

Preparation of Single Poly(lactic acid) Composites

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ABSTRACT: An approach for making poly(lactic acid) (PLA) single-polymer composites (SPCs) on the basis of PLA's slowly crystallizing characteristics was investigated. As a slowly crystallizing polymer, PLA can be processed with standard polymer processing techniques into end-use products with varied crystallinities, from amorphous films to highly crystalline fibers. In this study, amorphous PLA sheets and crystalline PLA fibers/fabrics were laminated and compression-molded to form an SPC at a processing temperature substantially lower than PLA's melting temperature. The effects of the major process conditions on the performance of the SPC were studied. The processing tempera-

ture played a profound role in affecting the fiber-matrix bonding properties. As the processing temperature increased, a drastic improvement in the interfacial bonding occurred at a temperature of around 135°C, which indicated the lower boundary of the process window. The compression-molded SPC exhibited enhanced mechanical properties; particularly, the tearing strength of the fabric-reinforced SPC was almost an order higher than that of the nonreinforced PLA. © 2007 Wiley Periodicals, Inc. *J Appl Polym Sci* 107: 2909–2916, 2008

Key words: biodegradable; composites; molding; recycling

INTRODUCTION

In general, composites are heterogeneous materials made from a combination of different matrix and fiber materials that are difficult to recycle. One promising approach to composite recycling is the single-polymer composite (SPC) approach. SPCs are composites with a matrix and reinforcement derived from the same polymer. The original concept of SPCs was presented by Capiati and Porter¹ 3 decades ago. The method used the noticeable difference in melting temperature (T_m) between the high-density polyethylene (HDPE) matrix and the HDPE reinforcement to fabricate an HDPE homocomposite. The resulting composite was made of a single polymer and could, thus, be recycled with the standard package recycling practice for HDPE. Furthermore, because the extent of adhesion between the matrix and fibers is largely influenced by their physical and chemical compatibilities, the SPCs approach is believed to be useful in the enhancement of matrix-fiber interfacial bonding.^{2–4}

Although the SPC approach did not attract much attention from the composites research community

in the earlier days following Capiati and Porter's pioneer work,¹ there has been consistently growing interest in the manufacture of new SPCs since the 1990s. SPCs have been successfully manufactured for a variety of different polymers, including polyethylene,^{3–7} polypropylene,^{8–14} poly(ethylene terephthalate) (PET),¹³ poly(ethylene naphthalate),¹⁵ poly(lactic acid) (PLA),¹⁶ polyamides,^{17,18} and poly(methyl methacrylate).^{19–21} This trend in the technological development of composite manufacturing has been primarily driven by the increasing concern for the environment and, thus, the need for environmentally friendly composite materials.²²

SPC manufacturing greatly benefits from the well-established practices of the traditional composite manufacturing industry. However, because a single polymer is involved in the composite, SPC manufacturing presents a unique set of technical problems that must be addressed for successful application. So far, the work in SPC manufacturing has almost been exclusively focused on a fiber hot-compaction process,^{10,14,23} where polymer fibers are compacted at a temperature very close to, but below, the polymer T_m so as to partially melt the fibers and fuse them into a single solid material. The essence of the process is to melt only the surface fraction of each fiber under a comparatively low contact pressure and then to apply a substantially higher pressure for a short time to achieve excellent consolidation of the structure. The recrystallized polymer acts to bind the fibers together like the resin matrix in a fiber/resin composite. The major challenge in this process is the small difference, typically about 5°C or below, between the feasible processing temperature and the

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fiber T_m . Within this small temperature window, it is difficult to process the SPC under normal processing conditions without significantly annealing the fiber. It is known that when polymer fibers are annealed at a temperature close to their T_m , the modulus of the fibers could be significantly reduced toward the bulk modulus.²

To enlarge the processing temperature window, we²⁴ recently proposed the use of the distinct physical forms of slowly crystallizing polymers in SPC manufacturing. The method was demonstrated with PET as a model system. As a slowly crystallizing polymer, the same PET could be processed into two distinct physical forms: amorphous PET and highly crystalline PET. The amorphous and crystalline materials were then rapidly heated to a temperature well above the glass-transition temperature (T_g) but considerably below the T_m and compression-molded. With this method, PET SPCs were prepared with a processing temperature window exceeding 70°C.²⁴

