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(54) Title: HEAT RESISTANT POLYLACTIC ACID COMPOUNDS

(57) Abstract: A significant disadvantage of the use of polylactic acid (PLA) has been overcome by the use of styrene maleic anhydride copolymer (SMAC) to cause an unexpected increase in the heat deflection temperature of the PLA compound, surpassing a delta improvement of 5 °C over the heat deflection temperature of the PLA alone, at 66 psi as measured using ASTM D648 when the blended compound is essentially dried prior to use. The compound also often exceeds a threshold of 65 °C in heat deflection temperature. Use of a compatibilizer and impact modifier further improves the industrial versatility of the heat resistant PLA compound. Alternatively, use of calcium carbonate in the heat resistant PLA compound also is industrially valuable.



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HEAT RESISTANT POLYLACTIC ACID COMPOUNDS

CLAIM OF PRIORITY

[0001] This application claims priority from both U.S. Provisional Patent Application Serial Number 61/047,460 bearing Attorney Docket Number 12008011 and filed on April 24, 2008 and U.S. Provisional Patent Application Serial Number 61/161,902 bearing Attorney Docket Number 12009006 and filed on March 20, 2009, both of which are incorporated by reference.

FIELD OF THE INVENTION

[0002] This invention relates to polylactic acid compounds which have a heat resistance modifier to improve structural integrity of the polylactic acid compounds during use.

BACKGROUND OF THE INVENTION

[0003] Plastic articles have replaced glass, metal, and wood articles because plastic can be engineered to not shatter, rust, or rot. The durability of plastic articles also creates a disposal dilemma. Also, many plastic resins are made from petrochemicals, which have long-term supply and cost issues.

[0004] Therefore, there is a considerable effort underway to find biologically-derived and sustainable sources of thermoplastic resins, preferably those which degrade or compost to also resolve the disposal dilemma.

[0005] Polylactic acid, also known as polylactide or PLA, has been explored as a thermoplastic resin from biologically sustainable origins which can replace petrochemically originated resins.

SUMMARY OF THE INVENTION

[0006] While polylactic acid is probably one of the three most popular bio-derived resins being explored, it has the distinct disadvantage, as when

compared to the fossil-derived resins it is meant to replace, in that it has a poor heat deflection temperature.

[0007] Heat deflection temperature (HDT) is a measurement of deflection of a sample under flexural load using the protocol of ASTM D648. The flexural load can be either of two settings. For purposes of this invention, 66 pounds per square inch (psi) or 455 kilo-Pascals (kPa) will be used for comparative measurements of heat deflection.

[0008] The problem with polylactic acid is that it has a heat deflection temperature under a 455 kPa flexural load of about 55°C or 131°F. In other words, inside a automobile on an Arizona summer day, PLA would not be sturdy enough to be used as a thermoplastic resin molded into a passenger compartment component, as the case for an electronic handheld device laying on the seat, or as a piece of packaging containing perishable food in a grocery bag on the floor inside the automobile.

[0009] The problem with PLA is that it does not have sufficient heat resistance to allow it to be considered as a practical replacement for fossil-derived thermoplastic resins now used in many common plastic articles.

[00010] The present invention solves that problem by finding and using a heat resistance modifier to be combined with PLA to increase the heat resistance of PLA so that it can be used ubiquitously.

[00011] The art has had a long-felt need for solving this heat resistance problem. Published literature of NatureWorks, LLC, a principal manufacturer of PLA reports that adding as much as 50% by weight of polymethyl methacrylate (PMMA) to PLA to create a 50/50 PLA-PMMA compound improves HDT by as little as 4 °C over the HDT of pure PLA polymer resin (63°C vs. 59°C).

[00012] Moreover, the art has had a long-felt need for solving this heat resistance problem, and it has been commonly characterized in some industries that a PLA compound should preferably have at least a 65°C HDT at 66 psi to be a practical thermoplastic compound of both biologically sustainable origin

and practical commercial use. At long last, the present invention has discovered also suitable combinations to achieve, and exceed, that goal of 65°C at 66 psi.

[00013] The art needs a means to increase the actual HDT values for PLA, while also retaining the resulting compound as principally significantly a PLA compound.

[00014] For purposes of this invention, the PLA must remain the "significant component", meaning that PLA is present in at least about thirty weight percent (30%) of the compound.

