Toward “Green” Hybrid Materials: Core–Shell Particles with Enhanced Impact Energy Absorbing Ability

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Supporting Information

ABSTRACT: Restricted properties of “green” degradable products drive the creation of materials with innovative structures and retained eco-attributes. Herein, we introduce the creation of impact modifiers in the form of core–shell (CS) particles toward the creation of “green” composite materials. Particles with CS structure constituted of PLA stereocomplex (PLASC) and a rubbery phase of poly(ε-caprolactone-oc-D,L-lactide) (P[CL-co-LA]) were successfully achieved by spray droplet atomization. A synergetic association of the soft P[CL-co-LA] and hard PLASC domains in the core–shell structure induced unique thermo-mechanical effects on the PLA-based composites. The core–shell particles enhanced the crystallization of PLA matrices by acting as nucleating agents. The core–shell particles functioned efficiently as impact modifiers with minimal effect on the composites stiffness and strength. These findings provide a new platform for scalable design of polymeric-based structures to be used in the creation of advanced degradable materials.

KEYWORDS: Polylactide, Biodegradable, Stereocomplex, Homocomposites, Impact modifier

INTRODUCTION

Environmental concerns drive the rapid expansion of new material design concepts as promising “green” alternatives for composite materials. The major attributes about “green” composites are that they are eco-friendly, can be fully degradable and sustainable. Among those, particulate “green” composites have gained much attention as unique properties, by synergetic combination of the diverse components on the molecular scale, can be achieved. In light of this, the creation and usage of functional particles and particles with core–shell (CS) structure has become an attractive choice as components in advanced materials. Structured CS particles combine the characteristics and properties of the shell and the core, where the surface properties of the shell are translated to the core, imparting new functionality to the final structure, causing a synergistic effect. Accordingly, CS particles have been extensively used in a number of applications such as surface coatings,10 catalysis11,12 drug delivery systems13–15 and more recently as impact modifiers.16–19

CS structured impact modifiers (IM) are an attractive method to incorporate a rubbery phase within a matrix, as in contrast to the straightforward use of the rubbery material, domains with regular size and shape are formed. Key parameters for achieving effective impact modifiers involve the design of its chemical composition, effectiveness at low loadings, miscibility/compatibility with the matrix, and the morphology of the resulting toughened material. Recently developed IM have been designed either as linear elastomers having low Tg or as cross-linked core–shell polymers consisting of a low Tg rubbery core encapsulated by a glassy phase that has a good interfacial adhesion with the matrix.20 Impact modifiers have been launched in order to provide an economic solution to the brittleness of some materials, particularly for the most famous biobased polymer, i.e., polylactide (PLA). The commercially attractive, biobased and degradable21,22 PLA indeed shows a key drawback with its limited toughness, which in some ways hinders its further industrial implementation. To overcome this issue, several impact modifiers have been investigated for PLA,23 among which poly(ε-caprolactone) (PCL)-based (co)polymers due to their biodegradable character,24 where P[CL-co-LA],25 P[CL-co-TMC]26 or P[CL-co-VL]27 are among the most common. To boost up the performances of IM modifiers, (in)organic nanoparticles have also been introduced as compatibilizing agents along with the IM in order to control their morphology within PLA matrix, while maintaining a high stiffness for the resulting blends. Association in a synergistic manner of rubber-like impact modifiers and (in)organic nanoparticles has shown to greatly improve the toughness of the PLA matrix by as much as a factor of 12.28 This is due to the specific localization of the

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(nano)particles at the matrix/IM interface, forming a CS-like structure and inducing modification in the morphology of the blended material. This solution could, however, affect the further use of PLA in certain fields of applications as its degradable profile could be altered.

In light of this, we previously reported homocomposites as “green” multiphase materials composed solely of PLA polymers, where a PLA matrix is reinforced with PLA stereocomplex (PLASC) particles. PLASC have attracted much attention as property modifiers due to their multifunctionality as reinforcing elements and nucleating activity, as well as their degradable character. The PLASC particles had high E-modulus (~3.2 GPa) and high crystallinity, increasing the stiffness of the PLA matrix. However, a decrease in the overall mechanical performance of the matrix was observed due to the presence of soft microdomains that could act as stress concentrators. In addition, we have previously incorporated soft rubbery microdomains within a PLA matrix, leading to an increase in impact strength but hampering the overall stiffness of the composites. By taking the next level, our aim is to produce “green” impact modifiers in the form of core–shell (CS) PLA-based particles to be used as reinforcing elements in PLA-based composite materials. Our hypothesis was that the use of core–shell structured particles in PLA-based composites will enhance the impact and thermo-mechanical properties of the PLA matrix through a synergistic effect between the components. The CS particles will combine stiffness induced by the presence of PLASC and elastic properties induced by the P[CL-co-LA] rubbery phase acting as an impact modifier. Furthermore, the low amounts of the PCL segments in the particle’s rubbery phase ensure the maintenance of a homocomposite formulation as promising alternatives in strive for eco-composites that can be easily chemical recycled or fully degradable.