In this study, PLA SPCs were prepared. Like PET, PLA as a slowly crystallizing polymer can be processed into physical forms with varied crystallinity, from amorphous films to highly crystalline fibers.^{25–27} However, compared to PET, PLA's half-time of crystallization does not follow a typical bell shape.^{25,26} Instead, PLA crystallizes extremely fast around 110°C. Furthermore, the difference between the T_g and T_m values is much smaller than that of PET (ca. 90°C smaller). Therefore, we expected that it would be more difficult to implement the slowly crystallizing method in the preparation of PLA SPCs. Accordingly, additional processing strategies may be needed in the processing of PLA SPCs. Because PLA is also a biodegradable polymer, PLA SPCs would be environmentally friendly and safe to dispose after a product life cycle. These were the main incentives for this study.

EXPERIMENTAL

Materials

PLA in different physical forms, including amorphous sheets and highly crystalline fibers, yarns, and fabrics, was used in the experiments. The sheets were extrusion grade (made of PLA from Natureworks LLC, (Minnetonka, MN) grade 4032D) and 0.1 mm thick and were provided by Plastic Suppliers, Inc (Columbus, OH). The PLA fabric, about 0.3 mm thick, made of Natureworks LLC Ingeo fibers, was supplied by Copland Industries (Burlington, NC). It had a cross-ply woven structure made of textured continuous filament yarns. Each yarn consisted of 135 bulked continuous filaments with a filament diameter of about 20 μm . The filaments were melt-spun, with a tensile strength of approximately 150

MPa, actually measured on a Instron tensile testing machine (Norwood, MA). The porosity of the fabric was about 50%, as measured on the basis of the volume and weight of the fabric and the density of the fiber. Some fabrics were dewoven, and recovered yarns and fibers were also used as reinforcing materials. All of these materials were made of PLA supplied by Natureworks, LLC. As disclosed by the resin supplier, the Natureworks extrusion and fiber-grade PLA was mainly poly(L-lactic acid), with a small portion of D-lactic acid existing as copolymer. The crystallinity of the PLA sheets and fibers used in the experiments were about 5 and 40%, respectively, as measured by differential scanning calorimetry (DSC). The T_g and T_m values of the PLAs used for the sheets and the fabric were approximately 60 and 167°C, respectively, as measured by DSC.

Fabrication

A similar experimental setup as used in a previous study²⁴ was used in this study. In that approach, a lamination of two amorphous PLA sheets and a layer of PLA fabric or yarns between was compressed between two heated platens on a Carver hydraulic press (Wabash, IN). It was important that the lamination was heated rapidly so that crystallization during the heating stage could be suppressed. Thin Teflon films (0.07 mm in thickness) were used on both sides for easy mold separation. Additional Teflon film was used in the middle of the lamination to create an unbonded region for peeling testing. Spacers were inserted between the heated platens to control the thickness of the molded composite sheet. The major process parameters, including the platen temperature, compression force, and heating time, were varied to study their effects on the fiber–matrix adhesion properties. The PLA SPCs obtained were rapidly quenched in ice water. Nonreinforced PLA was fabricated with the same setup by the compression of two amorphous PLA sheets without insertion of the PLA fabric.

Characterization

DSC was conducted on a TA Instruments DSC Q-100 (New Castle, DE). All samples were exposed to consecutive heating and cooling programs: first heating (30 to 200°C), cooling (200 to 30°C), and second heating (30 to 200°C). The DSC data were taken from the first heating cycle. The heating and cooling rates were 20°C/min, as typically used in the literature.²⁵ All scans were run under a N₂ atmosphere. Mechanical tests, including peeling, tearing, and tensile tests, were carried out at room temperature and a humidity of 63% on an Instron 5566 universal machine with a crosshead speed of 5 mm/min.

Compression-molded PLA and its SPCs were cut into tensile samples with a narrowed middle section with a width of 5 mm with a cutting die (supplied by Qualitest, Inc.) (Ft. Lauderdale, FL) according to DIN-53504-S2. For the yarn-reinforced SPCs, the tensile force direction was along the yarn direction. For fabric-reinforced SPCs, 50% of the fibers were aligned along the test direction, and the remaining 50% were aligned along the vertical direction. For the tearing tests, an SPC sheet was cut to an $80 \times 20 \text{ mm}^2$ rectangular shape. Then, an edge cut was made in the middle of the sample to form two arms, and the 40-mm arms were torn apart with the Instron machine. The failure surfaces on the broken samples from the mechanical tests were examined with stereoptical microscopy and scanning electron microscopy (SEM; Hitachi S-800) (Tokyo, Japan). SEM samples were sputter-coated with gold for a period of 5 min with current at 20 mA *in vacuo* at 0.7 Torr.

