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(54) Title: POLYLACTIDE MOLDING COMPOSITIONS AND MOLDING PROCESS

(57) Abstract: Molding compositions include a PLA resin, a nucleating agent and an accelerant. They may contain, in addition, a core-shell rubber and a reinforcing agent. These compositions are processed on injection molding equipment at temperatures above the T_g of the neat PLA resin to form semi-crystalline molded parts. A benefit of the invention is that short cycle times can be obtained.

POLYLACTIDE MOLDING COMPOSITIONS AND MOLDING PROCESS

This application claims priority from United States Provisional Patent Application No. 61/292,750, filed 6 January 2010.

5 This invention relates to polylactide resin molding compositions and to methods for producing molded polylactide resin articles.

Polylactide polymers (PLA, sometimes referred to as polylactic acid) are of increasing interest because they can be prepared from annually renewable resources such as corn sugars rather than oil or natural gas feedstocks. PLA
10 resins are also capable of degrading rapidly under some composting conditions to regenerate carbon dioxide. The ability to compost these materials can provide more disposal options for these resins, compared to most other organic polymers. As a result, PLA resins are finding uses in a variety of packaging applications. These packaging applications include a variety of rigid and semi-rigid articles such
15 as “clamshell” containers, deli and other food service trays and bottles or other containers. These packaging products are made mainly by extruding a sheet of the PLA resin and then thermoforming it.

PLA has certain characteristics which greatly affect how it is processed and the types of end-products that can be made from it. For example, the glass
20 transition temperature (T_g) of PLA is only about 55°C, which is significantly lower than those of commonly available, high-volume polymers that have use temperatures such that during use they are in the glassy state. This low T_g means that parts made from PLA resins tend not to be very heat-resistant, as even moderately elevated temperatures are sufficient to induce a phase transition and
25 soften the polymer.

One way to improve the heat resistance of a PLA resin is to partially crystallize it. A very significant improvement in heat resistance is seen when 20
J/g or more of crystallinity is induced in a PLA article. This can be done by annealing the part between the T_g and the crystalline melting temperature (T_m) of
30 the resin. However, another characteristic of PLA resins is that under quiescent conditions they crystallize very slowly compared to most other common semi-crystalline polymers. This slow crystallization is a practical problem in many manufacturing processes, because the slow crystallization rates lead to very long

cycle times. Equipment utilization is decreased and operating expenses are increased due to the slow crystallization rates.

This problem can be partially overcome if the PLA polymer chains are oriented as part of the manufacturing process. This is usually performed by stretching the part before or during the crystallization step. Thus, for example, in a thermoforming process, a sheet is first extruded, and then, in the thermoforming step, is drawn down into a mold. The drawing step stretches the sheet and orients the PLA resin, making crystallization easier and faster. Injection stretch blow molding processes, which are used to make bottles from PLA resins, also include steps in which the PLA resin is stretched to orient the polymer. In fiber manufacturing, orientation is performed by drawing the newly-spun fiber to several times its original length. In film manufacturing, the film is stretched uniaxially or biaxially to induce crystallization.

However, these processes are limited in the types of products that can be produced. Thermoforming, for example, is almost always limited to producing thin-wall articles that can be formed from a starting sheet material. Stretch blow molding processes are limited to producing certain types of hollow articles. In each case, thickness of the resulting parts is restricted. In addition, these processes are not amenable to forming complexly shaped parts.

Injection molding is a way in which thicker, more complex parts can be made. The injection molding process is fundamentally different than any of the processes just mentioned, in that injection molding starts with a molten polymer which is injected into the mold, and there is no simple way to further stretch the polymer within the mold in an injection molding process. Therefore, whereas crystallization is promoted in each of the aforementioned processes by stretching the part to orient the polymer chains, crystallization must take place in an injection molding process without the benefit of stretching the part. In other words, in the injection molding process quiescent crystallization dominates, rather than stress induced crystallization.

Therefore, PLA resins have been injection molded, but with only limited ability to form parts which are stable at elevated temperatures. The conventional injection molding process for PLA uses a cold mold, which is at or below the glass transition temperature of the PLA resin. In order to produce reasonable cycle times, the polymer is "quenched" in the mold by rapidly cooling it to below its T_g ,

so it hardens enough to be demolded. Little crystallization can occur in this process, especially because of the inherently slow crystallization of PLA under quiescent conditions, and so the molded part is not very resistant to elevated temperatures.

5 If better heat resistance is wanted, it becomes necessary for the PLA resin to become more highly crystallized. This can be done on injection molded parts after they have been demolded, by conducting a postcuring step during which the PLA resin is heated to about 70 to 130°C for a period of time. This annealing step can cause the part to warp or shrink if the part is not constrained. In addition,
10 this increases manufacturing costs very substantially because an extra process step is needed, and correspondingly higher equipment and energy costs are incurred. It is better to promote PLA crystallization while the part is still in the mold. This can be done by bringing the temperature of the part to 70 to 130°C for a period of time before the part is demolded.

15 However, because PLA is inherently slow to quiescently crystallize, and because there is no possibility to stretch the polymer, it takes a long time for the part to develop the wanted crystallinity. Furthermore, the part tends to be softer at the higher temperatures needed to crystallize it within the mold, because it is kept above its T_g . This can make the part more difficult to eject, because of
20 sticking to the mold and the possibility of distorting the part as it is removed. For these reasons, cycle times become very long in injection molding processes, if it is attempted to perform the crystallization step while the part is in the mold with conventional PLA molding compositions. PLA resins for injection molding processes generally have moderate molecular weights (such as a weight average
25 molecular weight (M_w) of 100,000 or less), to facilitate the process through a lower melt viscosity and faster crystallization rates. However, crystallization rates are still too slow to provide economically feasible cycle times.

A shorter cycle time is needed for the process to be economically viable.

30 Various nucleating agents and plasticizers have been used in some processes, in order to increase the crystallization rate of PLA. Among these are materials such as talc, ethylene bis(stearamide), polyethylene glycol, acetyl-tributyl citrate, tributyl citrate and even carbon dioxide. These can provide various levels of improvement in manufacturing processes which require the polymer to be crystallized quiescently. However, these have not been found to

reduce cycle times sufficiently, and manufacturing rates remain slow in an injection molding process.

Therefore, it is desirable to provide a PLA resin composition which can be processed rapidly in an injection molding process, to produce a semi-crystalline molded product. It is also desirable to provide an injection molding process that produces molded, semi-crystalline PLA resin parts within a commercially reasonable cycle time.

Still another issue is the physical properties of the PLA resins made in injection molding processes. Unmodified PLA resins have an inherent brittleness which can limit their use in some of these applications. It is therefore desirable to produce injection molded PLA resins parts that have higher impact resistance than does the neat resin, and to accomplish this without increasing cycle time or otherwise adding significant expense to the process. Core-shell rubbers have been used with some success in some processes, to improve the impact strength of a PLA resin. However, it has been found, very surprisingly, that the effectiveness of those core-shell rubbers falls very substantially, when the resin is injection molded into a mold that is at a temperature which is especially suitable for in-mold crystallization of the PLA resin (such as from 70 to 130°C). Another approach is needed to obtain significant impact strength improvement in an injection molded PLA resin.

In one aspect, this invention is a molding composition comprising, in admixture, (A) from 35.1-96.9% by weight a polylactic acid (PLA) resin having lactic acid repeating units that are (1) all L-enantiomers, (2) all D-enantiomers, or (3) a mixture of L- and D- enantiomers wherein the mixture of L- and D-enantiomers includes at least 97% of one enantiomer, and no more than 3% of the other enantiomer, (B) from 0.1 to 40% of at least one nucleating agent and (C) from about 3 to 24.9% by weight of an accelerant, wherein the weight percentages are based on the combined weights of components (A), (B) and (C).

In certain embodiments, the nucleating agent is an aromatic sulfonic acid salt or an aromatic phosphonic acid salt.

In other embodiments, the accelerant is an organic compound having a molecular weight of from 300 to 3000 and for which the dispersion component δ_{da} , polar component δ_{pa} and hydrogen bonding component δ_{ha} of its van Krevelen solubility parameter are such that $5 \leq \Delta\delta \leq 10$, wherein

$\Delta\delta = \left[(\delta_{da} - \delta_{dl})^2 + (\delta_{pa} - \delta_{pl})^2 + (\delta_{ha} - \delta_{hl})^2 \right]^{1/2}$ and δ_{dl} , δ_{pl} and δ_{hl} are the dispersion component, polar component and hydrogen bonding components of the van Krevelen solubility parameter of the polylactic acid resin.

Molding compositions in accordance with the invention have been found to crystallize rapidly in an injection molding process involving a mold which is at a temperature between the glass transition and crystalline melting temperatures of the (neat) PLA resin. This molding composition therefore can be injection molded using a mold that is held in such temperature range, and permitted to crystallize in the mold to the extent of at least 20 J/g of PLA resin, with surprisingly short cycle times.