**EXPERIMENTAL SECTION**

**Materials.** The monomers l- and d-lactide (Boehringer Ingelheim, France) were purified by recrystallization three times in dry toluene, and ε-caprolactone (Acros, Belgium) was dried for 48 h over calcium hydride and distilled under reduced pressure. Ethylene glycol (EG; Sigma-Aldrich, Sweden) and n-heptanol (Sigma-Aldrich, Belgium) were used as the initiators, which was dried over molecular sieves, and stannous 2-ethylhexanoate (SnOct); 95%, Sigma-Aldrich, Sweden) was used as the catalyst in the polymer synthesis. The solvents, i.e., heptane (Fisher Scientific, Sweden), toluene (Fisher Scientific, Sweden) and chloroform (Fisher Scientific, Sweden), were used as received. Commercially available extrusion-grade PLA (NatureWorks 4043D) with 4.8% d-lactide isomer content, $M_n = 219 \times 10^3$ Da and $D = 1.89$, as determined from SEC analysis, was used as received.

**Polymer Syntheses.** Poly(l-lactide) (PLLA) and poly(n-lactide) (PDLA) were synthesized by SnOct-catalyzed ring-opening polymerization (ROP) of l- and d-lactide initiated with EG. The reaction was performed in a thermostatically controlled oil bath at 110 °C for 72 h, as previously reported. The random copolymer poly(ε-caprolactone-co-d, l-lactide) (P[CL-co-LA]) (72/28 CL/LA % mol/mol) was synthesized by ROP of ε-caprolactone and d, l-lactide in one pot reaction. The catalyst used was SnOct, and n-heptanol as initiator in molar ratios [1]/[catalyst] and [M]/[l] of 100 and 200, respectively. The reaction was performed in a thermostatically controlled oil bath at 160 °C for 24 h, as previously reported.

**Particle Preparation Method.** The particles were obtained as dry powders by spray drying polymers solutions using a laboratory-scale spray-dryer (Rüch Mini Spray Dryer B-290, Switzerland).

PLASC particles were prepared by a two-fluid nozzle where 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 ± 3 °C for all samples, according to a previously reported procedure. PLASC particles were prepared from an equimolar mixture of the synthesized PLLA ($M_\text{n} = 1.32 \times 10^5$ g/mol and $D = 1.1$) and PDLA ($M_\text{n} = 1.25 \times 10^5$ g/mol and $D = 1.1$).

Core–shell (CS, i.e., P[CL-co-LA] as the core and PLASC as the shell) and inverse core–shell (ICS, i.e., PLASC as the core and P[CL-co-LA] as the shell) particles were prepared by means of a three-fluid nozzle where the solutions for the core and the shell were fed separately into the outer and inner sections of the three-fluid nozzle, respectively, while varying the ratio of their flow rates. The polymeric solutions contained an equimolar mixture of synthesized PLLA and PDLA, and P[CL-co-LA] ($M_\text{n} = 140 \times 10^4$ g/mol and $D = 1.4$), for the shell and the core depending on the formulation. The pump speeds were set to 20% and 30% for the solutions containing the core and the shell, respectively.

In all cases for both nozzles, the concentrations of the polymeric solutions were fixed to 0.5% w/w and the settings resulted in an outlet temperature of 65 ± 3 °C, and the air flow rate (700 Nl/h) and the aspirator at 100% (35 m3/min) were constant. The spray-dried particles in the form of powder were collected and stored in a desiccator at room temperature until further use.

**Composite Preparation Method.** Composites using PLA as matrix and the three types of PLA-based particles were prepared by extrusion using a twin-screw mini extruder (DWM- Xplore 15 cm³ Micro-Compounder). The different components were dried overnight at 60 °C under vacuum before compounding. The composites were prepared by extrusion using 180 °C from the feed throat to the die, at 80 rpm for 3 min in corotating mode. Thereafter, the materials were compression-molded at 180 °C for 10 min (9 min under contact and 1 min at 10 bar pressure). The composite systems were set with a final composition of 90/10 w/w matrix/particles.

