand for “green” degradable composite materials increases with growing environmental awareness. The key challenge is achieving the preferred physical properties and maintaining their eco-attributes in terms of the degradability of the matrix and the filler. Herein, we have designed a series of “green” homocomposites materials based purely on polylactide (PLA) polymers with different structures. Film-extruded homocomposites were prepared by melt-blending PLA matrixes (which had different degrees of crystallinity) with PLLA and PLA stereocomplex (SC) particles. The PLLA and SC particles were spherical and with 300–500 nm size. Interfacial crystalline structures in the form of stereocomplexes were obtained for certain particulate-homocomposite formulations. These SC crystallites were found at the particle/matrix interface when adding PLLA particles to a PLA matrix with α-lactide units, as confirmed by XRD and DSC data analyses. For all homocomposites, the PLLA and SC particles acted as nucleating agents and enhanced the crystallization of the PLA matrixes. The SC particles were more rigid and had a higher Young’s modulus compared with the PLLA particles. The mechanical properties of the homocomposites varied with particle size, rigidity, and the interfacial adhesion between the particles and the matrix. An improved tensile strength in the homocomposites was achieved from the interfacial stereocomplex formation. Hereafter, homocomposites with tunable crystalline arrangements and subsequently physical properties, are promising alternatives in strive for eco-composites and by this, creating materials that are completely degradable and sustainable.

KEYWORDS: Composites, Biodegradable, Morphology, Particles, Stereocomplexation, Interface

INTRODUCTION

Ecological trends work toward the use of “green” composites as substitutes for traditional plastics. These materials are environmentally compatible without sacrificing performance. Composites currently available on the market aim for long-term durability as prime requirement. Therefore, they often contain nondegradable polymers such as epoxies and polyurethane reinforced with fibers (graphite, aramid, and glass), and due to their inherent heterogeneous nature the recycling processes for these materials are limited. In light of this, biobased and degradable polylactide (PLA) polymers are an attractive “green” alternative for composite materials. PLA has proven to degrade in different profiles and rates depending on the applied bulk modification.1,2 The versatility of the lactide monomer has allowed the creation of new materials with unique architectures, mechanical and thermal properties.3–6 Furthermore, by taking advantage of the hydrolysis process suffered by PLA at elevated temperatures, chemical recycling has resulted in high yield of monomer recovery.7

Composites are materials that consist of two or more chemically and/or physically different phases separated by a distinct interface. The phases are combined to achieve properties that cannot be attained by the individual constituents. The constituents retain their separate identities in the composite materials and work together to result in the necessary mechanical strength.8 On this basis, we define a homocomposite as the combination of two physically distinct phases of the identical material separated by a particular interphase. The interfacial microstructure of a polymer composite (formed at the interface between solid-melt and solid—solid by thermomechanical mechanisms) is a research topic of great importance. For semicrystalline polymer matrixes, the crystalline structure near the interface needs to be considered as it affects the final properties of the composite.

Previous research has examined the crystalline structures near the interface between matrix and filler and their effect on interfacial adhesion and bond properties. Additionally, polymer processing methods such as extrusion and injection molding have been shown to influence the formation of interfacial crystalline arrangements.5,10 Interfacial crystalline structures were found in injection molded polypropylene (PP), originating combined effects of the thermomechanical properties.11 Leong et al. reported an increased interfacial adhesion between PP film and PP matrix when tuning the processing...
conditions and the interfacial crystalline structure was the decisive factor for controlling the mechanical properties.\textsuperscript{12,13} Zhong et al. investigated the nucleation rate changes induced under different shear-stress conditions for PLA materials. The crystallization process under shear was enhanced, and the crystallization kinetics were accelerated with increasing shear rate and time.\textsuperscript{14}

PLA-based composites have been reported with different fillers, including lignocellulosic materials,\textsuperscript{15–17} natural fibers,\textsuperscript{18–20} nanoclay,\textsuperscript{21–23} nanotubes,\textsuperscript{24,25} layered silicates\textsuperscript{26,27} and nanoparticles of metals.\textsuperscript{16,28} The successful preparation of multicomponent polymer-based materials relies on the strong interfacial adhesion from interactions between the phases.\textsuperscript{1,29} Composites materials having different phases, such as polar fibers and a nonpolar or hydrophobic polymer matrix, require a defined strategy to improve compatibility and interfacial adhesion. Furthermore, the properties of PLA-based nano-composites, such as PLA/nanoclay composites, strongly depend on the state of the filler in the composite where the dispersion in the matrix is one of the main problems. In this sense, PLA as filler could be a good candidate to be compatible within the PLA matrix. Single-polymer composites made from PLA materials have been previously reported with main focus on fiber type reinforcement, where the manufacturing process can significantly affect the fibers and by inference the properties of the composite.\textsuperscript{30–32} In addition, small sized fillers, in the nanorange, increase the interfacial area and create a significant volume fraction of the interfacial layer. This layer exhibits properties different from the bulk polymer, even at low loadings. Filler loading below 5\% (w/w) results in an effective enhancement of the nanocomposite properties.\textsuperscript{33}