The invention is also a process for forming injection molded articles, comprising

- a) heating a molding composition of the invention to a temperature above the crystalline melting temperature of the PLA resin;
- b) injecting the heated molding composition into a mold which is at a temperature of from 70 to 130°C,
- c) allowing the molding composition to cool and solidify in the mold until it has developed at least 20 Joules of crystallinity per gram of PLA resin in the molding composition; and then
- d) removing the resulting molded article from the mold.

The injection molding process of the invention is generally characterized by having surprisingly short cycle times, due to the rapid crystallization of the molding composition in the mold.

The mold temperature is preferably from 75 to 120°C, and more preferably from 80 to 110°C. An especially preferred temperature in some embodiments is from 85 to 95°C. It is preferred to permit the molding composition to remain in the mold until it has developed at least 30 J of crystallinity per gram of PLA resin.

In some embodiments, at least 15% by weight of the PLA resin consists of molecules that have molecular weights of at least 200,000, and the molding composition contains from 2 to 25% by weight of a core-shell rubber.

In other embodiments, the molding composition contains from 5 to 20% by weight of a particulate reinforcing agent, which is not a nucleating agent as described herein.

Especially preferred molding compositions of the invention contain (A) from 50 to 75% by weight of a PLA as described before, of which at least 15% by weight consists of molecules that have molecular weights of at least 200,000, (B) from 0.1 to 2% by weight of a dimethyl 5-sulfoisophthalate salt, (C) from about 3 to 24.9%
5 by weight of an accelerant, (D) from about 5 to 15% of a mineral particulate reinforcing agent different from the nucleating agent, and (E) from 5 to 15% of a core-shell rubber, all percentages based on the entire weight of the molding composition.

For the purposes of this invention, the terms “polylactide”, “polylactic acid”
10 and “PLA” are used interchangeably to denote polymers having at least 50% by weight of polymerized lactic acid repeating units (i.e., those having the structure $-\text{OC}(\text{O})\text{CH}(\text{CH}_3)-$), irrespective of how those repeated units are formed into the polymer. The PLA resin preferably contains at least 80%, at least 90%, at least 95% or at least 98% by weight of those repeating units.

The PLA resin may further contain repeating units derived from other
15 monomers that are copolymerizable with lactide or lactic acid, such as alkylene oxides (including ethylene oxide, propylene oxide, butylene oxide, tetramethylene oxide, and the like) or cyclic lactones or carbonates. Repeating units derived from these other monomers can be present in block and/or random arrangements. These
20 other repeating units suitably constitute up to about 10% by weight of the PLA resin, preferably from about 0 to about 5% by weight, especially from about 0 to 2% by weight, of the PLA resin.

The PLA resin may also contain residues of an initiator compound, which is often used during the polymerization process to provide control over molecular
25 weight. Suitable such initiators include, for example, water, alcohols, polyhydroxy compounds of various types (such as ethylene glycol, propylene glycol, polyethylene glycol, polypropylene glycol, other glycol ethers, glycerin, trimethylolpropane, pentaerythritol, sorbitol, hydroxyl-terminated butadiene
30 polymers and the like), polycarboxyl-containing compounds, and compounds having at least one carboxyl and one hydroxyl group (such a lactic acid or lactic acid oligomers). The initiator residue preferably constitutes no more than 10%, especially no more than 5%, and especially no more than 2% of the weight of the PLA resin.

The PLA resin may contain long-chain branching. Long-chain branching can be introduced in the PLA resin in various ways, such as by reacting carboxyl groups on the PLA resin with epoxide groups that are present on an acrylate polymer or copolymer. The acrylate polymer or copolymer is characterized in
5 being a solid or liquid at 23°C, containing an average of from about 2 to about 15 free epoxide groups/molecule (such as from about 3 to about 10 or from about 4 to about 8 free epoxide groups/molecule), and being a polymerization product of at least one epoxy-functional acrylate or methacrylate monomer, preferably copolymerized with at least one additional monomer. The acrylate polymer or
10 copolymer suitably has a number average molecular weight per epoxide group of about 150 to about 700, such as from 200 to 500 or from 200 to 400. The acrylate polymer or copolymer suitably has a number average molecular weight of from 1000 to 6000, such as from about 1500 to 5000 or from about 1800 to 3000. Other approaches to introducing long-chain branching are described in U. S. Patent Nos.
15 5,359,026 and 7,015,302 and WO 06/002372A2.

A preferred PLA resin is a random copolymer of L-lactic acid and D-lactic acid, a block copolymer of L-lactic acid and D-lactic acid, or a mixture of two or more of these, in each case optionally containing residues of an initiator compound and/or branching agent. The preferred PLA resin contains at least 95%, especially
20 at least 98% by weight repeating lactic acid units.

The lactic acid repeating units in the PLA resin may be either all L-enantiomers, (2) all D-enantiomers, or (3) a mixture of L- and D- enantiomers wherein the mixture of L- and D- enantiomers includes at least 97% of one enantiomer, and no more than 3% of the other enantiomer. The PLA resin may
25 contain at least 98% of either the L- or the D-enantiomer, and may contain at least 98.5% or at least 99% of either the L- or the D-enantiomer. The PLA resin may contain at least 0.3% of each the L-enantiomer and the D-enantiomer, or at least 1% of each the L- and the D-enantiomer.

The molecular weight of the PLA resin is sufficiently high that the PLA
30 resin is melt-processable. In general, weight average molecular weights of about 50,000 or more are suitable, and may be as much as 250,000 or more.

When short cycle times are of main interest and impact strength is of lesser concern, an impact modifier such as a core-shell rubber may be omitted from the molding composition. In such cases, relatively low molecular weight PLA resins

are generally preferable, as they have lower melt viscosities (which facilitate processing) and tend to crystallize more rapidly in the mold. In such cases, the weight average molecular weight of the PLA resin is preferably no greater than 110,000. PLA resin molecular weights are measured for purposes of this invention
5 by size exclusion chromatography, calibrated to linear polystyrene standards in a tetrahydrofuran mobile phase.

However, when a core-shell rubber is present in the composition, and good impact strength is desired, then it is preferred that the PLA resin has a significant fraction of molecules that have molecular weights of at least 200,000. Applicants
10 have unexpectedly discovered that when PLA resin molding compositions containing a core-shell rubber are injection molded as described herein, by permitting a significant amount of quiescent crystallization to occur in the mold, the molecular weight of the PLA resin has a strong effect on the performance of the core-shell rubber. This effect was not only previously unknown, but is
15 apparently unique to the case in which the part is produced using a mold heated above the PLA resin T_g ; parts made in a cooled (below PLA resin T_g) mold, as is conventional, show little effect of PLA molecular weight on impact strength. Even more surprisingly, applicants have found that when the PLA resin contains enough of a high molecular weight fraction, the impact strength of a core shell
20 rubber modified composition which is molded according to the invention can actually be higher than the impact strength when the same composition is molded in a mold with a temperature lower than the T_g of the polymer.

Therefore, a preferred molding composition in accordance with the invention is one which contains a core-shell rubber and in which at least
25 percent by weight of the PLA resin consists of molecules that have molecular weights of at least 200,000. This high molecular weight fraction may constitute at least 20%, or at least 30%, of the weight of the PLA resin, and may constitute as much as 100% thereof, but preferably constitutes no more than about 60% thereof. The PLA resin as a whole may have a weight average molecular weight (M_w) of at
30 least 110,000 or at least 140,000, up to 250,000 or more.

Blends of two or more PLA resins can be used to obtain a desired molecular weight distribution. If two or more PLA resins are used, then only the resin making up the major amount (at least 50%) by weight needs to have at least 97%

of one enantiomer present. The minor (less than 50% by weight) component PLA resin can be of any enantiomeric composition.

The PLA resin can be formed by polymerizing lactide. Lactide is a dimeric form of lactic acid, in which two lactic acid molecules are condensed to form a cyclic diester. Like lactic acid, lactide exists in a variety of enantiomeric forms, *i.e.*, “L-lactide”, which is a dimer of two L-lactic acid molecules, “D-lactide”, which is a dimer of two D-lactic acid molecules, and “meso-lactide”, which is a dimer formed from one L-lactic acid molecule and one D-lactic acid molecule. In addition, 50/50 mixtures of L-lactide and D-lactide that have a melting temperature of about 126°C are often referred to as “D,L-lactide” or “rac-lactide”. Any of these forms of lactide, or mixtures thereof, can be copolymerized to form a PLA resin for use in this invention. The L/D ratio in the PLA resin is controlled through the ratio of the enantiomeric forms of lactide that are used in the polymerization. In an especially preferred process, mixtures of L-lactide with meso-lactide and/or D-lactide are polymerized to form a polymer having a controlled level of D-lactic acid enantiomeric units. Suitable processes for polymerizing lactide to form PLA having controlled L/D ratios are described, for example, in U. S. Patent No. 5,142,023 and 5,247,059, both incorporated herein by reference.