**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 Vetrotech 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.

**Differential Scanning Calorimetry (DSC).** The thermal properties of the particles were measured using a DSC equipment (DSC Q2000, TA Instruments). Approximately 5 mg of polymer was encapsulated in 40 µL aluminum pans. The temperature program was: (I) heat from −20 to +200 °C, (II) cool to −20 °C and (III) heat for a second time to 200 °C. The heating and cooling rate was 10 °C/min under a nitrogen atmosphere (nitrogen flow rate 25 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 1.

$$w_c = \frac{\Delta H_f}{\Delta H_f} \times 100$$

where $w_c$ is the degree of crystallinity and $\Delta H_f$ is the heat of fusion of the sample. The heat of fusion, $\Delta H_f$ of a 100% crystalline PLA polymer was taken from the literature as 93 J/g.

**Thermogravimetric Analysis (TGA).** The thermal stability of the particles and composite materials was evaluated using a TGA instrument (TA Instruments Q5000). Approximately 5 mg of sample was loaded into crucibles and heated from 25 to 600 °C at a rate of 20 °C/min under a nitrogen atmosphere (the nitrogen flow rate was set to 60 mL/min).

**Tensile Testing.** The mechanical properties of the composites were evaluated by tensile testing. Tensile tests were performed using a Zwick universal tensile tester according to the standard ASTM D638-10 (preload = 5 N and speed = 1 mm/s).
Impact Testing. Notched Izod impact test on the composites were performed using a Ray-Ran 2500 pendulum impact tester (E = 4 J, mass = 0.668 kg and speed = 0.46 m/s). The samples with dimensions of 35 × 12 × 3 mm were preconditioned before testing and the measurements were performed according to ASTM D256.

X-ray Photoelectron Spectroscopy (XPS). The surface chemical compositions of the dried particles systems were obtained by means of X-ray photoelectron spectroscopy (XPS). XPS measurements were performed at room temperature with an achromatic Al Kα X-ray source operated at 15 kV and 20 mA. High-resolution scans of the carbon 1s (C 1s) were acquired at the takeoff angles of 45 and 80°. Quantitative XPS analyses were performed with the Kratos Vision software (version 2.1.2). The atomic concentrations were calculated from the photoelectron peak areas by using Gaussian–Lorentzian deconvolution. The C 1s spectra were taken from the literature and the spectra were charge-corrected by setting the carbon-without-oxygen-bond contribution in the C 1s emission at 285.0 eV.39

SEM. The morphology of the particles surfaces was evaluated using a Hitachi S-4800 SEM with an accelerating voltage of 1.5 kV. The morphology of the surfaces of the impact-fractured specimens was analyzed by scanning electron microscopy (SEM) using a Philips XL20 microscope (1−30 kV). The samples were sputter-coated with gold prior to analysis. The morphology of the particles was evaluated using a Hitachi S-4800 operated with an accelerating voltage of 1.5 kV. The samples were sputter-coated with a gold/palladium mixture (60% gold, 40% palladium) prior to the experiments. Analysis software ImageJ was used for the analysis of SEM images to estimate the particle size of the spray dried particles.48

Dynamic Light Scattering (DLS). The size of the particles was measured by dynamic light scattering (DLS) using a Zetasizer Nano ZS at 25 °C. Water solutions containing particles at a concentration of 1 mg/mL were sonicated for 10 min and filtered using 2 μm nylon syringe filters before evaluation.

RESULTS AND DISCUSSION

PLA-based “green” homocomposites reinforced with core−shell particles were herein achieved. The core−shell structure of the particles induced specific thermomechanical and impact properties in the materials. The particles with a core−shell structure, based on PLA and PCL-based (co)polymers, were prepared by spray-droplet atomization. The molar masses of the polymers used for the particles preparation were in the same range: PLLA (M_n = 132 × 10^3 g/mol; M_w = 287 × 10^3 g/mol; D = 1.1), PDLA (M_n = 125 × 10^3 g/mol; D = 1.1) and P[CL-co-LA] (M_n = 140 kg/mol; D = 1.4). Using these, three different types of particles were prepared: PLA stereocomplex (PLASC); core−shell (CS) particles having PLASC as outer shell and the rubbery type impact modifier (IM) P[CL-co-LA] as the core; and inverted core−shell (ICS) having IM as outer shell and PLASC as the forming core (Scheme 1). Pure P[CL-co-LA] is fully amorphous with a T_m of ~35 °C (Figure S1) and did not form particles by itself under the experimental conditions used, thus the sole material is only used as reference. The PLASC particles were prepared according to a previously reported procedure.47 The core−shell structure was obtained by spray drying the polymeric solutions using specific experimental conditions for each particle type (see the Experimental Section). The setup ensured that the collected material was dry, nonsticky and only a small amount of wasted material was deposited on the wall of the drying chamber. The dry powder produced in a single batch had white color and the production yield was between 60 and 70% for the different formulations.