Oriented toward “green” composite materials, we have previously created PLA-based particles with tunable crystalline structures by spray droplet atomization. These particles could function as reinforcement materials in “green” composites.\textsuperscript{3} Spherical PLA particles with a size of \(\sim 400\) nm and tunable crystalline arrangements were fabricated. By taking this to the next level, our aim is to use the well-defined PLA-based particles into PLA matrices to create “green” homocomposite materials based solely on PLA. We hypothesize that combined thermomechanical effects could be achieved by the development of interfacial crystalline structures between PLA particles and PLA matrices with different crystallinity. The relationship between the crystalline structures formed at the particle/matrix interface and the interfacial strength will enable greater control over the final properties of the material. Homocomposites with tunable physical properties are promising alternatives in strive for eco-composites to create materials that can be easily chemical recyled or fully degradable.

\section*{EXPERIMENTAL SECTION}

\textbf{Materials.} The monomers \(L\) - and \(n\)-lactide (Boehringer Ingelheim, France) were purified by recrystallization three times in dry toluene. Ethylene glycol (EG; Sigma-Aldrich, Sweden) was used as the initiator. Stannous 2-ethylhexanoate (Sn(Oct)$_2$; 95\%, Sigma-Aldrich, Sweden) was used as the catalyst. The solvents heptane (Fisher Scientific, Sweden) and toluene (Fisher Scientific, Sweden) were used as solvents. The catalyst was Sn(Oct)$_2$, and the initiator was EG. The reaction was performed in a thermostatically controlled oil bath at 110 °C for 72 h, as previously reported.\textsuperscript{34} The content of \(n\)-lactide in the monomer feed ratio was set to 0, 5 and 7.5\% (mol/mol) for the synthesis of PLA with varying isomeric compositions.

\textbf{Particle Preparation Method.} PLA particles were obtained as dry powders by spray drying polymers solutions using a laboratory-scale spray-dryer (Büchi Mini Spray Dryer B-290, Switzerland).\textsuperscript{3} The feed rate was adjusted by setting the pump speed to 30\%, the two-fluid nozzle had a diameter of 0.7 mm and the inlet temperature was maintained at 65 °C ± 3 °C for all samples. These settings resulted in an outlet temperature of 65 ± 3 °C. The air flow rate (700 NL/h) and the aspirator at 100\% (35 m$^3$/min) were constant. The spray-dried powders were collected and stored in a desiccator at room temperature. The polymer solutions were prepared in a concentration of 0.25 g material/100 mL chloroform. PLLA particles were prepared from the synthesized PLLA (\(M_w = 1.60 \times 10^5 \text{ Da} \) and \(D = 1.2\) ). SC particles were prepared from an equimolar mixture of the synthesized PLLA (\(M_w = 1.60 \times 10^5 \text{ Da} \) and \(D = 1.2\) ) and PDLA (\(M_w = 1.80 \times 10^5 \text{ Da} \) and \(D = 1.1\) ).

\textbf{Homocomposite Preparation Method.} The homocomposites were prepared by extrusion using a twin-screw mini extruder (DSM-Xplore 5 cm$^3$ Micro-Compounder, Model 2012). For the formulations that used matrices with higher melting temperatures, the gradient temperatures from the feed throat to the die were 168, 170 and 170 °C. For the formulations that used matrices with lower melting temperatures, the gradient temperatures were 158, 160 and 160 °C. The screw speed was 80 rpm during 3 min in counter-rotating mode. The homocomposites had a filler loading of 5\% (w/w) for both PLLA and PLASC particles. The samples were dried overnight at 40 °C under vacuum before compounding. This drying minimized degradation during processing. The extruded materials were obtained as films by forcing the material through a film die with dimensions 35 mm width and 0.2 mm thickness.