In certain aspects of the invention, the molding composition contains nucleating agent and an accelerant.

Nucleating agents are materials which promote crystallization in accordance with the following cooling crystallization test: one part of the candidate nucleating agent is dry-blended with 99 parts by weight of a PLA resin which contains $98.6 \pm 0.2\%$ of the L-enantiomer and $1.4 \pm 0.2\%$ of the D-enantiomer, and a weight average molecular weight of 100,000 to 110,000. The PLA resin should contain less than 0.3% by weight residual lactide. Such a resin is commercially available from NatureWorks LLC, Minnetonka, Minnesota as Ingeo™ 3251 resin. The PLA resin/nucleating agent mixture is added to a Brabender three-piece mixing bowl with roller blades, operated at 60 rpm and 210°C, and the mixture is mixed on the Brabender for six minutes. The mixture is then removed and cooled to room temperature. Differential scanning calorimetry (DSC) is performed to determine the crystallization temperature for the blend. A 4-5 mg sample of the resulting blend is placed into a sample pan. The sample is heated to 210°C at 50°C/minute, and then cooled to 0°C at a rate of 35°C/minute. The enthalpy of

crystallization is measured during the cooling cycle and the temperature of peak enthalpy of crystallization is taken as the temperature of crystallization (T_c). A suitable nucleating agent is a material that provides a T_c on this cooling crystallization test of at least 90°C, more preferably at least 100°C, still more preferably 105°C and even more preferably at least 110°C.

Examples of nucleating agents include certain particulate inorganic minerals, as well as certain organic materials such as melamine, alkali metal salts of stearic acid, and the like. Talc having an average particle size of less than 5 microns, preferably less than 2 microns, is an example of a particulate inorganic material which performs as a nucleating agent. A preferred type of nucleating agent is an aromatic sulfonic acid salt or aromatic phosphonic acid salt. The sulfonic acid or phosphonic acid group is bound directly to an aromatic ring carbon atom. The aromatic ring structure may be substituted with alkyl groups, or with groups that contain ester and/or ether linkages. Examples of aromatic sulfonic acid salts include salts of dimethyl 5-sulfoisophthalate, p-toluene sulfonate, dodecylbenzenesulfonic acid, 3-sulfo benzoic acid, phenylphosphonic acid and dimethyl 5-sulfoisophthalate. Alkali metal salts are useful, such as sodium or potassium salts, and zinc salts are useful as well. Dimethyl 5-sulfoisophthalate potassium salt is an especially preferred nucleating agent.

The nucleating agent generally constitutes at least 0.1% of the combined weight of PLA resin, nucleating agent and accelerant. It may constitute up to 40% of the combined weights of those materials. Preferred nucleating agents, which provide a T_c value of at least 100°C or at least 110°C on the cooling crystallization test described before, are preferably used in amounts of up to 3% or up to 2% of the combined weight of PLA resin, nucleating agent and accelerant. Less effective nucleating agents (those providing T_c values of less than 100°C on the cooling crystallization test) are preferably used in larger amounts of 3% or more, up to as much as 40%, preferably up to 20% and more preferably up to 10%, on the same basis. When large amounts of nucleating agent are present, the nucleating agent may perform a stiffening function, increasing the storage modulus of the molded part at the mold temperature, which can further assist in reducing cycle times.

The molding composition also contains an accelerant. Accelerants, for purposes of this invention, are organic compounds or polymers which further enhance the rate of quiescent crystallization of a mixture of a PLA resin and a

nucleating agent as described above. The accelerant preferably has a molecular weight of from 300 to 3000.

Various types of accelerants are useful. These include acylated polyols such as acylated 1,4:3,6-dianhydrohexitols and acylated pentaerythritol, in which
5 the acyl groups may be linear or branched and can contain from 1 to 24 carbon atoms. Another class of accelerants includes esters of aromatic acids, such as linear or branched C₁₋₁₂ alkyl benzoates, diesters of ortho-phthalates wherein the ester groups may be linear or branched and can contain from 1 to 24 carbon atoms, and triesters of benzenetricarboxylic acid, again wherein the ester groups are
10 linear or branched and contain from 1 to 24 carbon atoms. Another type of useful accelerant includes esters of alkyl acids such as diesters of adipic acid, diesters of cyclohexanedicarboxylic acid and esters of citric acid, wherein in each case the ester groups may be linear or branched and may contain from 1 to 24 carbon atoms. In any of the foregoing cases, the ester groups may contain substituent
15 groups that may contain heteroatoms. The substituent groups may include, for example, ester linkages and/or hydroxyl groups.

Other types of useful accelerants include polyether polyols, such as polymers of ethylene oxide or propylene oxide and copolymers of ethylene oxide. Polyesters of polyols and polyacids are also useful, as are poly(ketoacid-co-polyol)s.

20 A useful screening test for evaluating potential accelerants is a heating crystallization test, as follows: one part by weight of dimethyl 5-sulfoisophthalic acid potassium salt is dry-blended with 89 parts by weight of a PLA resin which contains $98.6 \pm 0.2\%$ of the L-enantiomer and $1.4 \pm 0.2\%$ of the D-enantiomer, and a weight average molecular weight of 100,000-110,000. The PLA resin should
25 contain less than 0.3% by weight residual lactide. Such a resin is commercially available from NatureWorks LLC, Minnetonka, Minnesota as Ingeo™ 3251 resin. The PLA resin/nucleating agent mixture is added to a Brabender three-piece mixing bowl with roller blades, operated at 60 rpm and 210°C and mixed for one minute. 10 parts by weight of the accelerant are then added and the mixture is
30 mixed on the Brabender for an additional five minutes. A 4-5 mg sample of the resulting blend is placed into a sample pan. The sample is heated to 210°C to erase its thermal history and then quenched by removing it from the oven and cooling it rapidly to 0°C or below, such as by placing it on a metal heat sink. The oven is cooled, and the sample is reinserted into it and heated from 0°C to 210°C at

100°C/minute. The enthalpy of crystallization and enthalpy of melting are measured during this second heating cycle. The temperature of peak enthalpy of crystallization is taken as the temperature of crystallization (T_c) and the temperature of peak enthalpy of melting is taken as the melting temperature (T_m).

5 An accelerant which provides a T_c of no higher than 115°C on this test is a preferred type. More preferred types provide a T_c of no higher than 110°C or no higher than 100°C on this test. The melting temperature (T_m) of the crystallites is also measured, as a measure of how well the material crystallizes. An accelerant which provides for a T_m of at least 140°C, more preferably at least 164°C, on this
10 test (in addition to a T_c of 115°C or less) is preferred. For convenience herein, this test is sometimes referred to as the “heating crystallization” test.

An especially preferred class of accelerants is characterized by molecular weight (from 300 to 3000, as above) and certain solubility parameter characteristics. Solubility parameters are calculated for purposes of this invention
15 using the group contribution method outlined by D. W. Van Krevelen in “*Properties of Polymers*”, 3rd edition, Elsevier (1990). The group contributions presented in Table 7.8 of Van Krevelen and the Hoftyzer-Van Krevelen method presented in example 7.2 of Van Krevelen are used to calculate the individual solubility parameter components, based on reported or estimated values of the
20 density. The dispersion component δ_{da} , polar component δ_{pa} and hydrogen bonding component δ_{ha} of the Van Krevelen solubility parameter of the accelerant(s) preferably are such that $5 \leq \Delta\delta \leq 10$, wherein

$$\Delta\delta = \left[(\delta_{da} - \delta_{dl})^2 + (\delta_{pa} - \delta_{pl})^2 + (\delta_{ha} - \delta_{hl})^2 \right]^{1/2}$$

and δ_{dl} , δ_{pl} and δ_{hl} are the dispersion component, polar component and hydrogen bonding components of the van
25 Krevelen solubility parameter of the polylactic acid resin. The individual solubility parameter components, as well as $\Delta\delta$, are for purposes of this invention expressed in units of $J^{0.5}/cm^{1.5}$.

Surprisingly, it has been found that, unlike the case with usual PLA plasticizers, the accelerant is most effective when it is not highly soluble in the
30 PLA resin. Thus, for example, known plasticizers for PLA resin which are highly soluble in the PLA resin (as indicated by a $\Delta\delta$ of less than 5 and especially less than four), tend to provide little benefit in terms of increasing quiescent crystallization rates and, correspondingly, reducing cycle times. Thus, it is

preferred that $\Delta\delta$ be at least 5 and more preferably at least 6. On the other hand, if the accelerant is too insoluble in the PLA resin, it will not disperse well within the PLA resin and may migrate out of the finished part. For that reason, $\Delta\delta$ should not exceed 10, preferably does not exceed 9 and still more preferably does not exceed 8.