RESULTS AND DISCUSSION

To form a PLA SPC by compression-molding of a lamination of amorphous sheets and crystalline fibers, we needed the amorphous PLA to fuse together into a matrix material at a temperature much lower than PLA's crystalline T_m . Otherwise, the fiber may have been significantly annealed or even melted during processing, which would thus deteriorate its mechanical performance. There are two competing processes occurring when amorphous PLA is heated. First, the amorphous phase will experience a glass transition at its T_g , and the polymer will become rubbery and sticky at temperatures well above T_g (e.g., 50°C above T_g). Two such sticky pieces can be fused together through chain diffusion at the interface. The second competing process is crystallization. The amorphous PLA will start to crystallize when its temperature is above T_g . Therefore, the just softened, rubbery, and sticky amorphous phase will be transformed into a hardened crystalline phase at the same processing temperature. When preparing PLA SPCs, we needed to promote the first mechanism while restraining the second one. To promote fusion, the amorphous PLA needed to be rapidly heated to well above T_g , preferably above the rubbery plateau termination temperature, within a short period of time, during which no significant crystallization occurred.

Peeling of the thermally bonded PLA sheets

Given the small thickness of the amorphous PLA sheets used in this study, the lamination was expected to be heated rapidly. With typical thermal properties of PLA, analytical calculations showed that the time needed for the center of the 0.5 mm thick PLA lamination to undertake 90% of the

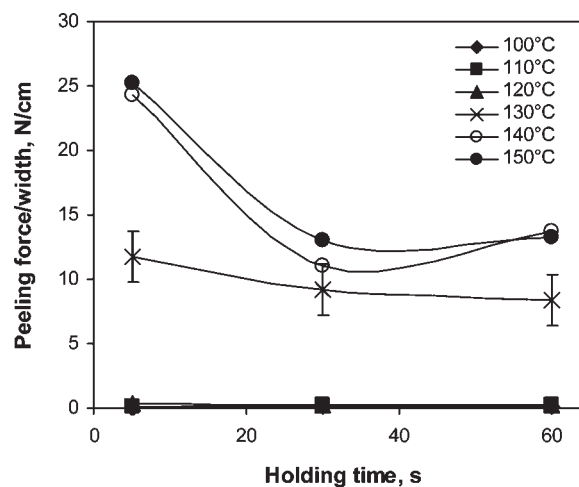


Figure 1 Effect of the platen temperature and holding time on the peeling failure force for samples prepared by the compression-molding of two PLA sheets.

imposed heating temperature difference was less than 0.5 s, about two orders faster than the typical half-time of crystallization of PLA. Therefore, rapid heating was not a problem. However, an appropriate heating temperature for the enhancement of fusion bonding needed to be determined. For prescreening purposes, different levels of platen temperatures were used during the hot-compression of the two-sheet laminations. The effects of platen temperature and holding time on the peeling force between two PLA sheets are shown in Figure 1. The compression pressure was set to about 1.5 MPa.

For a temperature of 120°C or below, good fusion bonding was not formed. The compressed sample could be peeled apart at the interface with hands. An increase in the holding time from 5 s and a change in the compression pressure did not significantly affect the bonding quality. A drastic increase in peeling force was observed at a platen temperature of 130°C . Compared with that at 120°C , the peeling force at 130°C was several orders higher. Such a significant improvement at 130°C deserves an explanation, as attempted next. Previous studies^{25,26} have shown that PLA crystallizes at the fastest rate at temperatures around 110°C . To greatly restrain the crystallization process, a higher temperature was desired. At a higher temperature, the characteristic fusion time is also reduced, which allows the two films to fuse together rapidly. When the lamination was compressed at 130°C , a significant amount of squeezing flow was observed; that is, liquid squeezed out in the lateral directions. The fluidity of the material suggested that the rubbery plateau termination temperature of amorphous PLA should have been in the vicinity of 130°C . This rapid liquefaction near 130°C was believed to be the main cause for the drastic increase in the fusion quality.