Scheme 1. Schematic Representation of the Particles Preparation Method Using a Two- and a Three-Fluid Nozzle

The core−shell configuration of the spray-dried particles was determined by elucidation of the particles surface composition by XPS analysis (Figure 1). The binding energies for carbon in the particle systems were correlated with the aimed core−shell configurations. In the high-resolution carbon spectra, the carbon signal can be resolved into several component peaks, which reflect the local environments of the carbon atoms: C—C, C—O and O—C=O functions. In all samples, the three component peaks are therefore categorized by the kind of bonds involved in PLA and PCL molecular structures. Corresponding peaks compared to the literature appeared at specific binding energies for each function of linear polymers: C—C at 285.0 eV; C—O at 286.5 eV and O—C=O at 289.0 eV.39,40 The distinctive peak corresponding to the O—C=O function at 289.0 eV shifts toward lower binding energy values for the P[CL-co-LA] copolymer compared to the PLASC. The CS showed the distinctive peak corresponding to the O—C=O function in the same region as for the PLASC, indicating that the surface is composed of PLASC for this formulation (blue arrows). In contrast, the ICS particle system resembled the P[CL-co-LA] showing a shift for the O—C=O function toward lower binding energy, indicating that this formulation indeed contains P[CL-co-LA] as the outer layer (red arrows).

Furthermore, the composition of the particles systems was determined from the first derivative of the decomposition traces (Table 1 and Figure 2). The particles had a composition of ~80% PLASC and ~20% of the IM, and ~70% SC and ~30% IM, for the CS and ICS formulations, respectively. For the production of the particles with core−shell structure, the variable parameter was the ratio of the volumetric flow rates of the external (PLLA/PDLA equimolar solution for the CS formulation) to the internal (IM solution for the CS formulation) liquids to 1:0.6. Hence, both the CS and ICS particle systems gave compositions close to the theoretical formulations, indicating that high encapsulation efficiency was achieved with the carefully chosen parameters. Decomposition traces of the particles varied depending on the composition (Figure 2). The decomposition trace of the pure particles demonstrated that the particles containing the P[CL-co-LA] used as impact modifier, i.e., CS and ICS particles, presented higher thermal decomposition temperature (T_m) than PLASC particles. Pure P[CL-co-LA] had a decomposition temperature around ~400 °C. This is probably due to the PLA segments that have lower thermal stability than do the PCL segments.41,42 In the CS particles, the first derivative of the decomposition trace demonstrated a two-step degradation where the highest intensity peak had a shift toward lower temperatures resemble the SC particles. The second degradation step (small intensity peak) is shifted toward higher
temperature values in the region of the pure P[CL-co-LA]. The ICS particles presented two degradation steps as well, but oppositely to the CS formulation, the highest intensity peak had a shift toward higher temperatures resembling the P[CL-co-LA] and a lower intensity peak appeared at lower temperatures toward the PLASC region. This corroborates the composition in the core–shell structured particles formulations.