\textbf{Characterization Techniques. Size Exclusion Chromatography (SEC).} The number-average molar mass (\(M_n\)) and the dispersity (\(D\)) of the PLA polymers were determined using a Verotech PL-GPC 50 Plus system with a PL-RI Detector and two Mixed-D (300 × 7.5 mm) columns from Varian. The samples were injected with a PL-AS RT Autosampler for PLGPC 50 Plus using chloroform as the mobile phase (1 mL/min, 30 °C). Polystyrene standards, with a narrow molar mass distribution in the range of 580–400 000 g/mol, were used for calibration. Corrections for flow rate fluctuations were performed using toluene as the internal standard.

\textbf{Polarimetry.} The \(\pm\)-isomer content in the synthesized PLA matrices was measured by polarimetry using an AUTOPOL IV Automatic Polarimeter (Rudolph Research Analytical, New Jersey). The PLA materials were dissolved in chloroform at a concentration of 1 g/100 mL. Sample solutions were transferred to 100 mm cells and analyzed at a standard wavelength of \(\lambda = 589\) nm. The \(\pm\)-isomer percentage was then calculated using the following equation:

\[
\% = \left[\frac{[\alpha]_{\text{PLLA}}}{[\alpha]_{\text{PDLA}}} \right] \times 100
\]

where \([\alpha]_{\text{PLLA}}\) is the specific rotation for PLLA and \([\alpha]_{\text{PDLA}}\) is the specific rotation for the unknown sample.\textsuperscript{35}

\textbf{Differential Scanning Calorimetry (DSC).} The thermal properties of the particles were measured using DSC equipment (Mettler Toledo DSC 820 module). Approximately 5 mg of polymer was encapsulated in 40 \(\mu\)L aluminum crucibles without a pin. The temperature program was (I) heat from \(–20\) to \(+270\) °C, (II) cool to \(-20\) °C and (III) heat for a second time to \(270\) °C. The heating and cooling rate was 10 °C/min under a nitrogen atmosphere (nitrogen flow rate 50 mL/min). The melting temperature (\(T_m\)) was noted as the maximum value of the melting peaks, and the glass transition temperature (\(T_g\)) was determined from the midpoint temperature of the glass transition. The approximate crystallinity of the materials was calculated according to eq 2.

\[
\psi = \frac{\Delta H_f}{\Delta H_f^c} \times 100
\]
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where $\gamma$ is the degree of crystallinity and $\Delta H_f$ is the heat of fusion of the sample. The heat of fusion of a 100% crystalline PLA polymer (93 J/g) and 100% PLA stereocomplex (102 J/g) is determined by DSC.

**Results and Discussion**

| matrix       | $M_w$ (Da, $\times 10^5$) | $D^*$ | $d$-content$^b$ (mol %) | particle size (nm)$^c$ | particle size dispersity (nm)$^c$ | $T_m$ (°C)$^d$ | $w_c$ (%)$^d$ |
|--------------|--------------------------|-------|--------------------------|------------------------|-------------------------------|----------------|--------------|
| matrix       | PLAhig         | 0.85  | 1.2                      |                        |                               | 171           | 57           |
| matrix       | PLAmed         | 1.51  | 1.1                      | 2.6 ± 0.4              |                               | 150           | 27           |
| matrix       | PLALow         | 1.02  | 1.1                      | 3.4 ± 0.1              |                               | 143           | 5            |
| filler       | PLLA           | 1.60  | 1.2                      |                        | 443.4                        | 176           | 57           |
| filler       | SC$^c$         |       |                          |                        | 364.8                        | 226           | 62           |

a Determined by SEC using CHCl$_3$ as the eluent and polystyrene standards. b Determined by polarimetry. c z-average value. d Determined by DSC. *PLLA with $M_w = 1.60 \times 10^5$ Da and $D = 1.2$ and PDLA with $M_w = 1.80 \times 10^5$ Da and $D = 1.1$.