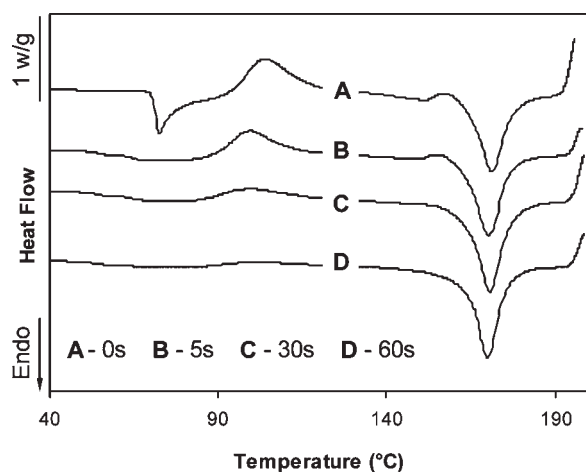


Figure 2 DSC thermograms of PLA prepared by the compression-molding of two PLA sheets at 140°C with different holding times. The four levels of holding time are labeled A, B, C, and D. A heating rate of around 20°C/min was used in the DSC experiments.

On the basis of the prescreening findings, the platen temperature for the focused study on SPC formation was set to 130°C or above. If successful, this would have resulted in a processing temperature window of about 40°C. A compression pressure around 1.5 MPa was found to be appropriate for the lamination of the PLA films and composites. At this pressure, the compression-molded samples were free from air bubbles, and the molded thickness could be well controlled.

Crystallinity development during hot compression

Figure 2 shows DSC thermograms at a heating rate of 20°C/min for samples prepared by the compression-molding of two laminated amorphous PLA sheets at 140°C with various holding times. The 0-s sample corresponded to the original PLA sheet. From the DSC thermograms, the amount of crystallinity for the samples with different holding times could be compared. The enthalpy of melting for a pure PLA crystal (i.e., 100% crystallinity) calculated through extrapolation of the experimental results was reported to be 93.7 J/g.²⁸ We determined the crystallinity of the molded sample by taking the ratio of the difference between the DSC melting and crystallization enthalpies to the single-crystal melting enthalpy. The results are summarized in Figure 3. For comparison purposes, the crystallinity of the PLA fibers used in this study is also shown in the figure. We observed that the crystallinity of the original PLA sheet was less than 5%, which indicated a nearly amorphous polymer. As the holding time increased, the compression-molded and quenched samples were transparent for short holding times

(e.g., 10 s) but became translucent for longer holding times (e.g., 50 s). This change in appearance signified an increase in crystallinity, which agreed with the data in Figure 3. Interestingly, when amorphous PLA was compression-molded, two solidification mechanisms existed. With a short holding time before quenching, vitrification of the amorphous phase was the main solidification mechanism, and therefore, the samples turned into a transparent amorphous glass. For longer holding times, the polymer experienced sequential fluidization (i.e., softening and liquefaction of the amorphous phase) and solidification (crystallization induced) under isothermal molding conditions. For the lamination of two thin PLA sheets, fluidization occurred almost instantaneously (within 1 s) when the sample came into contact with the two heated platens. On the contrary, crystallization occurred over a much longer period. For longer holding times (>60 s), the sample was substantially crystallized and became a solid between the two heated platens.

Fiber–matrix bonding

PLA SPCs were prepared by the compression-molding of a layer of PLA fabric sandwiched between two amorphous PLA sheets. Tensile specimens were cut from the molded SPC sheet and tested with an Instron machine. The surface topology of the broken samples were examined with SEM. Representatively, two different types of broken surface topology from samples prepared with different platen temperatures are shown in Figure 4. The holding time was set to 30 s. For SPC specimens molded at 130°C, very long pull-out fibers were observed at the broken surface, as indicated by arrows in Figure 4(a,c); the pull-out length was several times larger than the thickness of

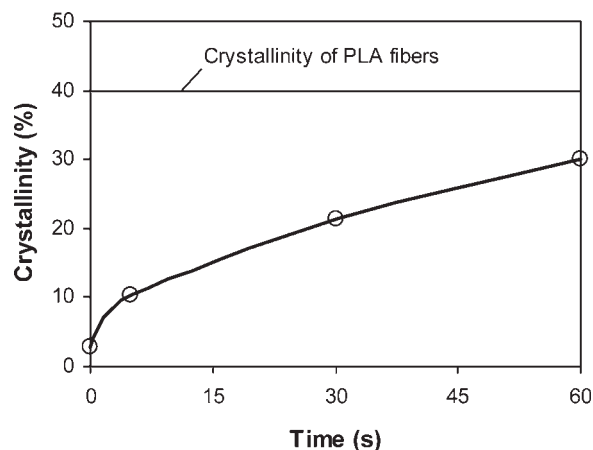


Figure 3 Crystallinity for the PLA samples prepared by the compression-molding of two as-received PLA sheets at 140°C with various holding times. For comparison, the crystallinity of the as-received PLA fibers is also given.