The size of the particles was determined by DLS and SEM microscopy (Table 1). The preparation method and the materials packing ability led to larger particles for the core–shell formulations, i.e., CS and ICS, in comparison to pure SC particles. This could be due to that an excess of the polymeric solution that will form the particle surface can not only enhance the encapsulation of the forming core within each particle but also lead to some type of buckling of the particles between them. This manifests itself by the span of the size distribution, especially for the ICS formulation. It can also be seen in the SEM micrographs in Figure 3, which shows that the individual particles are actually rather small, that they, however, form agglomerates. Accordingly, SEM images further showed that the CS and ICS particles had a bigger size and a more irregular spherical shape compared to the PLASC particles. This is probably due to fact that the PLASC particles were produced using a two-fluid nozzle, which influences the particle tendency to undergo buckling instability.43 Furthermore, the PLASC/P[CL-co-LA] ratio used for the CS and ICS formulations and the large molecule sizes, could have led to larger mean particle size. It was observed that different particle sizes were obtained by the two methods applied, where the smallest size was reported by DLS. This could be due to prior to DLS analysis of dry powder, the samples are sonicated to achieve suspended particles and avoid particles for sticking together. Moreover, particles adherence could lead to miscalculation of the mean particle size when analyzed by SEM, and image treatment of a large number of particles is needed to reach an average particle size.44 Besides the differences in sizes, the particle systems presented unique thermal properties within the formulations (Table 2 and related Figure S1). The core–shell particles thermal data demonstrated that the particles consisted of PLASC and the P[CL-co-LA] in the formulations. The CS particles showed two \( T_g \) values in the range of \(-34 \) and \(+59^\circ C\) corresponding to the P[CL-co-LA] and the PLASC component in the composition. Similarly, the ICS particles also showed two \( T_g \) values of \(-32 \) and \(+49^\circ C\) in the formulation. The lower \( T_g \)

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**Table 1. Particles Composition and Size**

|                | PLASC−content (%a) | IM−content (%a) | particle size (μm) | dispersity (μm) | particle size (μm) |
|----------------|--------------------|-----------------|--------------------|-----------------|--------------------|
| CS: core−shell | 79.8               | 20.2            | 0.7                | 0.5             | 1.1                |
| ICS: inversed core−shell | 33.3               | 66.7            | 1.2                | 0.5             | 1.5                |
| PLASC: stereocomplex | 100               | 0.6             | 0.2                | 0.6             |                    |

“Determined from the 1st derivative of the decomposition traces. *z-average value determined by DLS. *Particles average size determined from SEM micrographs.

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**Figure 1.** XPS high-resolution C 1s deconvolution spectra of the particles and the P[CL-co-LA] used as reference (5 nm penetration depth). Right: zoomed area of the specific function O—C═O at 289.0 eV.

**Figure 2.** 1st derivative of the decomposition traces of the PLASC, CS and ICS particles and the impact modifier, P[CL-co-LA], as reference.

**Figure 3.** SEM micrographs of the particles systems: CS, ICS and PLASC particles.
value of the PLA phase in the ICS in comparison to the CS structure could be due to the higher amount of P[CL-co-LA] in the formulation, lowering much more the glass transition of the structure. The endothermic peak observed for the PLASC, CS and ICS formulations at temperatures ~220 °C corresponded to the PLASC formed at the shell and core for the CS and ICS compositions, respectively. A decrease in the cold crystallization and fusion enthalpies was observed in the CS and ICS formulation compared to the PLASC particles. This is probably due to a decrease in the chain segment mobility for crystallization induced by the rubbery P[CL-co-LA] component. Because of the differences in crystallinity between the core and the shell in the particles, crystalline PLASC and fully amorphous P[CL-co-LA], the core–shell structure was examined by the presence or absence of crystalline structures at the particle surfaces by polarized optical micrographs of the dry particles (Figure S2). For the SC and CS particles, clear crystalline structures at the surface of the dry agglomerated particles were observed. Oppositely, the ICS formulation did not show crystalline domains at the particle surfaces. This further corroborates the obtained core–shell, CS, and inverted core–shell, ICS, structures in the particle formulations.

**Composite Formulations.** The carefully designed CS and ICS particles were used as reinforcement elements in the creation of PLA-based composites. The impact modifier used in the core–shell particles is like previously described a combination of PCL and PLA (72/28 CL/LA % mol/mol), which confirms the almost fully maintenance of a homo-composite formulation. The composites contained 10 w/w % of the CS particles in the composition and the CS particles contained ~20 w/w % of the P[CL-co-LA] in the formulation (Table 1 and Figure 2), indicating that the total amount of the impact modifier in the composites was of ~2 w/w %. Common contents of rubbery impact modifiers used in PLA matrices are around 10–20 w/w % as reported in the literature. Herein, only 2 w/w % of the rubbery phase in the PLASC matrix was sufficient to enhance the impact performance of the PLA composites, while ensuring compatibility between the phases and the composites eco-attributes maintained. Five different composite systems with composition of 90/10 w/w % matrix/particles were prepared as follow: PLA/CS (PLA/core–shell particles), PLA/ICS (PLA/inv/coreshell particles) and PLA/CS/ICS (PLA/core–shell/inv/coreshell particles in a composition 90/5/5% w/w). Additionally, PLA/IM (PLA/P[CL-co-LA]) and PLA/PLASC (PLA/PLA stereocomplex particles) blends were prepared as references.