Examples of specific accelerants for which $5 \leq \Delta\delta \leq 10$ include:

<u>Name</u>	<u>Molecular Weight</u>	δ_{da}	δ_{pa}	δ_{ha}	$\Delta\delta$
Acetyl dibutyl 2ethylhexyl citrate	458	15.97	4.36	7.89	5.22
Trihexyl citrate	470	15.56	3.30	9.34	5.47
Monobutyl di-2 ethylhexyl citrate	472	16.27	3.32	9.36	5.51
Acetyl trihexyl citrate	486	16.05	4.05	7.61	5.64
Acetyl butyl di-2-hexyl citrate	514	16.29	3.89	7.45	5.90
Butyl trihexyl citrate	528	16.12	3.69	7.26	6.15
Butyl trioctyl citrate	590	17.25	3.41	6.98	6.75
Triethylene glycol methyl adipate	434	12.83	4.26	8.27	5.70
Dibutoxyethyleneadipate	346	16.10	3.64	7.58	6.00
Diocetyl adipate	370	15.98	2.45	5.91	7.95
Di-isoocetyl adipate	370	15.91	2.44	5.90	7.96
N-octyl-n-decyl adipate	398	16.16	2.26	5.68	8.26
Diisodecyl adipate	426	16.12	2.11	5.49	8.48
Tall oil monoglyceride	345	16.18	2.99	11.23	5.57
Acylated glycerin	442	15.67	3.13	6.68	6.92
<u>Isosorbide-2,5-di-n-hexanoate</u>		14.15	3.70	7.65	6.02
<u>Isosorbide-2,5-di-2-ethylhexanoate</u>		14.67	3.18	7.09	6.67
<u>Hallgreen R4010*</u>	442	18.14	3.66	7.23	6.72
<u>Dibutyl sebacate</u>	341	15.94	1.23	4.19	10.00
<u>Adipic acid ester of benzyl alcohol and diethylene glycol monomethyl ether</u>	338	17.17	4.14	8.08	5.54
<u>Diethylene glycol dibenzoate</u>	314	18.11	4.06	7.99	6.00
<u>Dipropylene glycol dibenzoate</u>	342	17.29	3.54	7.45	6.38
<u>Butyl benzyl phthalate</u>	312	18.39	3.59	7.08	6.95

*An ester additive for PLA resins, available from Hallstar Company. **Values of 15.45, 8.51 and 11.02, respectively as δ_{dl} , δ_{pl} and δ_{hl} for the PLA resin in calculating $\Delta\delta$.

The PLA resin, nucleating agent and accelerant are present such that the accelerant constitutes from 3 to 24.9 percent of the combined weight of these materials. A preferred amount of accelerant is from 3.5 to 14.5 percent of the combined weight of these components.

5 The molding composition may also contain a particulate or fibrous reinforcing agent. This reinforcing agent is not a nucleating agent as described before, i.e., a material which provides a T_c on this cooling crystallization test of less than 90°C (or no T_c at all). The reinforcing agent is a material which does not melt or thermally degrade under the conditions of the molding process. It typically
10 will not melt or thermally degrade at a temperature of below 250°C and preferably not below 300°C. The reinforcing agent performs a stiffening function, increasing the storage modulus of the molded part at the mold temperature. If in the form of a particulate, the reinforcing agent preferably has a median particle size of no more than 50 microns and still more preferably no more than about 5 microns.
15 The median particle size may be as small as about 100 nanometers, but the particle size is preferably at least 250 nm. Mineral powders are suitable. Talc which has a large particle size, calcium carbonate, carbon black, fly ash and other particulate minerals are suitable particulate reinforcing agents. Fibrous reinforcing agents should have diameters of no more than 100 microns, preferably
20 no more than 10 microns, and include, for example, carbon fibers, glass fibers, boron fibers, cellulosic fibers, natural plant and animal fibers, aramid fibers and the like.

If present, the reinforcing agent may constitute from 5 to 40 percent by weight of the entire molding composition, and, if present, preferably constitutes
25 from 5 to 15 percent by weight thereof. The presence of a reinforcing agent has been found to stiffen the molded part, at the temperatures at which it is demolded in the inventive process, and thus can help in further reducing cycle time. In preferred embodiments, the molded product has a storage modulus E' , as measured on a three-point bend dynamic mechanical analyzer according to ASTM
30 D5023, of at least 5×10^7 Pa at 80°C, more preferably at least 1×10^8 Pa at 80°C.

Preferred molding compositions according to the invention also contain a core-shell rubber. The core-shell rubber particle contains at least one core portion, which is a rubbery material having a T_g of less than -10°C, and at least one shell portion that has a T_g of at least 50°C. By "core", it is meant an internal portion of

the core-shell rubber. The core may form the center of the core-shell particle, or an internal shell or domain of the core-shell rubber. The core may be crosslinked. A shell is a portion of the core-shell rubber that is exterior to the rubbery core. The shell portion (or portions) typically forms the outermost portion of the core-shell rubber particle. The shell material is preferably co-polymerized on to the core or grafted onto the core. The shell may be crosslinked.

The rubber core suitably constitutes from 50 to 90%, especially from 50 to 85% of the weight of the core-shell rubber particle.

The core-shell rubber may contain, in addition to the aforementioned materials, a central portion which is encapsulated by the rubber core. The central portion may be a hard ($T_g > 0^\circ\text{C}$, preferably $> 50^\circ\text{C}$) or soft ($T_g < 0^\circ\text{C}$, preferably $< -20^\circ\text{C}$) polymer.

The first or core stage rubbery latex is preferably a polymer or copolymer of a lower alkyl acrylate such as n-butyl-, ethyl-, isobutyl- or 2-ethylhexylacrylate. Homopolymers of such lower alkyl acrylates are suitable rubbery core materials. The rubbery core polymer optionally contains up to 20% by weight of other monounsaturated or conjugated dienic copolymerized monomers such as styrene, vinyl acetate, vinyl chloride, methyl methacrylate, butadiene, isoprene, and the like and optionally up to 5% of a crosslinking polyunsaturated monomer having two or more sites of approximately equal reactivity, such as ethylene glycol diacrylate, butylene glycol dimethacrylate, divinyl benzene, and the like. It also optionally contains up to 5% of a graft-linking monomer having two or more sites of unsaturation of unequal reactivity, such as diallyl maleate, monoallyl fumarate, allyl methacrylate, and the like, at least one of the reactive sites being non-conjugated.

The shell polymer, which is optionally chemically grafted or crosslinked to the core rubbery stage, is preferably polymerized from at least one lower alkyl methacrylate such as methyl-, ethyl- or t-butyl methacrylate. Homopolymers of such methacrylate monomers can be used. Further, up to 40% by weight of the shell polymer can be formed from other monovinylidene monomers such as styrene, vinyl acetate, and vinyl chloride, methyl acrylate, ethyl acrylate, butyl acrylate, methyl methacrylate and the like. The molecular weight of the grafted shell polymer is generally between 20,000 and 500,000.

Methods for making core-shell rubbers are well known and are described, for example, in U.S. Pat. Nos. 3,655,825, 3,678,133, 3,668,274, 3,796,771, 3,793,402, 3,808,180, 3,843,735, 3,985,703 and 6,989,190.

Commercially available core-shell rubbers that are suitable include those
5 sold as Paraloid™ KM 355 and Paraloid™ KM 365 by Rohm and Haas Company, and Biostrength™ 150 core-shell rubber from Arkema.

The molding composition of the invention may contain from 1 to 20% by weight of the core shell polymer, preferably from about 5 to about 15% thereof.

The molding composition may in addition contain various optional
10 ingredients, such as colorants, mold release additives, preservatives, antioxidants, flame retardants and the like. Materials that inhibit molecular weight loss via hydrolysis of the PLA resin are preferred type of additives. Such materials include, among other things, monomeric or polymeric carbodiimide compounds, isocyanate compounds, epoxide compounds, oxazoline compounds, and the like.

Additional resins may be blended into the molding composition. These may
15 include, for example, a high molecular weight polymer which is miscible in the PLA resin in the relative proportions thereof that are present. In some embodiments, this high molecular weight polymer does not crystallize in the polymer matrix. Examples of such polymers include “amorphous” grades of
20 polylactic acid that contain at least 5% by weight of each of the L- and D-enantiomers, polymethyl methacrylate, and the like. Block copolymers of lactic acid and a different monomer also can be used. The presence of these high molecular weight materials may increase the impact strength of the part in some cases.

The molding composition is useful for preparing molded parts, particularly
25 in an injection molding process. The molding composition can be used if desired in conventional injection molding processes, in which the mold is cooled to below the T_g of the neat PLA resin and the part is “quenched” in the mold by rapidly cooling it to below its T_g so that little or no crystallization develops in the PLA resin.