The incorporation of the particles into the matrixes, and the interfacial stereocomplex crystallites found at the particle/matrix interface of specific particulate-homocomposite materials, were confirmed by thermal analysis (Figure 2) and XRD diffraction patterns (Figure 3). PLa$_{high}$(SC) demonstrated two endothermic peaks at 174 and 223 °C. The latter peak corresponded to the SC particles with a $T_m$ of 226 °C (Table 1 and Figure S2). No significant changes were observed when PLLA particles were added to the PLa$_{high}$ matrix. A broadening in the endothermic melting peak was observed when PLa$_{med}$...
was compared with PLA<sub>high</sub>. This broadening most likely occurred because of the melting of different crystal conformations in the materials. PLA<sub>med</sub> and PLA<sub>low</sub> are a combination of l-lactide and d-lactide isomers (Table 1) that disrupts crystal formation and results in a double endothermic peak in the thermogram. The addition of PLLA particles to PLA<sub>med</sub> (PLA<sub>med</sub>(PLLA)) induced the formation of a second endothermic melting peak at 220 °C. This indicates that SC crystallites were formed at the particle/matrix interface during the melt-processing of the homocomposites. For PLA<sub>med</sub>(SC), two clear endothermic peaks were observed at 151 °C (matrix) and 217 °C (SC particles). PLA<sub>low</sub> and PLA<sub>med</sub> demonstrated a double melting peak that was more pronounced with the addition of particles. For PLA<sub>low</sub>(PLLA), three endothermic peaks were observed at temperatures of 144 °C, 176 and 211 °C, corresponding to the PLA matrix, the PLLA particles and the SC crystallites, respectively. In the case of PLA<sub>low</sub>(SC), two clear endothermic peaks appeared at 143 and 223 °C, corresponding to the matrix and the SC particles, respectively. Additionally, cold crystallization (CC) was observed in some of the formulations. Pure PLA<sub>med</sub> exhibited CC, and a shift toward lower temperatures in the CC was observed after particle addition for PLA<sub>med</sub>(PLLA) and PLA<sub>med</sub>(SC). This finding is most likely because of a facilitated crystallization after particle addition. The identical phenomenon was observed for the PLA<sub>low</sub> formulations. PLA<sub>low</sub>(PLLA) and PLA<sub>low</sub>(SC) demonstrated CC. The lowest temperature was exhibited by PLA<sub>low</sub>(PLLA).

SC crystallites were formed in the PLA<sub>med</sub>(PLLA) and PLA<sub>low</sub>(PLLA) homocomposites, but not in the pure PLA<sub>med</sub> and PLA<sub>low</sub> matrices, which are composed of nonequimolar l- and d-lactide units. This finding is explained by an oriented overgrowth of the SC crystalline phase on the surface of the particles. The particle surface acts as a substrate that is also crystalline. Therefore, SC crystallites are formed at the interface between the PLLA particles and the PLA<sub>med</sub> and PLA<sub>low</sub> matrices when the l-lactide units at the particles surface meet the d-lactide units in the matrix. This specific interfacial interaction between two distinct components is enhanced by an increase in chain mobility upon melting. The orientation of the particles as substrates may enhance the subsequent nucleation at the interface. These special crystallization conditions have been reported for homocrystallites of PLLA on the stereocomplex crystallites of PLLA and poly(1-lactide-co-d-lactide) (20/80) in a ratio of 80/20 that is crystallized from the melt.

The particles enhanced the nucleation of a second crystalline phase, i.e., SC crystallites, by lowering the free energy of activation through the force field near the surface, which also depends on their spatial arrangements. The shear under extrusion facilitated the dispersion of the particles in the matrix and thus enhanced the interfacial complex formation. Simple physical blending of the components did not result in an interfacial complex upon melting during thermal analysis for PLA<sub>med</sub>(PLLA). Furthermore, SC crystallites were not found in the pure matrices, PLA<sub>med</sub> and PLA<sub>low</sub> after melt-blending even when these matrices are composed of l-lactide and d-lactide units. PLLA particles showed purely homocrystallites under thermal analysis. This confirms that the SC crystallites are only formed at the particle/matrix interphase. The SC crystallites could have also been formed during the DSC heating process. However, the thermograms represent the first heating scans that report the thermal history of the materials.

The interfacial complex formation is then explained by the increased crystallization of SC crystallites compared with homocrystallites because of the higher growth rate and density of the SC spheronites and the shorter induction period. SC is preferred over homopolymer crystallization, even at the lower d-content in the PDLA phase in a PLLA-rich matrix. The crystallization of the SC at the interface is most likely completed before the crystallization of the homopolymer begins. The excess of l-units in the interaction between the chains with identical configuration prevails, and they assemble separately to form homocrystallites in the matrix.