[00015] For some situations when it is desirable to market plastic articles made from the compound as made principally from bio-renewable materials, the PLA can be present as the "principal component", meaning that it has the highest or equal to highest weight percent of the compound among all ingredients employed. For example, PLA will be the "principal component" in a two-ingredient compound if it has 50% or more weight percent of the total compound. PLA will also be the "principal component" in a three-or-more-ingredient compound if it has a plurality weight percent in excess of any other ingredient, e.g., 34% PLA in a compound with two other ingredients each having 33 weight percent. PLA is also the "principal component" for this invention if its weight percent is equal to the weight percent of one other ingredient, such as in a 30 (PLA) -30-20-20 (other ingredients) in a four-ingredient compound.

[00016] It has been found, unexpectedly, that styrene maleic anhydride copolymer can increase the HDT of a PLA compound by at least 5 °C more than the HDT for PLA alone. A blend of PLA and styrene maleic anhydride copolymer can also preferably have a HDT of more than 65°C.

[00017] One aspect of the present invention is a heat resistant polylactic acid compound, comprising: a blend of (a) polylactic acid and (b) styrene maleic anhydride copolymer; wherein the compound has polylactic acid as a significant component; wherein polylactic acid and styrene maleic anhydride copolymer have a weight ratio of 2.3:1.0 or less; and wherein if the blended

compound is essentially dried before shaping into a plastic article, then the blended compound after shaping into the plastic article has a heat deflection temperature increase of at least 5°C more than the heat deflection temperature of the polylactic acid alone, when both are measured at 66 pounds per square inch using the protocol of ASTM D648.

[00018] Alternatively, the heat resistant polylactic acid compound also includes a compatibilizer, such as polymethyl methacrylate of any crystallinity (PMMA), to assist the blending of polylactic acid and the styrene maleic anhydride copolymer (SMAC).

[00019] Optionally, the heat resistant polylactic acid compound also includes a rubbery impact modifier, such as a styrene butadiene rubber (SBR) with the PLA, SMAC, and PMMA to enhance impact resistance or toughness of a plastic article made from the compound.

[00020] Alternatively to the option of using a compatibilizer, with or without impact modifier, the heat resistant polylactic acid compound can include filler, such as calcium carbonate (CaCO₃) and also achieve the goal of 5°C HDT differential at 66 psi.

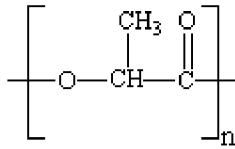
[00021] Preferably, the HDT of the compound of the present invention not only has a 5°C differential HDT at 66 psi but also has a HDT of at least 65°C.

[00022] Features and advantages of the compound of the present invention will be further explained with reference to the embodiments and the examples showing the unexpected results.

EMBODIMENTS OF THE INVENTION

[00023] Polylactic acid

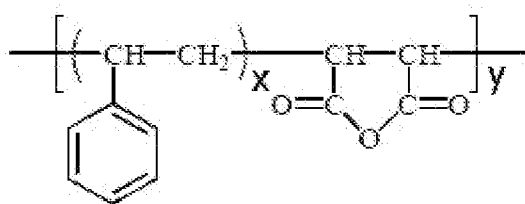
[00024] PLA is a well-known biopolymer, having the following monomeric repeating group:



[00025] The PLA can be either poly-D-lactide, poly-L-lactide, or a combination of both. PLA is commercially available from NatureWorks, LLC located in all manufacturing regions of the world. Any grade of PLA is a candidate for use in the present invention. The number average molecular weight of PLA can be any which is currently available in a commercial grade or one which is brought to market in the future. To the extent that a current end use of a plastic article could benefit from being made from PLA and from having the heat resistance of the compound of the present invention, then that suitable PLA should be the starting point for constructing the compound of the present invention.

[00026] Styrene Maleic Anhydride Copolymer

[00027] SMAC is a copolymer having the following co-monomeric repeating group:



[00028] Candidates of SMAC for the present invention can be based on a combination of two different factors: percentage maleic anhydride content and molecular weight.

[00029] One set of candidates relies on a low molar ratio of styrenic moiety to maleic anhydride moiety and a low molecular weight of SMAC. This set of candidate SMACs can have a molar ratio of styrenic moiety to maleic anhydride moiety ranging from about 4:1 to about 1:1, and preferably about 1:1. Likewise, such candidates should have a number average molecular weight

ranging from about 1000 to about 50,000, and preferably from about 2000 to about 10,000. Most preferably, the SMAC has a number average molecular weight of 2000.

[00030] SMAC of this first set of candidates is commercially available in a number of grades under the SMA[®] brand of SMAC from Sartomer Company of Exton, PA, USA. Of them, SMA[®] 1000 is preferred.