In a preferred molding process, the molding composition is heated to above
30 the melting temperature of the neat PLA resin to form a melt, and the melt is introduced into the mold. Any reinforcing agent and/or core shell rubber particles which may be present in the composition become dispersed within the molten PLA resin phase. The mold is at a temperature of from 70 to 130°C, preferably from 75

to 120°C, and more preferably from 80 to 110°C. The mold temperature in some embodiments is from 75 to 85°C. It is often necessary to supply cooling to the mold to maintain the temperature within this range throughout the cooling and solidification step, as the molten molding composition typically will have a
5 temperature of 170°C or more when introduced into the mold.

Once introduced into the mold, the molding composition is retained there, with the mold temperature maintained within the specified temperature range, until it cools below the crystalline melting temperature of the neat PLA resin, solidifies and develops at least 20 Joules of crystallinity per gram of PLA resin. It
10 is preferred to allow the molding composition to develop at least 30 Joules of crystallinity per gram of PLA resin in this step, and still more preferred to allow it to develop at least 40 Joules of crystallinity per gram of PLA resin.

Once the resulting molded part has achieved the desired amount of crystallinity, it is removed from the mold. It is possible to cool the part down to
15 below the T_g of the neat PLA resin, before removing it from the mold, but this has the disadvantage of requiring more cooling and of extending cycle time while the part cools. To minimize cycle times and reduce manufacturing costs, it is preferred to demold the part while hot, *i.e.*, above the T_g of the neat resin, suitably from 70 to 130°C, preferably from 70 to 120°C, more preferably from 70 to 110°C.
20 Further cooling and post-demold operations such as trimming can then be conducted as needed.

Surprisingly short cycle times can be achieved with the molding compositions of the invention. By “cycle” time, it is meant the total time required to inject the molding composition into the mold, cool and crystallize the
25 composition in the mold, demold the resulting part and prepare the mold to receive the next subsequent injection of molding composition. Heretofore, attempts to produce semi-crystalline PLA parts in an injection molding have required long cycle times, because of the slow rate of crystallization of the PLA resin. The molding composition of the invention crystallizes rapidly in the mold, and so the
30 cycle time is reduced quite substantially.

The cycle time in any particular process will depend on many factors, including the particular manufacturing equipment that is used, the size and shape of the mold, the mass of the part, the specifics of the molding composition, and the efficiency of heat removal from the filled mold. For relatively small parts of simple

design, cycles times less than one minute often can be achieved, to produce a part having 20 Joules or more of crystallinity per gram of PLA resin. The presence of a particulate reinforcing agent often helps to further reduce cycle times, because the reinforcing agent increases the modulus of the part, stiffening it so it can be removed from the mold more easily at the elevated temperatures. To this end, the molding composition is suitably formulated to provide the composition with a storage modulus (E') of at least 5×10^7 Pa at 80°C , as described before. Cycles times often can be reduced to 10-50% of those required in prior art processes.

When a core-shell rubber is present in the molding composition, the molded part will generally have a higher impact resistance, compared to when no core-shell rubber is present, particularly when the PLA resin has a significant (15% or more by weight) fraction of molecules that have molecular weights of 200,000 or more. A useful measure of impact strength is the ASTM D 256 notched impact test. PLA by itself exhibits an impact strength (at room temperature) of about 0.3 foot-pound/inch (0.16 Joules/cm) on this test. Impact-modified PLA resins made in accordance with the invention may have an impact strength of 1.75 foot-pounds/inch (0.93 J/cm) or greater. For many applications, an impact strength of from about 2 to 15 foot-pounds/inch (1.06-7.95 J/cm) is desirable.

Especially preferred molded products according to the invention have a room temperature impact strength of at least 1.75 foot-pounds/inch (0.93 J/cm), preferably at least 2 foot-pounds/inch (1.06 J/cm) and a storage modulus E' , at 80°C , of at least 5×10^7 Pa, more preferably at least 1×10^8 Pa.

As mentioned before, applicants have found that the molecular weight of the PLA resin plays a very significant role in impact strength, when a core-shell rubber is present and the mold temperature is in the range of 70 to 130°C . Under these molding conditions, the PLA resin does not contain a significant high (200,000+) molecular weight fraction, impact strengths tend to remain low. This finding is unexpected, because in conventional PLA injection molding processes, in which the mold temperature is below the T_g of the neat PLA resin, the resin molecular weight has at most a small effect on impact strength.

Therefore, another aspect of this invention is a process for forming injection molded articles, comprising

a) heating a molding composition containing (A) from 35.1 to 94% by weight a polylactic acid (PLA) resin having lactic acid repeating units that are (1) all L-

enantiomers, (2) all D-enantiomers, or (3) a mixture of L- and D- enantiomers wherein the mixture of L- and D- enantiomers includes at least 97% of one enantiomer, and no more than 3% of the other enantiomer, and wherein the PLA resin contains at least 15% by weight of the PLA resin has a molecular weight of at least 200,000 and (D) at least one core-shell rubber, to above the crystalline melting temperature of the PLA resin;

b) injecting the heated molding composition into a mold which is at a temperature of from 70 to 130°C,

c) allowing the molding composition to cool and solidify in the mold until it has developed at least 20 Joules of crystallinity per gram of PLA resin in the molding composition; and then

d) removing the resulting molded article from the mold.

The mold temperature is preferably from 70 to 110°C and more preferably from 85 to 95°C during step b) and c), in this aspect of the invention.

The molding composition in this aspect of the invention preferably contains from 75 to 94% by weight of the PLA resin.

In this aspect of the invention, the molding composition may contain a nucleating agent, as described before, an accelerant as described before, a particulate or fibrous reinforcing agent as described before, and/or other optional materials as described before.

In this aspect of the invention, the molding composition preferably contains a nucleating agent which provides a T_c of at least 90°C, more preferably at least 100°C, still more 105°C and even more preferably at least 110°C on the cooling crystallization test. The nucleating agent is preferably a salt of an aromatic sulfonic acid or of an aromatic phosphonic acid, and more preferably contains a salt of dimethyl 5-sulfoisophthalate, p-toluene sulfonate, dodecylbenzenesulfonic acid, 3-sulfo benzoic acid, phenylphosphonic acid or dimethyl 5-sulfoisophthalate, or a mixture of two or more such salts. The molding composition in this aspect of the invention suitably contains from 0.1 to 40% by weight, based on the combined weight of the PLA resin, nucleating agent, and any accelerant that may be present, of the nucleating agent. Preferably, a molding composition of this aspect of the invention contains from 0.1 to 3% by weight, on the same basis, of a nucleating agent that provides a T_c of at least 105°C on the cooling crystallization test. In the last case, the molding composition may in addition contain a second

nucleating agent such as talc which provides a T_c of from 90 to less than 105°C on the cooling crystallization test. It is preferred that such second nucleating agent, if present at all, constitute no more than 20%, more preferably no more than 10% of the combined weight of the PLA resin, all nucleating agents and any accelerant
5 as may be present.

In this aspect of the invention, the molding composition preferably contains an accelerant, which preferably provides a T_c of no more than 115°C on the heating crystallization test. The accelerant, if present may constitute from about 3 to 24.9% of the combined weight of the PLA resin, any nucleating agent as may be
10 present, and accelerant.

In this aspect of the invention, the molding composition suitably contains from 2 to 25%, preferably from 2 to 15% by weight of the core-shell rubber, based on the total weight of the composition.

Molding parts made in accordance with the invention are useful in a wide
15 range of applications, including computer housings, appliance housings, other office electronic equipment, machine parts, bearings, rollers, hand-held electronic devices, electrical faceplates, automotive and construction structural and decorative trim, appliances, kitchen utensils and the like.

The following examples illustrate the invention, but are not intended to
20 limit it in any way. All parts and percentages are by weight unless otherwise indicated.

PLA resins

The following PLA resins are described in the following examples:

PLA resin A is a copolymer that contains about 98.6% of the L-enantiomer
25 and 1.4% of the D-enantiomer. It has a weight average molecular weight of about 104,000, as determined by GPC against a polystyrene standard. Its T_g is about 55°C.

PLA resin B is a copolymer that contains 99.7% of the L-enantiomer and 0.3% of the D-enantiomer. Its molecular weight (M_w) is about 135,000 Daltons and
30 its T_g is 55-60°C.

PLA resin C contains 98.6% of the L-enantiomer and 1.4% of the D-enantiomer. Its molecular weight (M_w) is about 143,000. It contains about 22% by weight of molecules of 200,000 molecular weight or more.

the mold. All parts show some sticking on the B side, and those molded at mold temperatures from 90 to 105°C also stick on the A side or fail to eject altogether.

These results show that the neat resin is incapable of being injection molded with reasonable cycle times at mold temperatures sufficient to promote in-
5 mold crystallization of the PLA resin.

Screening of nucleating agents

Blends of PLA resin A and various candidate nucleating agents are evaluated using the cooling crystallization test described above. T_c is measured as
10 an indication of the potential efficacy of the candidate nucleating agent. Results for various aromatic sulfonic acid or phosphonic acid salts are indicated in Table 1, as well as results for talc and melamine, two known PLA nucleating agents.