The thermal properties of the particulate composites varied depending on the composition (Table 3). For the composites with SC particles in the PLA matrix, two endothermic peaks were observed at temperatures around 146 and 223 °C, corresponding to the homocrystallites in the PLA matrix and to the racemic crystallites in the PLASC particles, respectively. Only one \( T_g \) was detected at temperatures around 57 °C, typical for PLA materials. An increased crystallinity in the PLA matrix was observed, most probably because of the heterogeneous nucleation effect induced by the PLASC particles. It has been previously shown that small concentrations of PLASC induced a nucleating effect in PLA homocrystallization. This lowers the surface free energy barrier toward nucleation and allows crystallization to occur at higher temperatures upon cooling. For the composites containing CS particles, two \( T_g \) values were detected at temperatures around ~35 and ~57 °C corresponding to the P[CL-co-LA] impact modifier and to the PLA component present both at the PLASC shell and at the PLA matrix. Similarly, two endothermic peaks were observed at 148 and 222 °C, ascribed to the PLA matrix and to PLASC particles, and the degree of crystallinity of the matrix increased with the addition of the particles. Analogous trend was observed for the composites with ICS, i.e., PLA/ICS, and with the combinations of both CS and ICS particles, i.e., PLA/CS/ICS. Interestingly, the cold crystallization temperature shifted toward higher temperatures when the particles systems made of the impact modifier were added. The same phenomenon was observed when blending pure P[CL-co-LA] impact modifier into the PLA matrix. This is caused by the inhibition of chain segment motion during crystallization by the rubbery phase, which decreases the crystalline phase and leads to the melting of the crystals at slightly lower temperatures.

Concurrently, the mechanical and impact properties of the composites also varied depending on the formulation (Table 4). The impact strength (IS) of the PLA matrix increased with the addition of both ICS and CS particles (Table 3). The IS increased around 2 times with the addition of the CS and ICS particles within PLA, i.e., PLA/CS and PLA/ICS, in comparison with neat PLA. Adding only PLASC particles

### Table 2. Thermal Properties of the Particle Systems

| particle systems | \( T_1 \) (°C) | \( T_2 \) (°C) | \( T_m \) (°C) | \( \Delta H_m \) (J/g) | \( w_c \) (%) | \( T_g \) (°C) |
|------------------|-------------|-------------|-------------|----------------|--------|-------------|
| PLASC            | 58.8 ± 2    | 83.0 ± 1    | 14.9 ± 2    | 31.2 ± 0.2     | 223.5 ± 0.3 |
| CS               | −34.2 ± 0.5 | 59.2 ± 0.7  | 4.2 ± 0.2   | 24.2 ± 1       | 222.3 ± 0.0 |
| ICS              | −32.8 ± 0.2 | 49.6 ± 0.5  | 3.8 ± 0.2   | 23.5 ± 0.1     | 223.2 ± 0.1 |

“Determined by DSC from the 1st heating scan.

### Table 3. Particulate Composite Materials Thermal Properties

| material          | \( T_1 \) (°C) | \( T_2 \) (°C) | \( T_m \) (°C) | \( \Delta H_m \) (J/g) | \( T_m \) (°C) | \( w_c \) (%) |
|-------------------|-------------|-------------|-------------|----------------|------------|--------|
| PLA               | 57.8 ± 0.5  | 113.2 ± 0.0 | 23.1 ± 1    | 146.7 ± 0.3   | 0.8 ± 1    |
| PLA/CS            | −34.6 ± 1   | 57.0 ± 0.0  | 15.2 ± 3    | 148.4 ± 0.2   | 222.4 ± 0.2 | 2.3 ± 0.9 |
| PLA/ICS           | −39.4 ± 3   | 57.5 ± 0.1  | 11.8 ± 2    | 145.5 ± 4     | 222.4 ± 0.0 | 1.6 ± 0.6 |
| PLA/CS/ICSa       | −39.0 ± 0.0 | 56.3 ± 0.0  | 9.7 ± 0.4   | 148.7 ± 0.1   | 222.5 ± 0.4 | 5.4 ± 0.8 |
| PLA/SC            | 57.0 ± 0.1  | 114.1 ± 0.3 | 19.9 ± 2    | 146.8 ± 0.2   | 223.3 ± 0.0 | 1.8 ± 0.5 |
| PLA/IM            | −36.9 ± 0.5 | 56.2 ± 0.7  | 8.3 ± 2     | 149.1 ± 0.1   | 2.5 ± 2    |