The thermal properties of the homocomposites were different depending on the composition (Table 2). For PLA<sub>high</sub>, SC particles slightly increased the T<sub>g</sub> and no variation was observed for PLA<sub>high</sub>(PLLA). The SC particles may reduce the chain mobility in the PLA<sub>high</sub> matrix, thereby resulting in an increase in the T<sub>g</sub>. The enthalpy of fusion (ΔH<sub>fus</sub>) increased for both PLA<sub>high</sub>(PLLA) and PLA<sub>high</sub>(SC) and resulted in increased crystallinity. The enhanced crystallization is because of the heterogeneous nucleation effect induced by the particles. This lowers the surface free energy barrier toward nucleation and allows crystallization to occur at higher temperatures upon cooling. Small content of high molar mass PDLA chains in a PLLA-rich matrix induces the formation of SC crystallites under nonisothermal crystallization. Racemic crystallites are formed over homocrystallites. These crystallites acted as nucleation sites and increased the number of PLLA spheronites and thus the overall crystallization rate. In the case of PLA<sub>med</sub>, the T<sub>g</sub> did not vary with the addition of particles compared with the pure matrix. The ΔH<sub>fus</sub> and the ω<sub>c</sub> increased with the addition of both PLLA and SC particles. The highest values were observed for PLA<sub>med</sub>(SC). The SC particles acted then as better nucleating agents than the PLLA particles. The smaller particle size demonstrates a higher nucleating effect (SC particles are smaller than the PLLA particles, Table 1). An identical trend was observed for PLA<sub>low</sub>(PLLA) and PLA<sub>low</sub>(SC). The T<sub>g</sub> of PLA<sub>med</sub>(PLLA) and PLA<sub>med</sub>(SC), and PLA<sub>low</sub>(PLLA) and PLA<sub>low</sub>(SC) slightly decreased in comparison with their respective matrices. The nucleating effect of the
particles enhances the crystallization process, lowers the crystallization temperature and results in lower $T_m$ values.

**Interfacial Crystalline Structure.** The presence of SC crystallites in the homocomposites, formed at the interface between the PLLA particles and the $\text{PLA}_{\text{med}}$ and $\text{PLA}_{\text{low}}$ matrixes, was revealed by X-ray scattering profiles (Figure 3) confirming the results obtained from DSC data (Figure 2). The peaks in the X-ray patterns of the matrix materials, $\text{PLA}_{\text{high}}$, $\text{PLA}_{\text{med}}$ and $\text{PLA}_{\text{low}}$ appeared at $2\theta$, with values of 17 and 19°. These peaks correspond to the $\alpha$ form of PLLA and PDLA crystallized in a pseudo-orthorhombic unit cell. SC crystallites were observed at $2\theta$, with values of 12, 21 and 24°. These peaks correspond to PLA crystallized in a triclinic unit cell, in which the $\text{L}$- and $\text{D}$-lactide segments are packed parallel in a helical conformation. SC crystallites formed at the interface. The crystallites are formed during the processing between pure PLLA particles mixed with a PLA matrix with $\text{D}$-lactide segments. Their presence is additionally confirmed by the thermograms of the homocomposites (Figure 2). This interfacial crystallite formation was induced during the film-making process. The films were obtained by hot-drawing directly after melt-blending. This process causes an increase in the surface area per unit molecule. This increase is achieved through the expansion of the chains, which in turn increases the probability of interaction between the PLLA chains at the particles surface and the PDLA segments in the matrix. The PLLA chains at the particle surface and the PDLA segments at the matrix arrange themselves side by side through strong hydrogen bonding interactions at the particle/matrix interface under the shear stress of processing (Scheme 1). This tight chain packing at the particle/matrix interface is referred to the SC structure. SC crystallites formed from the melt have been reported in hot-drawing PLA fibers. SC or racemic crystallites can also be formed from the melt when PLLA and PDLA segments are in nonequimolar concentration. This formulation results in a mixture of racemic and homocrystallites because the racemic crystallites form more rapidly than do the homocrystallites. Bai et al. reported SC crystallites at the interphase in blends of PLLA/elastomers containing PDLA units through melt-blending.

**Mechanical Properties.** The formation of interfacial crystalline structures influences the mechanical properties (Figure 4). Incorporating a small weight percentage (5% (w/w)) of PLLA and SC particles into the different PLA matrixes resulted in significant variations in the mechanical properties.
between the homocomposites. The mechanical properties of the particulate-homocomposite materials demonstrated differences that depended on the particle size, particle nature (rigid or soft) and particle/matrix interfacial adhesion. These factors are discussed for each of the properties examined: Young’s modulus, tensile strength and fracture toughness.