[00031] The second set of candidates relies on a high molar ratio of styrenic moiety to maleic anhydride moiety and a high molecular weight of SMAC. This set of candidate SMACs can have a molar ratio of styrenic moiety to maleic anhydride moiety ranging from about 20:1 to about 5:1, and preferably about 10:1. Likewise, such candidates should have a number average molecular weight ranging from about 75,000 to about 250,000, and preferably from about 100,000 to about 200,000. Most preferably, the SMAC has a number average molecular weight of 150,000.

[00032] SMAC of this second set of candidates is commercially available in a number of grades under the Dylark[®] brand of SMAC from Nova Chemicals of Pittsburgh, PA, USA. Of them, Dylark[®] FG7300 and FG2500 are preferred. Another source is from Polyscope Polymers BV of Roermond, the Netherlands bearing the Xiran[®] brand in a number of grades with Mn of 80,000 – 180,000 and a styrenic/maleic anhydride moiety ratio range of 4.54:1 -- 2.94:1. Presently, Xiran SZ22110 and Xiran SZ26080 grades are preferred.

[00033] Presently, there is no set of commercially available SMAC candidates which have both a high molecular weight SMAC and a low styrenic/maleic anhydride moiety ratio. If there were, that set of candidates could also be useful.

[00034] Optional Compatibilizer

[00035] To assist in the blending of PLA and SMAC, a compatibilizer can be used. Any dual-affinity compound or molecule with affinity for lactide moieties and either styrenic or anhydridic moieties can be a candidate for use as a compatibilizer.

[00036] Of possible candidates, poly (meth)acrylates of any crystallinity are desirable because compatibility and flexibility of synthesis. Of them, polymethyl methacrylate is preferred because the possibility of recycling, the possibility of being made from biomass, its globally available and lower cost.

[00037] Optional Impact Modifier

[00038] Any conventional impact modifier is a candidate for use in compounds of the present invention. Core/shell impact modifiers, rubbery impact modifiers, etc. are suitable.

[00039] Optional Filler

[00040] Any conventional filler is a candidate for use in compounds of the present invention. Fillers increase mass without adversely affecting the physical properties of the compound. It has been found that a precipitated calcium carbonate marketed under the Emforce[®] from Specialty Minerals, a business unit of Mineral Technologies, Inc. of New York City is suitable for use in the present invention.

[00041] Other Optional Additives

[00042] The compounds of the present invention can include other conventional plastics additives in an amount that is sufficient to obtain a desired processing or performance property for the compound. The amount should not be wasteful of the additive nor detrimental to the processing or performance of the compound. Those skilled in the art of thermoplastics compounding, without undue experimentation but with reference to such treatises as Plastics Additives Database (2004) from Plastics Design Library (www.williamandrew.com), can select from many different types of additives for inclusion into the compounds of the present invention.

[00043] Non-limiting examples of optional additives include adhesion promoters; biocides (antibacterials, fungicides, and mildewcides), anti-fogging agents; anti-static agents; bonding, blowing and foaming agents; dispersants; fire and flame retardants and smoke suppressants; initiators; lubricants; pigments, colorants and dyes; plasticizers; processing aids; release agents; slip

and anti-blocking agents; stabilizers; stearates; ultraviolet light absorbers; viscosity regulators; waxes; and combinations of them.

[00044] Table 1 shows acceptable, desirable, and preferable ranges of ingredients useful in the present invention, all expressed in weight percent (wt. %) of the entire compound.

Table 1			
	Acceptable	Desirable	Preferable
PLA Matrix	10-80	20-75	30-70
SMAC Heat Resistance Modifier*	7-54	14-50	20-47
Optional Compatibilizer	0-20	0-20	0-20
Optional Impact Modifier	0-20	0-20	0-20
Optional Filler	0-20	0-20	0-20
Other Optional Additives	0-10	0-10	0-10

*with the weight ratio of PLA:SMAC being 2.3:1.0 or less.

[00045] Processing

[00046] The preparation of compounds of the present invention is uncomplicated. The compound of the present can be made in batch or continuous operations.

[00047] Mixing in a continuous process typically occurs in an extruder that is elevated to a temperature that is sufficient to melt the polymer matrix with addition either at the head of the extruder or downstream in the extruder of the solid ingredient additives. Extruder speeds can range from about 50 to about 500 revolutions per minute (rpm), and preferably from about 100 to about 300 rpm. Typically, the output from the extruder is pelletized for later extrusion or molding into polymeric articles.

[00048] Mixing in a batch process typically occurs in a Banbury mixer that is also elevated to a temperature that is sufficient to melt the polymer matrix to permit addition of the solid ingredient additives. The mixing speeds

range from 60 to 1000 rpm and temperature of mixing can be ambient. Also, the output from the mixer is chopped into smaller sizes for later extrusion or molding into polymeric articles.