Table 1

<u>Nucleating Agent</u>	<u>Nucleating Agent level, wt-%</u>	<u>T_c (°C)</u>	<u>T_m (°C)</u>
None	0	None detected	None detected
Dimethyl 5-sulfoisophthalate, potassium salt	1.0	112.6	169.8
Dimethyl 5-sulfoisophthalate, sodium salt	1.0	97.6	168.4
Sodium phenyl phosphonate	1.0	88.8	165.7
3-sulfo benzoic acid, sodium salt	1.0	94.1	166.6
Zinc phenylphosphonate	1.0	114.9	167.4
Talc*	1.0	95.9	170.1
Ground melamine	1.0	95.3	159.8

15 *Mistron® Vapor R talc.

In this cooling crystallization test, higher T_c values generally indicate better performance in accelerating crystallization under quiescent conditions, as are encountered in injection molding processes. Under this test, the dimethyl 5-sulfoisophthalate potassium salt and zinc phenylphosphonate are identified as
20 excellent nucleating agent candidates.

Screening of accelerants

Blends of 89% PLA resin A, 1% dimethyl 5-sulfoisophthalic acid potassium salt (LAK-301 from Takemoto Oil & Fat) and 10% of various candidate accelerants are evaluated using the heating crystallization test described above.

5 T_c is measured as an indication of the efficacy of the candidate nucleating agent. Results for various accelerants are indicated in Table 2. In addition, the solubility parameter components δ_{da} , δ_{pa} and δ_{ha} are ascertained with respect to each of the candidate accelerants. Those values are used to calculate $\Delta\delta$ in the manner described before, using values of 15.45, 8.51 and 11.02, respectively as δ_{dl} , δ_{pl} and δ_{hl}
 10 for the PLA resin. These values are also reported in Table 2.

Table 2

<u>Accelerant Candidate</u>	<u>Accelerant level, wt-%</u>	<u>T_c (°C)</u>	<u>T_m (°C)</u>	<u>δ_{da}</u>	<u>δ_{pa}</u>	<u>δ_{ha}</u>	<u>$\Delta\delta$</u>
None	0	141.1	172.6	NA	NA	NA	NA
Hallgreen R4010 ¹	10	110.0	164.5	18.14	3.66	7.23	6.72
Diocetyl adipate ²	10	101.6	164.5	14.83	2.45	5.91	7.95
Daifatty 1010 ³	10	111.0	161.2	17.17	4.14	8.08	5.54
Citric Acid Ester A ⁴	10	120.1	162.9	16.02	5.11	8.55	4.24
Citric Acid Ester B ⁵	10	123.1	162.1	16.15	7.00	10.00	1.95
Citric Acid Ester C ⁶	10	123.8	162.1	16.13	6.39	12.99	2.97
Citric Acid Ester D ⁷	10	115.9	163.4	16.00	4.48	10.88	4.06

¹An ester additive for PLA resins, available from Hallstar Company ²Plasthall DOA, from Hallstar Company. ³Fatty ester available from Daihachi Chemical Industry Co., Ltd. ⁴Citroflex A4 from Vertellus Specialties. ⁵Citroflex A2 from Vertellus Specialties. ⁶Citroflex 2 from Vertellus Specialties. ⁷Citroflex 4 from Vertellus Specialties.

20 The Halgreen R4010 and dioctyl adipate each dramatically lower the T_c , which is desired, while having only a small effect on T_m . The other materials are less effective at reducing T_c on this test, and/or have a greater adverse effect on T_m , and these are considered as less desirable candidates as the accelerant. The citric acid esters are known PLA plasticizers; however, this test indicates that they will be less effective as accelerants and unlikely to provide for very low cycle times.

The solubility parameter data also shows how a closer match in solubility parameter (as indicated by lower $\Delta\delta$ values) correlates with higher T_c and thus slower crystallization. Contrary to ordinary plasticizers, good accelerants for use in this invention have solubility parameters which are distanced from that of the PLA resin.

Examples 1-4

Four molding compositions are made and injection molded according to the general procedure described above. Mold temperature is 90°C. Cycle times are varied to determine the shortest cycle time that can be used in each case, consistent with a clean ejection of the part from the mold (*i.e.*, without sticking on either the A- or B-sides), and without deforming the part.

The formulations and cycle times are as indicated in Table 3.

Table 3

Component	Ex. 1	Ex. 2	Ex. 3	Ex. 4
PLA resin B	89	9	79	9
PLA resin A	0	80	0	70
Hallgreen R4010 ¹	10	10	10	10
Dimethyl 5-Sulfoisophthalic acid Potassium Salt ²	1	1	1	1
Talc ³	0	0	10	10
Cycle time, s ⁴	32	49	32	36

¹See Table 2. ²Takemoto Oil and Fat LAK-301. ³Mistron™ Vapor R talc. ⁴Minimum cycle time for clean ejection without part distortion.

These results illustrate the dramatic reduction in cycle time provided by this invention. These cycle times are in the range of 3-5% of those of Comparative Sample A, with better release from the mold. These results also illustrate the effect of the enantiomer composition of the PLA resin. Example 1, in which the PLA resin is very enantiomerically pure, crystallizes especially rapidly to form a part having a modulus that is high enough for the part to be demolded. The addition of talc (a second nucleating agent) to this formulation, which contains the dimethyl 5-sulfoisophthalic acid salt as a nucleating agent, has little or no effect on the cycle time, as shown in Example 3. When the PLA resin is less enantiomerically pure, as with PLA resin A, modulus develops a bit more slowly, although the cycle time is nonetheless excellent. In this case, the addition of talc

provides a further improvement in cycle time due mainly to its stiffening function (Example 4 vs. Example 2). In general, the use of a reinforcing agent such as talc in combination with dimethyl 5-sulfoisophthalic acid potassium salt is especially preferred when the PLA resin contains 97-99% of one enantiomer and from 1-3% of the other enantiomer.

Examples 5-7 and Comparative Samples B, C and D

Six more molding compositions are made and injection molded according to the general procedure described above. Mold temperature is 90°C. Cycle times are varied to determine the shortest cycle time that can be used in each case, consistent with a clean ejection of the part from the mold (i.e., without sticking on either the A- or B-sides), and without deforming the part.

The formulations and cycle times are as indicated in Table 4.

Table 4

Component	Comp. B	Comp. C	Ex. 5	Comp. D	Ex. 6	Ex. 7
PLA resin B	0	0	9	9	70	0
PLA resin A	100	90	80	80	9	80
Hallgreen R4010 ¹	0	0	10	0	10	10
Dimethyl 5-sulfoisophthalic Potassium Salt ²	0	0	1	1	1	0
Talc ³	0	10	0	10	10	10
Cycle time, s ⁴	1025	106	49	106	34	46

¹See Table 2. ²Takemoto Oil and Fat LAK-301. ³Mistron™ Vapor R talc. ⁴Minimum cycle time for clean ejection without part distortion.

Comparative Sample B is a baseline case which shows that very long cycle times are needed with the neat resin. In this case, there is still some sticking, even after 1025 second cycle time. Comparative Sample C shows the effect of adding talc, which is known to function as a nucleating agent, as well as a reinforcing agent for PLA. The presence of talc as the nucleating agent, without an accelerant being present, reduces the cycle time to 106 seconds, mainly due to its stiffening function. Comparative Sample D shows the effect of adding dimethyl 5-sulfoisophthalic acid potassium salt without an accelerant being present. Cycle

time is reduced to 106 seconds. Examples 5 and 6 show very short cycle times. Example 7 shows that a relatively ineffective nucleating agent (talc) can yield short cycle times, if used in large quantities and if a highly effective accelerant is present.

5

Example 8

A molding composition containing 79% of PLA resin A, 10% talc, 10% dioctyl adipate and 1% of dimethyl 5-sulfoisophthalate, potassium salt is injection molded according to the general procedure described above. Mold temperatures are varied from 85 to 110°C and cycle times are varied to determine the lowest cycle time that can be achieved at each temperature.

At 110°C mold temperature, the parts eject cleanly at a cycle time as low as 35 seconds.

At 105°C mold temperature, the parts eject cleanly at a cycle time as low as 29 seconds.

At 95-100°C, the parts eject cleanly at a cycle time as low as 34 seconds.

At 90°C, the parts eject cleanly at a cycle time as low as 40 seconds.

At 85°C, the parts eject cleanly at a cycle time as low as 44 seconds.

These results demonstrate that low cycle times can be obtained with this invention across a range of mold temperatures.

Examples 9-12

Duplicate molding compositions are made and injection molded according to the general procedure described above. The compositions are as indicated in Table 5 below. Mold temperature is either 90°C or 110°C. Notched Izod impact testing is performed according to ASTM D256 on the demolded and cooled samples.

The formulations and impact resistance results are as indicated in Table 5.