The E-modulus, after the addition of PLLA and SC particles, was improved for all homocomposites compared with the neat matrixes (Figure 4a). The E-modulus relates to the stiffness of the material in the elastic region during tensile testing. The stiffness is improved by the addition of particles that are more rigid than the matrix. PLA(SC) homocomposites demonstrated a higher E-modulus than did the PLA(PLLA) homocomposites. The E-modulus is less dependent on the particle size until a critical particle size is reached. Below this value, the effect of particle size on the E-modulus is more significant.51 The differences in the E-modulus between PLA(SC) and PLA(PLLA) are attributed to the rigidity of the particles rather than the variation in size (∼80 nm). Additionally, the particle/matrix interfacial adhesion has shown to have little effect in the E-

Table 2. Thermal Properties of the Particulate-Homocomposite Materials after Extrusion

| material     | $T_g$ (°C) | $T_m$ (°C) | $\Delta H_f$ (J/g) | $\Delta H_m$ (J/g) | $w_c$ (%) |
|--------------|------------|------------|---------------------|---------------------|-----------|
| PLA<sub>high</sub> | 54.7 ± 0.3 | 169.7 ± 0.2 | 55.6 ± 0.9          | 23.1 ± 2             | 39.7 ± 1  |
| PLA<sub>high</sub>(PLLA) | 54.7 ± 0.2 | 170.4 ± 0.5 | 54.9 ± 0.2          | 23.1 ± 2             | 58.9 ± 0.2 |
| PLA<sub>med</sub>(SC) | 56.6 ± 0.6 | 174.0 ± 0.3 | 56.9 ± 1.9          | 12.6 ± 1.2           | 61.2 ± 1.0 |
| PLA<sub>med</sub>(PLLA) | 53.6 ± 0.1 | 153.7 ± 0.3 | 26.7 ± 1.5          | 12.6 ± 1.2           | 15.7 ± 0.8 |
| PLA<sub>low</sub>(SC) | 53.4 ± 0.3 | 150.5 ± 0.1 | 27.9 ± 0.5          | 9.6 ± 0.7            | 20.1 ± 1.0 |
| PLA<sub>low</sub>(PLLA) | 53.3 ± 0.5 | 151.0 ± 0.4 | 31.4 ± 0.1          | 11.8 ± 0.8           | 23.7 ± 0.1 |
| PLA<sub>med</sub> | 49.8 ± 0.2 | 144.3 ± 0.1 | 9.6 ± 0.3           | 10.3 ± 0.4           | 14.9 ± 1.6 |
| PLA<sub>low</sub>(SC) | 46.1 ± 0.3 | 143.9 ± 0.4 | 26.9 ± 1.5          | 15.2 ± 3             | 20.7 ± 0.7 |
| PLA<sub>low</sub>(PLLA) | 46.6 ± 0.4 | 143.9 ± 0.4 | 35.1 ± 0.6          | 12.5 ± 3             | 20.7 ± 0.7 |

$^a$Determined by DSC from the 1st heating scan.

Figure 3. XRD patterns of the particulate-homocomposite materials: (a) PLA<sub>high</sub>-based, (b) PLA<sub>med</sub>-based and (c) PLA<sub>low</sub>-based homocomposites.

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Small differences in the E-modulus were observed for PLA med and PLA low after the addition of PLLA particles, although these materials demonstrated interfacial crystallite formation (Figures 2 and 3). The E-modulus is measured at relatively low deformation in which there is no sufficient dilation to cause interfacial separation between the matrix and the particle.

The rigidity of the particles resulted in clear differences in the E-modulus for the PLA(PLLA) and the PLA(SC) homocomposites. The SC particles demonstrated higher E-modulus (Figure 5) than did the PLLA particles most probably because of the high crystallinity values obtained during the stereocomplexation. During stereocomplexation, intermolecular crystallization dominates when blending PLLA and PDLA. This phenomenon results in increased tie chains between the crystallites. Analysis of the pure PLLA and SC particles demonstrated average height values of 1.2 and 3.2 GPa (Figure 5), respectively.

Depending on the filler particles, the tensile strength of the homocomposites demonstrated a large variation within the matrixes (Figure 4b). The tensile strength is the maximum stress that the material can bear under uniaxial tensile loading.