[00049] Optionally prior to batch or continuous blending, one can dry the ingredients to help reduce the possibility of a moisture-activated degradation or reaction in the blending vessel. Alternatively, one can use other ways to reduce degradation possibilities, such as incorporating a moisture scavenger or desiccant into the formulation, applying a vacuum within the blending vessel, etc. Any of these techniques, or combination of techniques, results in the ingredients being dried before or during blending. These are optional techniques because it has been found, as seen in the Examples below, that an un-dried set of ingredients can be extruded and later molded into a plastic article which meets the goal of at least a 5 °C HDT differential and preferably a 65°C HDT at 66 psi flexural load.

[00050] Subsequent extrusion or molding techniques are well known to those skilled in the art of thermoplastics polymer engineering. Without undue experimentation but with such references as "Extrusion, The Definitive Processing Guide and Handbook"; "Handbook of Molded Part Shrinkage and Warpage"; "Specialized Molding Techniques"; "Rotational Molding Technology"; and "Handbook of Mold, Tool and Die Repair Welding", all published by Plastics Design Library (www.williamandrew.com), one can make articles of any conceivable shape and appearance using compounds of the present invention.

[00051] Regardless of drying or other techniques during blending, it has been found that drying the blended compound before molding has a direct effect on performance properties, including heat deflection temperature. As the Examples below demonstrate, the amount of drying should be much closer to about 48 hours than about 4 hours, in order to achieve an essentially dry blended compound prior to molding, i.e., having a moisture content of less than 0.1%. To reduce the possibility of drying at a temperature approaching the heat

deflection temperature of 65°C, the temperature can be up to about 60°C without vacuum. Indeed, without undue experimentation, one can identify the best combination of time, temperature, and atmospheric pressure to reduce the time of drying while maximizing the amount of drying, without approaching a temperature which would degrade or otherwise affect performance of the compound as a molded or extruded product.

USEFULNESS OF THE INVENTION

[00052] Any plastic article is a candidate for use of the compounds of the present invention. With the heat durability of PLA now achieved, all types of plastic articles which required at least a 5 °C HDT differential (and preferably a HDT of at least 65°C at 66 psi), previously made from fossil-derived polymers, can now be made from a sustainable PLA polymer compound.

[00053] Plastic articles made from compounds of the present invention can be shaped via molding or extruding for use in the transportation, appliance, electronics, building and construction, biomedical, packaging, and consumer markets.

[00054] For example, food packaging can now be made from a PLA compound of the present invention and retain sufficient heat resistance to withstand storage or transport at temperatures approaching 60°C. The plastic article made from a compound of the present invention will retain its structural integrity at least 5 °C higher than with PLA alone and preferably at temperatures below 65°C.

[00055] Examples prove the unexpected nature of the present invention.

EXAMPLES

[00056] Comparative Examples A -D and Examples 1-19

[00057] Neat PLA resin was obtained and 18 different compounds were prepared.

[00058] Comparative Example A is neat PLA resin undergoing the same extrusion and molding heat histories as do Comparative Examples B-D and Examples 1-19. Comparative Example B demonstrates that neither a delta HDT of 5°C nor a HDT of 65°C at 66 psi can be achieved by attempting to crosslink the PLA. Thus, the obvious approach to improving HDT does not work.

[00059] All of Examples 1-19 meet and exceed the >5°C delta HDT goal, and many of them exceed the 65°C HDT goal. Unexpectedly, for the first known time, because of the use of SMAC as a heat resistance modifier, PLA can be compounded to have a delta HDT meeting or exceeding 5°C with PLA remaining as the principal component in the compound and also often meeting or exceeding a HDT of 65°C at 66 psi flexural load.

[00060] Table 2 shows the raw material ingredients employed.

Table 2 Ingredients				
Name	Brand	Composition	Manufacturer	Function
PLA	NatureWorks® Polylactide Resin 4042D	Poly lactide Resin	NatureWorks LLC	Matrix
SMAC	SMA 1000P	Styrene Maleic Anhydride resin, cumene end- capped	Sartomer Company, Inc.	Heat Resistance Modifier
PMMA	Plexiglas® VS-100 Acrylic Resin	Poly(Ethyl acrylate/Methyl methacrylate)	Arkema Inc.	Compatibilizer
ABS	Blendex® 338	Acrylonitrile- butadiene- styrene polymer	Chemtura	Impact Modifier
Peroxide	Trignox® 101	2, 5-Dimethyl- 2,5-di(tert- butylperoxy) hexane	Akzo Nobel Polymer Chemicals LLC	Crosslinking Agent
Silane	Silquest® A171	Vinyl Trimethoxy Silane	Momentive	Crosslinking Agent