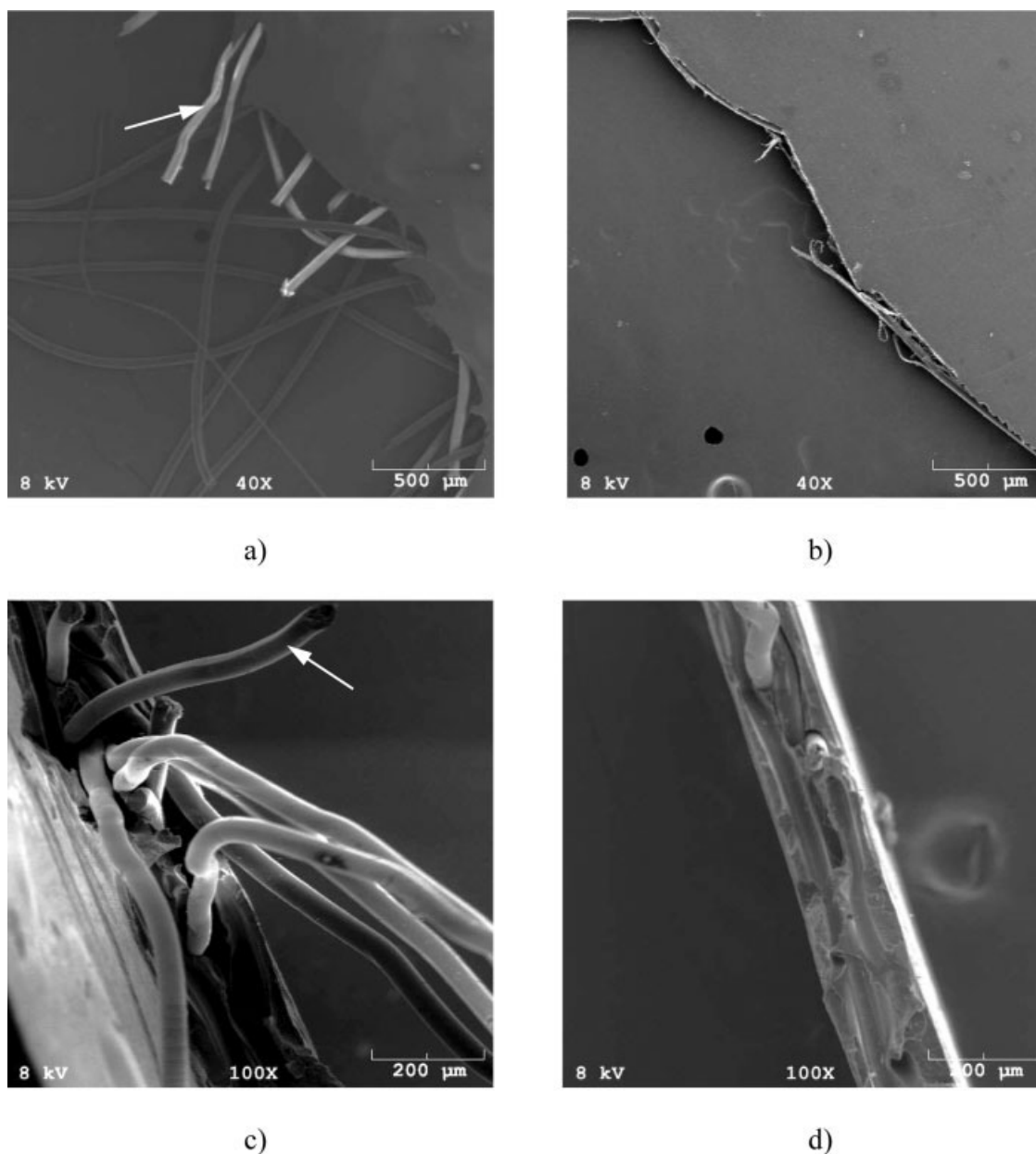


Figure 4 Topography at the tensile failure surface of the compression-molded PLA SPCs: (a) side view with the platen temperature at 130°C, (b) side view with the platen temperature at 140°C, (c) front view with the platen temperature at 130°C, and (d) front view with the platen temperature at 140°C. The holding time was 30 s.