Table 5

Component	Ex. 9	Ex. 10	Ex. 11	Ex. 12
PLA resin A	67.15	7.65	67.15	7.65
PLA resin C	0	59.5	0	59.5
Diethyl adipate ¹	8.5	8.5	8.5	8.5
Dimethyl 5-sulfoisophthalic acid potassium salt ²	0.85	0.85	0.85	0.85
Talc ³	8.5	8.5	8.5	8.5
Core-shell rubber ⁴	15	15	15	15
Mold temperature, °C	90	90	110	110
Notched Impact Str., ft-lb/in (J/cm)	1.8 (0.96)	3.0 (1.6)	0.8 (0.43)	1.2 (0.64)

¹Plasthall DOA, from Hallstar Company. ²Takemoto Oil and Fat LAK-301. ³Mistrion™ Vapor R talc. ⁴Arkema Biostrength™ 150 core-shell rubber.

5 These results show the effect of mold temperature and PLA resin molecular weight on impact strength. Final extruder barrel temperature is 190°C. The parts molded at 110°C have significantly lower impact strengths than do parts molded from the same composition at 90°C. However, increasing the molecular weight of the PLA has a significant positive effect on impact strength, at both molding
10 temperatures. This is considered to be unusual, as impact strengths using a conventional, ambient temperature mold (26°C) show very little dependence on the molecular weight of the PLA resin.

Example 13

15 A molding composition is made and injection molded according to the procedure described above, with the final barrel temperature being 190°C. The composition is as indicated in Table 6 below. Mold temperatures are varied to evaluate the effect of temperature on cycle time. Notched Izod impact testing is performed according to ASTM D256 on the demolded and cooled samples.

20 The cycle times and notch impact strengths at different mold temperatures are indicated in Table 7.

Table 6

<u>Component</u>	<u>Ex. 13</u>
PLA resin A	8.1
PLA resin C	63
Diethyl adipate ¹	9
Dimethyl 5-sulfoisophthalic acid potassium salt ²	0.9
Talc ³	9
Core-shell rubber ⁴	10

¹Plasthall DOA, from Hallstar Company. ²Takemoto Oil and Fat LAK-301.
³Specialty Minerals Ultratalc™ 609. ⁴Arkema Biostrength™ 150 core-shell rubber.

5

Table 7

<u>Mold Temperature, °C</u>	<u>Cycle time, s</u>	<u>Notched Impact Str., ft-lb/in (J/cm)</u>
80	80	3.9 (2.1)
85	60	3.2 (1.7)
90	50	2.5 (1.3)
95	50	2.0 (1.1)
100	50	1.8 (1.0)
105	45	1.6 (0.9)
110	50	1.1 (0.6)

These results show the effect of mold temperature on cycle time and impact strength. An optimum in cycle time is seen at about 90-105°C mold temperature. Impact strength decreases with increasing mold temperature, as seen before.

Example 14

A molding composition is made and injection molded according to the procedure described above, except the final barrel temperature is 185°C. The composition is as indicated in Table 8 below. Mold temperatures are varied to evaluate the effect of temperature on cycle time. Notched Izod impact testing is performed according to ASTM D2456 on the demolded and cooled samples.

The cycle times and notch impact strengths at different mold temperatures are indicated in Table 9.

Table 8

<u>Component</u>	<u>Ex. 14</u>
PLA resin C	59.88
PLA resin A	7.7
Dioctyl adipate ¹	8.55
Dimethyl 5-sulfoisophthalic acid potassium salt ²	0.86
Talc ³	13.5
Core-shell rubber ⁴	9.51

¹Plasthall DOA, from Hallstar Company. ²Takemoto Oil and Fat LAK-301.

³Specialty Minerals Ultratac™ 609. ⁴Arkema Biostrength™ 150 core-shell rubber.

5

Table 9

<u>Mold Temperature, C</u>	<u>Cycle time, s</u>	<u>Notched Impact Str., ft-lb/in (J/cm)</u>
85	45	2.4 (1.3)
90	45	2.0 (1.07)
95	45	1.8 (0.96)

Examples 15-16 and Comparative Samples E-H

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This series of experiments illustrates the effect of PLA molecular weight and mold temperature on impact strength.

15

A series of molding compositions are injection molded using the general process described before. In Comparative Samples F, G and H, the mold temperature is 26°C, well below the T_g of the neat PLA resin. In Examples 14-15 and Comparative Sample E, the mold temperature is 110°C. The composition in each case is 84% of a PLA resin, 1% of the LAK-301 material described before, and 15% of a core-shell rubber (Arkema Biostrength™ 150). The PLA resin in each case is as follows:

20

Comparative Samples E and F: A 104,000 M_w PLA resin that contains less than 9% of molecules at or above 200,000 molecular weight.

Comparative Sample G and Example 15: A 143,000 M_w PLA resin that contains about 22% of molecules at or above 200,000 molecular weight.

Comparative Sample H and Example 16: A 195,000 M_w PLA resin that contains more than 41% of molecules at or above 200,000 molecular weight.

The impact strength of each molded product is measured, with results as indicated in Table 10.

5

Table 10

Example or Sample No.	Wt. fraction, PLA \geq 200,000 molecular weight	Mold temperature, °C	Impact strength, ft-lb/in (J/cm)
F*	9	26	5.3 (2.81)
G*	22	26	6.3 (3.34)
H*	41	26	6.1 (3.23)
E*	9	110	2.9 (1.54)
15	22	110	6.5 (3.45)
16	41	110	11.5 (6.10)

Comparative Samples F, G and H show how polymer molecular weight plays only a minor role in impact strength when the mold temperature is below resin T_g. This is the expected outcome, as in many systems impact strength tends to vary only slightly with polymer molecular weight above a certain threshold. However, Comparative Sample E and Examples 15 and 17 show that once the mold temperature is raised above the T_g of the neat resin, there is a very large molecular weight effect that is not seen at the lower mold temperature. The presence of a significant high molecular weight fraction in this case leads to a very significant increase in impact strength, to the point that impact strengths can significantly exceed those which are obtainable in the lower mold temperature.

Examples 17 and 18 and Comparative Sample I

Using the injection molding general procedure, neat PLA resin A is molded at a mold temperature of 26°C. The storage modulus E' for the molded material (Comparative Sample I) is measured at 60°C, and found to be about 6.2 X 10⁶ Pa. The modulus drops off steeply with increasing temperature.

A blend of 79% PLA resin A, 10% Mistron™ Vapor R Talc, 10% dioctyl adipate and 1% of the LAK-301 salt is injection molded using the injection molding

general procedure, with a mold temperature of 90°C. The storage modulus of this material (Example 17) at 80°C is 2.73×10^8 Pa.

A blend of 71.1% PLA resin C, 9% Ultratac™ 609 Talc, 10% dioctyl adipate, 10% Biostrength™ 150 core-shell rubber and 0.9% of the LAK-301 salt is
5 injection molded using the injection molding general procedure, with a mold temperature of 95°C. The storage modulus of this material (Example 18) at 80°C is 4.49×10^8 Pa.

WHAT IS CLAIMED IS:

1. A molding composition comprising, in admixture, (A) from 35.1 to
5 96.9% by weight a polylactide (PLA) resin having lactic acid repeating units that
are (1) all L-enantiomers, (2) all D-enantiomers, or (3) a mixture of L- and D-
enantiomers wherein the mixture of L- and D- enantiomers includes at least 97%
of one enantiomer, and no more than 3% of the other enantiomer, (B) from 0.1 to
40% of at least one nucleating agent and (C) from about 3 to 24.9% by weight of an
10 accelerant, wherein the weight percentages are based on the combined weights of
components (A), (B) and (C).

2. The molding composition of claim 1, wherein component (B) includes
at least one nucleating agent that provides a T_c of at least 110°C on the cooling
15 crystallization test.

3. The molding composition of claim 2 which contains from 0.1 to 3%
by weight of a nucleating agent that provides a T_c of at least 110°C on the cooling
crystallization test, based on the combined weights of components (A), (B) and (C).

20

4. The molding composition of any of claims 1-3, wherein component
(B) includes an aromatic sulfonic acid salt or an aromatic phosphonic acid salt.

5. The molding composition of any of claims 1-4, wherein component
25 (B) includes talc.

6. A molding composition of any of claims 1-5 wherein the accelerant is
an organic compound or polymer having a molecular weight of from 300 to 3000
and for which the dispersion component δ_{da} , polar component δ_{pa} and hydrogen
30 bonding component δ_{ha} of its van Krevelen solubility parameter is such that
 $5 < \Delta\delta < 10$, wherein $\Delta\delta = \left[(\delta_{da} - \delta_{dl})^2 + (\delta_{pa} - \delta_{pl})^2 + (\delta_{ha} - \delta_{hl})^2 \right]^{1/2}$ and δ_{dl} , δ_{pl} and δ_{hl}
are the dispersion component, polar component and hydrogen bonding components
of the van Krevelen solubility parameter of the polylactic acid resin.

7. The molding composition of any of claims 1-6, which contains from 5 to 40% by weight of a particulate reinforcing agent that is not a nucleating agent.