Table 2 Ingredients				
Name	Brand	Composition	Manufacturer	Function
CaCO ₃	Emforce® Bio additive	Precipitated Calcium Carbonate	Specialty Minerals	Filler

[00061] Table 3 (in two parts) shows the recipes for the compounds. Table 4 (in two parts) shows the extrusion conditions to produce pellets for later molding. Table 5 (in two parts) shows the molding conditions to produce molded articles as needed for the HDT testing. Table 6 (in two parts) shows the average of HDT results using four different samples of each Example and Comparative Example, with a standard deviation provided.

[00062] In Table 3, Comparative Example B and Examples 3-8 and 15-17 had the resins dried before extrusion commenced using the following technique: all of the polymeric resins were dried overnight at 80°C in a convection oven without a vacuum applied. The other Comparative Examples and Examples were not dried before extrusion.

[00063] As shown in Table 4, extruder conditions for all Examples and Comparative Examples were very similar. As shown in Table 5, molding conditions for all Examples and Comparative Examples were very similar. Processing variability was minimized.

[00064] Table 6 shows several features of the invention arising from the HDT results as measured in degrees Celsius under flexural load of 66 psi according to the protocol of ASTM D648.

Table 3 Recipes												
	A	1	2	B	3	4	5	6	7	8	9	10
PLA	100.0	70.0	60.0	98.5	60.0	52.2	54.0	48.0	42.0	30.0	54.0	48.0
SMAC		30.0	40.0		40.0	34.8	36.0	32.0	28.0	30.0	36.0	32.0
Peroxide				0.5								
Silane				1.0								
PMMA							10.0	20.0	20.0	20.0	10.0	20.0
ABS									10.0	20.0		
CaCO ₃						13.0						
PLA:SMAC Ratio	NA	2.3:1.0	1.5:1.0	NA	1.5:1.0	1.5:1.0	1.5:1.0	1.5:1.0	1.5:1.0	1.0:1.0	1.5:1.0	1.5:1.0
Resin Dried at 80°C for 8 hours prior to extrusion	N	N	N	Y	Y	Y	Y	Y	Y	Y	N	N
Drying time prior to molding	4h	4h	4h	48h	48h	48h	48h	48h	48h	48h	48h	48h
Drying temperature prior to molding	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C

Table 3 Recipes (Continued)											
	11	12	C	D	13	14	15	16	17	18	19
PLA	63.0	56.0	72.0	64.0	70.0	60.0	70.0	58.5	52.0	58.5	52.0
SMAC	27.0	24.0	18.0	16.0	30.0	40.0	30.0	31.5	28.0	31.5	28.0
Peroxide											
Silane											
PMMA	10.0	20.0	10.0	20.0				10.0	20.0	10.0	20.0
ABS											
CaCO ₃											
PLA:SMAC Ratio	2.3:1.0	2.3:1.0	4.0:1.0	4.0:1.0	2.3:1.0	1.5:1.0	2.3:1.0	1.86:1	1.86:1	1.86:1	1.86:1
Resin Dried at 80°C for 24 hours prior to extrusion	N	N	N	N	N	N	Y	Y	Y	N	N
Drying time prior to molding	48h	48h	48h	48h	48h	48h	48h	48h	48h	48h	48h
Drying temperature prior to molding	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C	60 °C

Table 4 Extruder Conditions												
Extruder Type	Prism 16mm Counter-Rotating Twin Screw Extruder											
Order of Addition	All ingredients mixed together and fed into the extruder hopper.											
	A	1	2	B	3	4	5	6	7	8	9	10
Zone 1 (°C)	201	200	201	210	210	210	210	210	210	210	210	210
Zone 2 (°C)	210	200	201	210	210	210	210	210	210	210	210	210
Zone 3 (°C)	199	201	200	200	200	200	200	200	200	200	200	200
Zone 4 (°C)	199	200	200	200	200	200	200	200	200	200	200	200
Zone 5 (°C)	200	200	200	210	210	210	210	210	210	210	210	210
Zone 6 (°C)	200	201	200	200	200	200	200	200	200	200	200	200
Zone 7 (°C)	200	200	201	200	200	200	200	200	200	200	200	200
Zone 8 (°C)	200	200	200	200	200	200	200	200	200	200	200	200
Zone 9 (°C)	200	200	200	200	200	200	200	200	200	200	200	200
Die (°C)	200	200	200	199	199	199	199	199	199	199	199	199
RPM	300	300	300	500	500	500	250	250	250	250	250	250