the SPC sheet. As the platen temperature increased to 140°C, the fibers pulled out at the broken surface were short; most fibers were broken at the same broken surface of the matrix. This indicated that a strong bonding between the fiber and the matrix occurred. Because an abrupt change in the bonding quality occurred during the manufacture of the SPC in a small temperature window of 10°C, we could define a bonding transition temperature using the median temperature, that is, 135°C. This transition temperature specified the low boundary of the processing temperature window for successful PLA SPC manufacturing.

SPCs with PLA fabric as reinforcement

The as-received PLA fabric was used as a reinforcing material in the SPC. Figure 5 compares the tensile behavior of three SPC sheets compression-molded under different conditions. The weight fraction of the fabric in the SPC was 50%. The SPC molded at a platen temperature of 140°C and with a holding time of 50 s exhibited a considerably higher strength (almost twice higher) than the SPC molded at a platen temperature 130°C and with a holding time of 20 s. In the former case, the fiber and the matrix broke simultaneously, with a composite failure strain

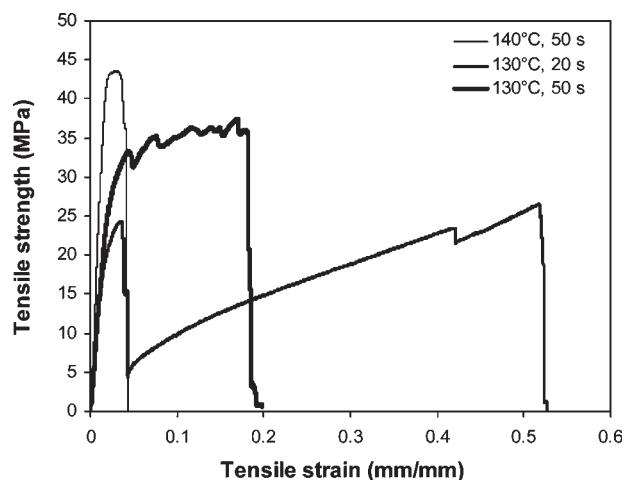


Figure 5 Tensile behavior of PLA SPCs prepared by the compression-molding of a lamination of two PLA sheets and one layer of PLA fabric.

of about 0.03. In the latter case, the matrix and the reinforcement broke at different strains, about 0.03 and 0.5, respectively; after the matrix broke, the fabric was pulled out and continued to elongate until failure occurred. The difference in the tensile behavior could be correlated with the different fiber–matrix bonding conditions in the two different samples. Because the fabric was more ductile than the matrix, the concurrent failure of the matrix and the fabric signified a strong adhesion between them. An intermediate case with a platen temperature of 130°C and a holding time of 50 s is also given in Figure 5. Some intermediate tensile behavior was seen in this case.

For better understanding of the composite behavior, the tensile behaviors of the matrix and the rein-

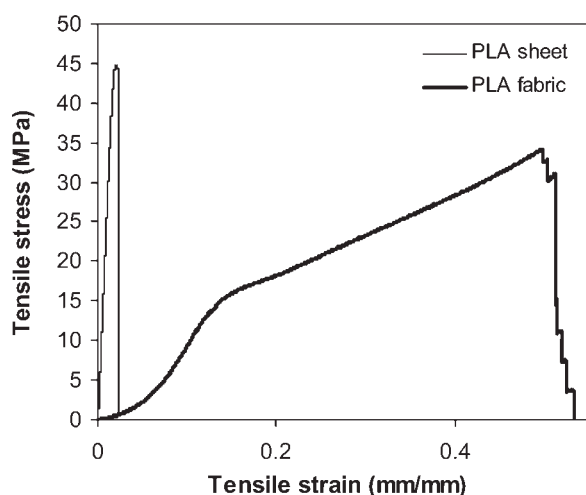


Figure 6 Tensile behavior of a PLA sheet and PLA textile fabric. The PLA sheet was prepared by the compression-molding of two as-received PLA sheets at 140°C with a holding time of 50 s.