**Figure 4.** Homocomposite materials mechanical properties: (a) Young’s modulus, (b) tensile strength and (c) toughness.
For these homocomposites, the strength depends on the stress transfer between the matrix and the particle filler. Particle size and the particle/matrix interfacial adhesion affect the strength of the material. For PLA high, the strength of the materials increased with decreasing the particle size: PLA high ≪ PLA high (PLLA) < PLA high (SC). Smaller particles (such as SC particles) have a higher surface area, which results in a more efficient stress transfer. PLA med (PLLA) and PLA low (PLLA) had higher tensile strengths compared to PLA med (SC) and PLA low (SC). The interfacial adhesion had a larger effect than did the particle size. The adhesion strength at the particle/matrix interface defines the load transfer between the particle and the matrix. SC crystallites are formed at the interface between the PLLA particles and the PLA med and PLA low (Figures 2 and 3). The crystal formation at the interface contributed to the improved adhesion of the particles to the matrix. This adhesion increased the stress transfer between the components. Particle agglomeration may have affected the stress transfer between the particles and the matrix. The SC particles coalesced more readily than the PLLA particles in the homocomposites (Figure 1). This behavior resulted in the lower tensile strength values obtained for PLA med (SC) compared with PLA med (PLLA). The strong interfacial interaction between the PLLA particles in PLA med (PLLA) and the matrix may facilitate the dispersion of the filler in the matrix and obstructing possible agglomeration. This behavior was observed for the PLA low-based materials. The tensile strengths of these homocomposites were PLA low < PLA low (PLLA) > PLA low (SC). The introduction of rigid SC particles into a polymer matrix results in a reduction in the strength of the material, but at the same time the crack propagation becomes more difficult. The particle loading also affects the strength of the material (Figure S3). Different amounts of SC particles, i.e., 5 and 10 wt %, were added to the PLA high matrix. Increased brittleness was observed in the homocomposites that contained an increased particle amount. Mechanical testing was not possible for the film of PLA high (SC) with 10 wt % particles because of increased brittleness probably due to agglomeration of the particles. Smaller sized particles have a higher coalescent tendency that interrupts the stress transfer between the particle and the matrix and induce brittleness.54

The fracture toughness of the homocomposites differed for all of the particle–matrix combinations (Figure 4c). For PLA high, the fracture toughness increased with the addition of PLLA particles. The addition of SC particles had no effect: PLA high ≪ PLA high (PLLA) >> PLA high (SC). For PLA med and its homocomposites, the toughness slightly decreased with the addition of both particles in comparison with the matrix: PLA med ≥ PLA med (PLLA) > PLA med (SC). This decrease may have occurred because brittleness increases when there is poor interfacial adhesion between components. Rigid fillers, such as SC particles, increase the stiffness of the composite but decrease the fracture toughness, which results in a more brittle material. This phenomenon explains the decreased toughness observed for PLA med (SC). For PLA low, an increase in toughness was observed when PLLA particles were added to the matrix. A decrease in toughness compared with the neat matrix was obtained for PLA low (SC): PLA low < PLA low (PLLA) > PLA low (SC). The increased toughness values for PLA med (PLLA) and PLA low (PLLA) is explained by the strong interfacial adhesion between the PLLA particles and the PLA matrices with D-lactide segments. This adhesion affects the fracture toughness. Strong adhesion leads to the increased toughness of the homocomposite. The interfacial adhesion between the particles and the matrix was confirmed by particle/matrix interfacial debonding and the subsequent appearance of voids with the strain of the crystalline matrix after tensile testing (Figure 6, blue lines). PLA med (PLLA) and PLA low (PLLA) demonstrated better adhesion of the particles to their respective matrixes because of the interfacial complex crystalline structures (Figure 6, green lines). Bai et al. demonstrated improvements in PLA toughness by increasing the interfacial strength through SC crystallites.60 In PLA med (SC) and PLA low (SC), cavities in the matrix were observed after tensile testing indicating poor adhesion between the SC particles and the matrixes. In PLA high (PLLA), small cavities were observed that may be attributed to nonmelted PLLA particles during the melt-blending process that was performed close to the Tm of the PLLA particles.