Table 4 Extruder Conditions (Continued)											
Extruder Type	Prism 16mm Counter-Rotating Twin Screw Extruder										
Order of Addition	All ingredients mixed together and fed into the extruder hopper.										
	11	12	C	D	13	14	15	16	17	18	19
Zone 1 (°C)	200	200	199	199	200	201	200	200	199	200	199
Zone 2 (°C)	200	201	200	200	200	201	200	200	199	199	200
Zone 3 (°C)	200	199	201	201	201	201	201	200	199	200	200
Zone 4 (°C)	200	200	200	199	200	200	200	199	200	200	200
Zone 5 (°C)	201	200	200	200	200	200	200	200	200	200	200
Zone 6 (°C)	200	201	200	200	201	201	201	200	200	200	199
Zone 7 (°C)	200	200	201	200	200	200	200	199	200	200	199
Zone 8 (°C)	200	200	200	200	200	200	200	199	199	200	199
Zone 9 (°C)	200	200	200	200	200	200	200	199	199	200	200
Die (°C)	200	200	200	200	200	200	200	200	200	199	200
RPM	300	300	300	300	300	300	300	250	250	250	250

Table 5												
Molding Conditions												
88 ton Nissei molding machine												
	A	1	2	B	3	4	5	6	7	8	9	10
Drying Conditions:												
Temperature (°C)	60	60	60	60	60	60	60	60	60	60	60	60
Time (h)	48	4	4	48	48	48	48	48	48	48	48	48
Temperatures:												
Nozzle (°F)	395	396	396	397	397	397	406	406	406	406	406	406
Zone 1 (°F)	396	395	395	390	390	390	395	395	395	395	395	395
Zone 2 (°F)	399	394	394	380	380	380	404	404	404	404	404	404
Zone 3 (°F)	394	395	395	375	375	375	395	395	395	395	395	395
Mold (°F)	100	100	100	89	89	89	99	99	99	99	99	99
Oil Temp (°F)	86	86	86	100	100	100	100	100	100	100	100	100
Speeds:												
Screw RPM (%)	65	65	65	65	65	65	65	65	65	65	65	65
% Shot - Inj Vel Stg 1	60	60	60	80	80	80	60	60	60	60	60	60
% Shot - Inj Vel Stg 2	50	50	50	70	70	70	50	50	50	50	50	50
% Shot - Inj	40	40	40	60	60	60	40	40	40	40	40	40

Table 5												
Molding Conditions												
88 ton Nissei molding machine												
	A	1	2	B	3	4	5	6	7	8	9	10
Vel Stg 3												
% Shot - Inj Vel Stg 4	35	35	35	55	55	55	35	35	35	35	35	35
% Shot - Inj Vel Stg 5	30	30	30	50	50	50	30	30	30	30	30	30
Pressures:												
Hold Stg 1 (PSI) - Time(sec)	300 7	300 7	300 7	440 9	440 9	440 9	300 7	300 7	300 7	300 7	300 7	300 7
Hold Stg 2 (PSI) - Time(sec)	240 7	240 7	240 7	360 9	360 9	360 9	240 7	240 7	240 7	240 7	240 7	240 7
Timers:												
Injection Hold (sec)	7	7	7	8	8	8	7	7	7	7	7	7
Cooling Time (sec)	25	25-30	25-30	25	25	25	25	25	25	25	25	25
Operation Settings:												
Shot Size (mm)	50	50	50	40	40	40	50	50	50	50	50	50
Cushion (mm)	1.5	1.5	1.5	1.3	1.3	1.3	1.0	1.0	1.0	1.0	1.0	1.0

Table 5											
Molding Conditions (Continued)											
88 ton Nissei molding machine											
	11	12	C	D	13	14	15	16	17	18	19
Drying Conditions:											
Temperature (°C)	60	60	60	60	60	60	48	60	60	60	60
Time (h)	48	48	48	48	48	60	48	48	48	48	60
Temperatures:											
Nozzle (°F)	395	395	395	395	395	395	395	396	396	396	396
Zone 1 (°F)	396	396	396	396	396	396	396	398	398	398	398
Zone 2 (°F)	399	399	399	399	399	399	399	395	395	395	395
Zone 3 (°F)	394	394	394	394	394	394	394	395	395	395	395
Mold (°F)	100	100	100	100	100	100	100	108	108	108	108
Oil Temp (°F)	86	86	86	86	86	86	86	86	86	86	86
Speeds:											
Screw RPM (%)	65	65	65	65	65	65	65	65	65	65	65
Inj Vel Stg 1 (inch/sec)	60	60	60	60	60	60	60	60	60	60	60
Inj Vel Stg 2 (inch/sec)	50	50	50	50	50	50	50	50	50	50	50
Inj Vel Stg 3	40	40	40	40	40	40	40	40	40	40	40