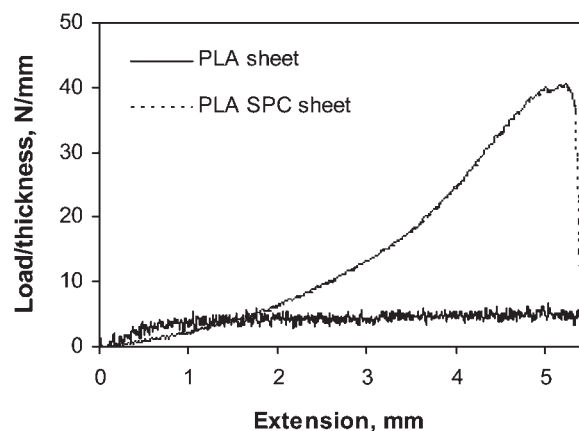


Figure 7 Tearing tests of nonreinforced PLA and PLA SPC sheets, both molded at a platen temperature of 140°C and with a holding time of 50 s.

forcement were obtained, as shown in Figure 6. The matrix PLA had a failure strain at around 0.03. The fabric appeared to be much more ductile, with a failure strain of about 0.5. This ductile behavior was attributed to the fabric's textured structures and porosity. For poor interfacial bonding, fabric will slip in the matrix and deform freely. When the bonding is strong, the matrix and fabric will assume the same strain during deformation. In this case, the structural elasticity of the fabric was suppressed, and the composite exhibited a single point of failure.

The tearing behavior of the SPC sheet and the original PLA sheet were also tested and compared. An edge cut was made in the middle of the sample to form two arms, and the arms were then torn apart with the Instron machine. Figure 7 shows that the tearing strength of the SPC sheet was about eight times higher than that of the nonreinforced PLA sheet. Both samples were molded at a platen temperature of 140°C and with a holding time of 50 s. The nonreinforced PLA appeared to be a notch-sensitive material. The propagation of the crack was greatly suppressed by the fabric in the SPC. This substantial increase in tearing strength would be desired in many membrane and packaging applications.²⁹ Figure 8 shows the formability of the fabric-reinforced PLA SPC sheet. A dome shape with a 50-mm diameter was successfully molded on a 0.5 mm thick PLA SPC sheet.

SPCs with PLA yarns as reinforcement

Although the tearing strength was significantly improved, the tensile strength of the fabric-reinforced SPC remained almost unchanged, at about 45 MPa both before and after reinforcement. Because the fabric was in a cross-ply configuration, only 50% yarns were involved in the load transfer. The

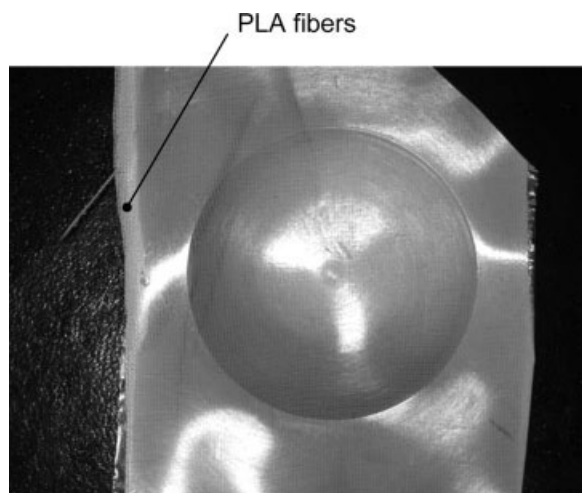


Figure 8 Dome-shaped sample (with a 50-mm-diameter dome) made of PLA SPCs and compression-molded at a platen temperature of 140°C.

remaining yarns orientated in the transverse direction to the loading direction contributed little to the strength of the SPC, although they accounted for about 25 wt % of the SPC. To create a stronger PLA SPC, yarns were separated from the fabric and used to make a uniaxially reinforced SPC. The resulting yarn was made of 135 textured continuous filaments in a diameter of about 20 μm . Figure 9 shows the tensile stress–strain curve of the yarn. Because of the texturing structure, the yarn showed structurally elastic behavior, exhibited by a low modulus, at the beginning of the stress–strain curve. During this initial period, the curled yarn was uncurled. The ultimate tensile strength of the yarn was about 130 MPa, which was considerably lower than that reported by Natureworks,³⁰ which was above 300 MPa. The reduced strength might have resulted from damage during yarn postprocessing and dur-