5 8. The molding composition of any preceding claim, which contains from 2 to 25% by weight of a core-shell rubber.

9. The molding composition of any preceding claim, wherein at least 15% by weight of the PLA resin consists of molecules having a molecular weight of at least 200,000.
10

10. The molding composition of any preceding claim, wherein component B includes a dimethyl 5-sulfoisophthalate salt.

11. The molding composition of any preceding claim, wherein component C includes a long-chain diester of an aliphatic dicarboxylic acid.
15

12. The molding composition of any preceding claim, wherein component C includes dioctyl adipate.
20

13. The molding composition of any preceding claim, which contains from 75 to 94% by weight of the PLA resin, based on the combined weights of components (A), (B) and (C).

14. The molding composition of any preceding claim, further comprising one or more colorants, mold release additives, preservatives, antioxidants, flame retardants or any two or more thereof.
25

15. The molding composition of any preceding claim, further comprising at least one monomeric or polymeric carbodiimide compound, isocyanate compound, epoxide compound or oxazoline compound.
30

16. A molding composition comprising (A) from 50 to 75% by weight of a polylactide (PLA) resin having lactic acid repeating units that are (1) all L-

enantiomers, (2) all D-enantiomers, or (3) a mixture of L- and D- enantiomers wherein the mixture of L- and D- enantiomers includes at least 97% of one enantiomer, and no more than 3% of the other enantiomer, of which at least 15% by weight has a molecular weight of at least 200,000, (B) from 0.1 to 2% by weight of a dimethyl 5-sulfoisophthalate salt, (C) from about 3 to 24.9% by weight of an accelerant, (D) from about 5 to 15% of a mineral particulate reinforcing agent, and from 2 to 15% of a core-shell rubber, all percentages based on the entire weight of the molding composition.

10 17. The molding composition of claim 16 wherein the accelerant is an organic compound or polymer having a molecular weight of from 300 to 3000 and for which the dispersion component δ_{da} , polar component δ_{pa} and hydrogen bonding component δ_{ha} of its van Krevelen solubility parameter is such that $5 < \Delta\delta < 10$, wherein $\Delta\delta = \left[(\delta_{da} - \delta_{dl})^2 + (\delta_{pa} - \delta_{pl})^2 + (\delta_{ha} - \delta_{hl})^2 \right]^{1/2}$ and δ_{dl} , δ_{pl} and δ_{hl} are the dispersion component, polar component and hydrogen bonding components of the van Krevelen solubility parameter of the polylactic acid resin.

18. The molding composition of claim 16 or 17 wherein the accelerant is long-chain diester of an aliphatic dicarboxylic acid.

20

19. A process for forming injection molded articles, comprising

a) heating a molding composition of any of claims 1-18 to a temperature above the crystalline melting temperature of the PLA resin;

b) injecting the heated molding composition into a mold which is at a temperature of from 70 to 130°C,

c) allowing the molding composition to cool and solidify in the mold until it has developed at least 20 Joules of crystallinity per gram of PLA resin in the molding composition; and then

d) removing the resulting molded article from the mold.

30

20. The process of claim 19 wherein in steps b) and c), the mold temperature is from 75 to 120°C.

21. The process of claim 20 wherein in steps b) and c), the mold temperature is from 80 to 110°C.

22. The process of any of claims 19-21 wherein in step c) the molding composition develops at least 30 J of crystallinity per gram of PLA resin.

23. A process for forming injection molded articles, comprising

a) heating a molding composition containing (A) from 35.1-94% by weight a polylactide (PLA) resin having lactic acid repeating units that are (1) all L-enantiomers, (2) all D-enantiomers, or (3) a mixture of L- and D- enantiomers wherein the mixture of L- and D- enantiomers includes at least 97% of one enantiomer, and no more than 3% of the other enantiomer, and wherein the PLA resin contains at least 15% by weight of the PLA resin has a molecular weight of at least 200,000 and (E) at least one core-shell rubber to above the crystalline melting temperature of the PLA resin;

b) injecting the heated molding composition into a mold which is at a temperature of from 70 to 130°C,

c) allowing the molding composition to cool and solidify in the mold until it has developed at least 20 Joules of crystallinity per gram of PLA resin in the molding composition; and then

d) removing the resulting molded article from the mold.

24. The process of claim 23, wherein the molding composition includes at least one nucleating agent.

25. The process of claim 24, wherein the nucleating agent includes at least one nucleating agent that provides a T_c of at least 110°C on the cooling crystallization test.

26. The process of claim 25, wherein the nucleating agent that provides a T_c of at least 110°C on the cooling crystallization test is an aromatic sulfonic acid salt or an aromatic phosphonic acid salt.

27. The process of claim 25 or 26, wherein the nucleating agent that provides a T_c of at least 110°C on the cooling crystallization test is present in an amount from 0.1 to 3 percent of the combined weight of the PLA resin, nucleating agent(s) and any accelerant as may be present.

5

28. The molding composition of any of claims 24-27, wherein the nucleating agent includes talc.

29. The process of any of claims 23-28, wherein the molding composition
10 includes an accelerant.

30. The process of claim 29, wherein the accelerant is an organic compound or polymer having a molecular weight of from 300 to 3000 and for which the dispersion component δ_{da} , polar component δ_{pa} and hydrogen bonding
15 component δ_{ha} of the van Krevelen solubility parameter is such that $5 < \Delta\delta < 10$, wherein $\Delta\delta = \left[(\delta_{da} - \delta_{dl})^2 + (\delta_{pa} - \delta_{pl})^2 + (\delta_{ha} - \delta_{hl})^2 \right]^{1/2}$ and δ_{dl} , δ_{pl} and δ_{hl} are the dispersion component, polar component and hydrogen bonding components of the van Krevelen solubility parameter of the polylactic acid resin

20 31. The process of claims 29 or 30, wherein the accelerant includes a long-chain diester of an aliphatic dicarboxylic acid.

32. The process of any of claims 23-31, wherein the molding composition further contains a particulate or fibrous reinforcing agent.

25

33. An injection molded PLA resin part made according to the process of any of claims 19-32.

34. An injection molded PLA resin part of claim 33 which has an impact
30 strength of at least 1.75 foot-pounds/inch (2.4 J) and a storage modulus E' , at 80°C, of at least 5×10^7 Pa.

35. An injection molded PLA resin part that has an impact strength of at least 1.75 foot-pounds/inch (2.4 J) and a storage modulus E', at 80°C, of at least 5×10^7 Pa.

5 36. A molding composition comprising, in admixture, (A) from 75-94% by weight a polylactide (PLA) resin having lactic acid repeating units that are (1) all L-enantiomers, (2) all D-enantiomers, or (3) a mixture of L- and D- enantiomers wherein the mixture of L- and D- enantiomers includes at least 97% of one enantiomer, and no more than 3% of the other enantiomer, (B) at least one
10 nucleating agent and (C) from about 3 to 24.9% by weight of an accelerant, wherein the weight percentages are based on the combined weights of components (A), (B) and (C).

37. A process for forming injection molded articles, comprising
15 a) heating a molding composition of claim 36 to a temperature above the crystalline melting temperature of the PLA resin;
b) injecting the heated molding composition into a mold which is at a temperature of from 70 to 130°C,
c) allowing the molding composition to cool and solidify in the mold until it
20 has developed at least 20 Joules of crystallinity per gram of PLA resin in the molding composition; and then
d) removing the resulting molded article from the mold.

38. A process for forming injection molded articles, comprising
25 a) heating a molding composition containing (A) from 75-94% by weight a polylactide (PLA) resin having lactic acid repeating units that are (1) all L-enantiomers, (2) all D-enantiomers, or (3) a mixture of L- and D- enantiomers wherein the mixture of L- and D- enantiomers includes at least 97% of one enantiomer, and no more than 3% of the other enantiomer, and wherein the PLA
30 resin contains at least 15% by weight of the PLA resin has a molecular weight of at least 200,000 and (E) at least one core-shell rubber to above the crystalline melting temperature of the PLA resin;
b) injecting the heated molding composition into a mold which is at a temperature of from 70 to 130°C,

c) allowing the molding composition to cool and solidify in the mold until it has developed at least 20 Joules of crystallinity per gram of PLA resin in the molding composition; and then

d) removing the resulting molded article from the mold.

5

39. An injection molded PLA resin part made according to the process of claim 37 or 38.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
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According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C08L C08K C08J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	DATABASE WPI Week 200952 Thomson Scientific, London, GB; AN 2009-L47642 XP002631757, - & JP 2009 155489 A (TORAY IND INC) 16 July 2009 (2009-07-16) abstract paragraph [0014] paragraph [0016] paragraph [0115] paragraph [0032] examples 20-24; table 4 examples 25,26; table 5 ----- -/--	1-39

Further documents are listed in the continuation of Box C.

See patent family annex.

* Special categories of cited documents :

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- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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