Table 5											
Molding Conditions (Continued)											
88 ton Nissei molding machine											
	11	12	C	D	13	14	15	16	17	18	19
(inch/sec)											
Inj Vel Stg 4 (inch/sec)	35	35	35	35	35	35	35	35	35	35	35
Inj Vel Stg 5 (inch/sec)	30	30	30	30	30	30	30	30	30	30	30
Pressures:											
Hold Stg 1 (PSI) - Time(sec)	300 7	300 7	300 7	300 7	300 7	300 7	300 7	300 7	300 7	300 7	300 7
Hold Stg 2 (PSI) - Time(sec)	240 7	240 7	240 7	240 7	240 7	240 7	240 7	300 7	300 7	300 7	300 7
Timers:											
Injection Hold (sec)	7	7	7	7	7	7	7	8	8	8	8
Cooling Time (sec)	25	25	25	25	25	25	25	25-30	25-30	25-30	25-30
Operation Settings:											
Shot Size (mm)	50	50	50	50	50	50	50	60	60	60	60
Cushion (mm)	1.5	1.5	1.5	1.5	1.5	1.5	1.5	2.0	2.0	2.0	2.0

Table 6 Deflection Temperature in °C Under Flexural Load of 66 psi according to ASTM D648

	A	1	2	B	3	4	5	6	7	8	9	10
Ratio	NA	2.3:1.0	1.5:1.0	NA	1.5:1.0	1.5:1.0	1.5:1.0	1.5:1.0	1.5:1.0	1.0:1.0	1.5:1.0	1.5:1.0
% Moisture	0.057	0.040	0.055		0.078	0.086	0.060	0.000	0.016	0.000	0.024	0.000
HDT #1	53.6	62.5	73.5	54.6	95.5	78.5	87.0	82.0	77.2	85.9	73.2	77.6
HDT #2	54.3	60.0	61.6	53.1	84.4	80.6	82.3	80.2	71.5	89.8	74.6	78.9
HDT #3	54.0	59.6	62.7		87.3	83.5	83.8	79.8	72.6	89.8	68.4	77.7
HDT #4	55.1	58.8	58.3		78.0	86.2	80.1	83.0	77.2	86.6	71.3	80.5
Average	54.3	60.2	64.0	53.9	86.3	82.2	83.3	81.3	74.6	88.0	71.9	78.7
Std. Dev.	0.6	1.6	6.6	1.1	7.3	3.4	2.9	1.5	3.0	2.1	2.7	1.4

	11	12	C	D	13	14	15	16	17	18	19
Ratio	2.3:1.0	2.3:1.0	4.0:1.0	4.0:1.0	2.3:1.0	1.5:1.0	2.3:1.0	1.9:1.0	1.9:1.0	1.9:1.0	1.9:1.0
% Moisture	0.019	0.035	0.007	0.022	0.010	0.031	0.023	Essentially Dried Before Shaping			
HDT #1	60.7	61.3	59.0	58.2	66.7	72.3	74.1	60.8	72.8	63.5	73.1
HDT #2	59.2	59.8	57.5	58.0	63.0	75.4	66.4	63.1	69.7	61.4	70.7
HDT #3	58.3	57.4	56.2	57.6	61.3	62.1	64.0	64.3	67.8	61.0	63.0
HDT #4	59.9	58.1	57.6	58.4	60.2	59.7	61.9	62.6	65.9	59.9	67.1
Average	59.5	59.2	57.6	58.1	62.8	67.4	66.6	62.7	69.1	61.5	68.5
Std. Dev.	1.0	1.8	1.1	0.3	2.8	7.6	5.3	1.5	2.9	1.5	4.4

[00065] Table 6 provides several comparisons to understand the invention. All Examples demonstrated at least a 9% improvement in HDT and some demonstrated as much as a 62% improvement while retaining PLA as the principal component.

[00066] Comparative Example B, the attempted crosslinking of the PLA, did not work. The average HDT was worse, not better than Comparative Example A, neat PLA resin. Therefore, Comparative Example B proved what was obvious to try does not work.