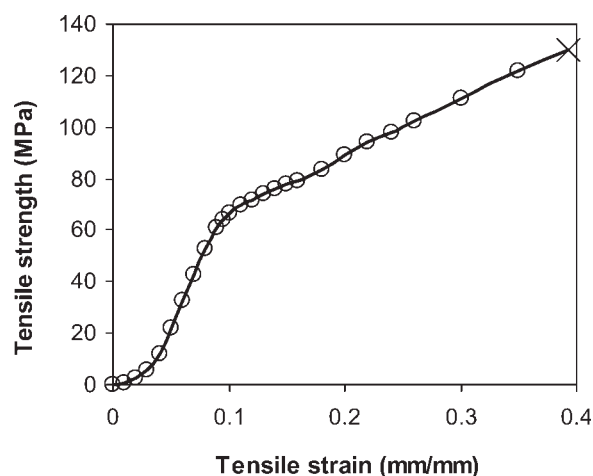


Figure 9 Tensile behavior of PLA yarns. Each yarn was made of about 130 textured continuous filaments with a diameter of about 20 μm .

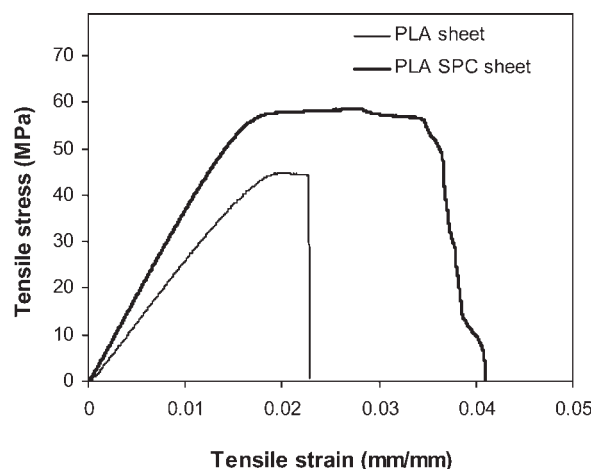


Figure 10 Comparison of the tensile properties of a non-reinforced PLA sheet and a PLA SPC sheet reinforced by 25 wt % unidirectional PLA yarns. Both samples were compression-molded at a platen temperature of 140°C and with a holding time of 50 s.

ing the fabric knitting and weaving steps because PLA's properties are sensitive to thermal and mechanical influences. Figure 10 compares the tensile behavior of the yarn-reinforced SPC with that of the nonreinforced PLA. The percentage of yarns by weight in the SPC was 25%. Both samples were compression-molded at a platen temperature 140°C and with a holding time of 50 s. Again, the structurally elastic behavior of the yarn (due to texturing) was suppressed in the SPC, which indicated strong bonding between the fiber and the matrix. An improvement of about 30% in tensile strength was observed for the SPC. We expect that with the employment of stronger PLA fibers and an increased fiber percentage, the tensile strength could be further improved. The tensile properties for the PLA SPCs described previously are summarized in Table I.

CONCLUSIONS

Single PLA composites were prepared by compression-molding of a lamination of PLA fibers in yarns

TABLE I
Tensile Properties of PLA Materials with Different Physical Forms

Type of PLA material	Young's modulus (GPa)	Tensile strength (MPa)	Failure strain (%)
Nonreinforced sheet ^a	2.5	44.8	2.3
Textile fabric	<0.1	34.2	50
Yarn	~1.1	133	40
SPC with 50 wt % fabric ^a	2.3	43.6	5
SPC with 25 wt % yarns ^a	3.7	58.6	4

^a The sample was compression-molded at a platen temperature of 140°C and with a holding time of 50 s.

or fabrics sandwiched between thin amorphous PLA sheets. With the slowly crystallizing characteristics of PLA, a processing temperature window greater than 30°C was obtained. The fusion quality of the matrix and the bonding between the matrix and the fiber were evaluated by a peeling test and microscopic examination of the failure surface and the optical appearance of the SPC. An abrupt improvement in matrix–fiber bonding quality was observed at 135°C, which signified the low boundary of the processing temperature window. With strong interfacial bonding, the PLA SPC showed a single point of failure during tensile testing, and the original texturing-induced structural elasticity of the reinforcement was restrained. The SPC exhibited a significant improvement in mechanical properties. Particularly, with 50 wt % fabric as reinforcement, the tearing strength was improved by almost an order. Increases in the tensile strength and modulus were also obtained for uniaxially reinforced PLA SPCs. The improved mechanical properties, together with the formability of the resulting SPC sheet, indicated its potential applications in the packaging industry.

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