“Determined by DSC from the 1st heating scan. Normalized values to the weight fraction. Blend composition 90/10 w/w % matrix/reinforcing element. PLA/CS/ICS blend composition 90/5/5 w/w %.
into PLA showed little effect on the IS of the composites in comparison with neat PLA. The direct use of the IM, P[CL-co-LA], in the PLA matrix showed lower IS values in the composites for the same content (i.e., 2% w/w) than those obtained with the core−shell structures. This indicates that the core−shell structure composed of PLASC and the rubber-type P[CL-co-LA], for both CS and ICS formulations, provided a synergistic enhancement in the IS of the composites than the use of its components separately. The IS of the resulting composite is then increased when both the rubbery type IM in combination with PLASC are present in the particles formulation. In such a structure, the synergetic association between the components promoted the stress absorbance within the matrix. It has been shown that a synergic association between rubbery-like P[CL-co-LA] used as an impact modifier and silica nanoparticles surrounding the rubber phase in PLA composites significantly improved the IS of the composite material. In addition, the effect on the impact properties with the addition of CS particles in PLA matrices with varying crystallinity was analyzed. The CS particles improved the IS of PLA composites in comparison to neat PLA independent of the crystallinity of the PLA matrix used (Figure S3).

By definition, synergy refers to the combined action of different components where each can increase the effectiveness of the other when joint together. In this sense, a positive synergistic effect is a reflection of improved properties compared with those of the simple mixing of the components in composites with hybrid fillers. Typical examples of a positive synergistic effect are observed in currently developed polymer/nanocarbon composites when adding carbon fillers with different geometries and electrical properties. In this sense, the synergistic effect obtained in the CS formulation was further confirmed by testing the PLASC and IM components separately added in the composite formulation, i.e., PLA/SC/IM, in a ratio of 90/8/2% w/w, which can be compared to the formulation within the CS particles. Impact strength values of 2.695 and 2.448 kJ/m² for PLA/IM and PLA/SC/IM, respectively, were obtained, which are ~50% lower than the IS values obtained with the addition of CS particles. The strong interaction between the components enhanced the impact strength of the composite material.

| material   | E (MPa) | σy (MPa) | εb (%) | IS (kJ/m²) |
|------------|---------|----------|--------|------------|
| PLA        | 2932.6 ± 20 | 63.8 ± 0.6 | 4.0 ± 0.6 | 2.8 ± 0.2 |
| PLA/CS     | 2658.6 ± 20 | 56.3 ± 1 | 7.6 ± 0.5 | 4.5 ± 0.5 |
| PLA/ICS    | 2584.6 ± 36 | 52.5 ± 0.7 | 15.2 ± 2 | 5.3 ± 0.6 |
| PLA/CS/ICSb | 2527.3 ± 44 | 52.3 ± 0.8 | 8.0 ± 2 | 4.4 ± 0.7 |
| PLA/SC     | 2636.8 ± 64 | 54.1 ± 1 | 4.1 ± 2 | 2.5 ± 0.4 |
| PLA/IM     | 2421.6 ± 60 | 47.4 ± 0.4 | 8.9 ± 1.6 | 4.1 ± 0.5 |

*a* Blend composition 90/10 w/w % matrix/reinforcing element. bPLA/CS/ICS blend composition 90/5/5 w/w %.

Figure 4. SEM micrographs of the notched surfaces of neat PLA, PLA/CS, PLA/ICS, PLA/SC and PLA/IM, in a composition 90/10 w/w % matrix/reinforcement element.
strength and the mechanical performance of the composite materials than when adding the components individually.