**Heat Resistance.** The thermal resistance of the homocomposite was improved with the addition of particles (Figure 7). The decomposition trace of the pure particles (Figure 7a) demonstrated that SC particles have a slightly higher thermal decomposition temperature (Tmax) than do pure PLLA particles. The helical conformation in SC is stable at temperatures higher than the Tm because of the strong interactions between the L- and D-lactide chains. These chains reduce the molecular mobility and delay the thermal degradation. However, at temperatures much higher than the Tm of the SC, these interactions have little effect resulting in slight difference in the thermal stability between PLA and PLA low (PLLA).
stereocomplex crystallites and PLA homocrystallites. In PLAhigh(SC), the first derivative of the decomposition trace demonstrated a shift toward higher temperatures with the addition of SC particles compared to PLAhigh. No shift was observed for PLAhigh(PLLA). PLAmed demonstrated double decomposition traces because of the different crystal formations. PLAmed(PLLA) and PLAmed(SC) exhibited an increase in the decomposition peak toward higher temperatures that corresponded to the decomposition of SC crystals. This peak is an indication of SC crystals formed at the interfaces between the PLLA particles and the PLAmed matrix. For PLAlow(PLLA), a small shoulder at higher temperatures appeared after the addition of PLLA particles. This shift represents SC crystal formation at the interface between the PLLA particles and the matrix. The second decomposition peak becomes more accentuated toward higher temperatures in PLAlow(SC) after the addition of SC particles.

**Surface Topography.** The surface topography of the films confirmed the particle distribution in the matrixes (Figure 8). A good distribution of both the PLLA and SC particles in the matrixes was observed. Particles were observed in PLAhigh(PLLA). These particles are likely nonmelted PLLA particles even when the extrusion temperature for the PLAhigh formulations was close to the $T_m$ of the PLLA particles. The surface topography of the films depicted a specific pattern of horizontal lines in the entire area. This pattern may be attributed to the film die that was used during the extrusion.

The stereocomplexation, formed at the particle/matrix interface in PLAmed(PLLA) and PLAmed(PLLA), provided a strong matrix/filler interaction. This stereocomplexation facilitated...
the dispersion of particles in the matrix and affected the mechanical properties of the homocomposites (Figure 4).

**CONCLUSIONS**

Homocomposites, based solely on polylactide (PLA), that were composed of a matrix of PLA and poly-l-lactide (PLLA) or PLA stereocomplex (SC) particles were successfully prepared. Interfacial complex crystalline arrangements were obtained in various combinations of homocomposite formulations and resulted in specific thermal and mechanical properties. The stereocomplexation for some of the homocomposites formulations after processing was confirmed to occur only at the particle/matrix interface. The stereocomplexation at the particle/matrix interface was not achieved by simple physical blending of the components in the specific formulations, and nor in the pure matrices composed of l-lactide and d-lactide units. The PLLA and SC particles functioned as nucleating agents for all matrices and enhanced the crystallization. The E-modulus of the matrices increased with the addition of PLLA and SC particles. Pure SC particles had a higher E-modulus than did PLLA particles. Homocomposites with rigid SC particles demonstrated a higher E-modulus than did homocomposites with PLLA particles. The tensile strength of the homocomposites was improved through the interfacial complex formation. The highest tensile strength among the homocomposites formulations was obtained when having PLLA particles into PLA matrices due to the interfacial complex formation. The SC crystallites formed at the particle/matrix interface for the specific homocomposite formulations improved the stress transfer between the particles and the matrix. Strong interfacial adhesion was exhibited by homocomposites of PLLA particles and PLA matrices through the interfacial stereocomplex formation. SC particles demonstrated higher decomposition trace temperatures than PLLA particles. Therefore, the heat resistance of the homocomposites was enhanced when SC particles were added to the matrices. The strong interfacial complex adhesion in homocomposites of PLLA particles and PLA matrices facilitated the dispersion of the particles in the matrix. The conception of homocomposites, using different structures instead of different materials, in combination with the understanding of interfacial crystalline structures formation, will enable more control over the material properties. Finally, the development of “green” homocomposites will expand the use of biobased materials in the creation of composite products, which can be chemical recycled or fully degradable, and by this contributing in the achievement of a more sustainable society.

**ASSOCIATED CONTENT**

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Particle SEM micrographs, particulate-homocomposite molar masses after film extrusion, DSC thermograms of the 2nd heating scan, representative tensile strength curves and the images of the formulations with varying particle loading (PDF).

**AUTHOR INFORMATION**

**Corresponding Author**

*A.-C. Albertsson. E-mail: aila@polymer.kth.se. Tel.: +46-8-790 82 74. Fax: +46-8-20 84 77.

**Notes**

The authors declare no competing financial interest.

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