It was observed that the addition of the particles slightly reduced the Young’s modulus, \( E \), of the PLA-based composites in comparison to neat PLA. The lowest value was observed when adding the pure IM, giving an \( E \)-modulus of \( \sim 20\% \) lower than neat PLA, which is expected due to the lower modulus and strength of the rubbery IM. It is well-known that the IS decrease with an increase in the \( E \)-modulus and vice versa, especially with the use of elastomeric based structures as impact modifiers. Nevertheless, a less pronounced decrease in the material stiffness was obtained when adding the CS and ICS particles in the formulations, most probably because of the more rigid PLASC segments in the formulations. The tensile yield stress decreased in all cases when adding the particles into the PLA matrix in comparison with unfilled PLA (Table 3). However, the introduction of CS particles, i.e., PLA/CS composite, only induced a decreased of \( \sim 12\% \) in the tensile yield stress in comparison to neat PLA. The lowest value was seen when adding the pure IM into the matrix, which decrease in \( \sim 25\% \) the tensile yield stress of the composite in comparison with neat PLA. The particulate composites PLA/ICS, PLA/SC and PLA/CS/ICS, gave tensile yield stress values of \( \sim 15\% \) lower than that of unfilled PLA material. The elongation at break, \( \varepsilon_b \), of the composites improved in all cases with the addition of particles, in comparison with the neat PLA (Table 3). The CS and ICS particles in the composites, i.e., PLA/CS and PLA/ICS, increased the \( \varepsilon_b \) of the PLA by a factor of 2 and 3, respectively, in comparison with unfilled PLA. Pure IM and the combination of CS and ICS, i.e., PLA/IM and PLA/CS/ICS composites, had \( \varepsilon_b \) values in the same range of the PLA/CS formulation. SC particles in the PLA/SC did not demonstrate significant changes in the \( \varepsilon_b \) of the PLA, most probably due to the rigidity of the PLASC particles. The results indicate that the core–shell structure is more effective in enhancing the overall mechanical performance of the particulate composites than using its components separately.

Morphological analysis of the impact-fractured surfaces gave further insights on the differences obtained for the mechanical and impact properties of the composites. The morphology of the notched surfaces showed cavities corresponding to the reinforcement elements in the composite formulations (Figure 4). The morphology is clearly altered by the type of particle added to the formulation. The surfaces of the composite materials with CS and PLASC particles displayed spherical voids within the matrix. However, the PLA/CS sample showed higher plastic deformation which explains the toughness improvement. In the case of the composites with ICS, PLA/ICS, the morphology is to some extent similar to that when having the pure IM, PLA/IM, where voids with irregular shape are observed. More regularly dispersed voids within the PLA matrix are perceived for PLA/ICS as well as for PLA/CS, in comparison with PLA/IM. This is most probably due to the high interaction between the components within the CS and ICS particles formulation that contributed to a more regular shape, facilitating the dispersion within the matrix and enduring greater plastic deformation under stress. The size of the voids can be also correlated to the impact strength, where in most cases the bigger the size the higher the impact strength. In this case, it was observed that the void sizes in the composites correlate with the differences in toughness obtained with the different particle systems (Figure 4), where PLA/CS and PLA/ICS had the higher IS values.

**CONCLUSIONS**

Successful preparation of PLA-based core–shell particles containing PLA stereocomplex (PLASC) and the rubbery type \( P[\text{CL-co-LA}] \) in the formulation was achieved. Subsequently, PLA-based composite materials reinforced with the carefully designed core–shell particles with enhanced impact strength and mechanical performances were achieved. A versatile and industrially scalable approach to create the core–shell particles in high yield production was developed by spray-droplet atomization. Three particles systems were effectively obtained: core–shell (CS) particles having PLASC as the shell and the rubbery type impact modifier \( P[\text{CL-co-LA}] \) as the core; inversed core–shell (ICS) with \( P[\text{CL-co-LA}] \) as shell and PLASC as the forming core, and pure PLASC particles. The particles had sizes ranging from 0.6 to 1.2 \( \mu \text{m} \) depending on the formulation. PLA-based composites were achieved using the designed particle systems. The CS and ICS particles showed improved mechanical performance and impact properties in the composites compared to simple use of \( P[\text{CL-co-LA}] \) and PLASC separately, showing a synergistic effect. The particles increased the crystallization of the composites acting as nucleating agents. The impact strength increased around two times with the addition of the CS and ICS, respectively, in comparison with neat PLA. The elongation at break of the PLA increased along with the impact strength with the addition of the CS, ICS and PLASC particles. The strength of the materials was slightly affected, with a decrease of \( \sim 10\% \) with the addition of the CS and ICS particles. Similarly, the stiffness was slightly affected by the addition of the CS and ICS particles, with a decrease of \( \sim 10\% \), respectively. Finally, the core–shell particle formulations acted as satisfactory impact modifiers with minimal effect on the mechanical performance and stiffness of the composites making these designed structures suitable reinforcing elements for the creation of more advance degradable and sustainable materials.

**ASSOCIATED CONTENT**

- **Supporting Information**
  The Supporting Information is available free of charge on the ACS Publications website at DOI: [10.1021/acssuschemeng.6b00397](http://doi.org/10.1021/acssuschemeng.6b00397).

- **Notes**
  The authors declare no competing financial interest.

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