[00067] All except Comparative Example B were "essentially dried before shaping." For purposes of this invention, "essentially dried before shaping" means a duration of drying at elevated temperature of sufficient duration to reduce moisture to less than 0.1%. The elevated temperature can be above 40°C and up to about 60°C. In some cases, the duration can be as short as 4 hours if a higher elevated temperature is used. More likely, the duration is more than 6 hours, desirably between 12-24 hours, and as much as 40-48 hours to be totally thorough. One skilled in the art, without undue experimentation, can determine for a particular recipe found in blended compound the amount of time necessary to achieve sufficient drying to less than 0.1% moisture content, so that the blended compound is "essentially dried before shaping" into a plastic article.

[00068] A comparison of Examples 1 and 2 with Comparative Example A shows at least a 5°C increase in HDT, a significant advance with retention of PLA as the principal component. Indeed, use of 40 weight percent SMAC with PLA while retaining PLA as the principal component produced a 17.8% improvement in HDT, while use of 30 weight percent produced 10.8% improvement. Examples 1 and 2 also demonstrated that as little as four hours of pre-molding drying, at the upper limit drying temperature of 60 °C was sufficient to reduce moisture content to below 0.1%.

[00069] Examples 3-19 and Comparative Examples C and D all had samples which were essentially dried before shaping (below 0.1% moisture content), although the actual values for Examples 16-19 were not obtained.

[00070] What distinguished Examples 3-19 from Comparative Examples C and D was the ratio of PLA:SMAC, with Comparative Examples C and D having a ratio exceeding 2.3:1.0.

[00071] Therefore, the two requirements for achieving the 5 °C HDT goal for a compound in which PLA is the principal component are a weight ratio of PLA:SMAC of 2.3:1.0 or less and a compound which is essentially dried before shaping.

[00072] The variations among Examples 1-19 show that compatibilizer is optional, that impact modifier is optional, and that pre-extrusion drying of resins is optional. Therefore, without undue experimentation and recognizing the robust alternatives shown, one skilled in the art can construct a variety of modified PLA compounds which improve HDT by 5 °C or more over neat PLA resin and often have a HDT of at least 65°C and approaching 90°C, almost 200°F and beyond habitable conditions for any length of time.

[00073] Table 6 also reports standard deviation of the four HDT tests on different samples of each Example and Comparative Example. Examples 5-12 and 16-19 also contained PMMA as a compatibilizer. The presence of compatibilizer in these Examples reduced the variability in the performance of the four samples of each Example tested. The standard deviation was smaller, resulting in a current preference for a recipe such as Example 10, rather than Example 14, which is inventive but subject to greater variability than a commercial production might tolerate.

[00074] The compounds of the present invention, Examples 1-19, have unexpectedly greatly surpassed the previously unattainable goal of a delta HDT increase of at least 5 °C and preferably a 65°C HDT at 66 psi.

[00075] Examples 20-25

[00076] Table 7 shows the raw material ingredients employed.

Table 7 Ingredients				
Name	Brand	Composition	Manufacturer	Function
PLA	NatureWorks [®] Polylactide Resin 4042D	Polylactide Resin	NatureWorks LLC	Matrix
SMAC	Xiran SZ 22110	Styrene Maleic Anhydride resin	Polyscope	Heat Resistance Modifier
SMAC	Xiran SZ 26080	Styrene Maleic Anhydride resin	Polyscope	Heat Resistance Modifier
SMAC	Dylark FG2500	Styrene Maleic Anhydride resin	Nova Chemicals	Heat Resistance Modifier
SMAC	Dylark FG7300	Styrene Maleic Anhydride resin	Nova Chemicals	Heat Resistance Modifier
PMMA	Plexiglas [®] VS- 100 Acrylic Resin	Poly(Ethyl acrylate/ Methyl methacrylate)	Arkema Inc.	Compatibi- lizer
ABS	Blendex [®] 338	Acrylonitrile- Butadiene- Styrene Polymer	Chemtura	Impact Modifier

[00077] Table 8 shows the recipes for the compounds. Table 9 shows the extrusion conditions to produce pellets for later molding. Table 10 shows the molding conditions to produce molded articles as needed for the HDT testing. Table 11 shows the average of HDT results using four different samples of each Example.

Table 8						
Recipes						
Example	20	21	22	23	24	25
PLA	54.0	54.0	54.0	50.0	50.0	40.0
SMAC SZ22110	36.0					
SMAC SZ26080		36.0			15.0	
SMAC FG7300			36.0			
SMAC FG2500				50.0	35.0	60.0
PMMA	10.0	10.0				
PLA:SMAC Ratio	1.5:1	1.5:1	1.5:1	1:1	1:1	0.67:1
Resin Dried at 80°C for 8 hours prior to extrusion	Yes					
Drying time prior to molding	48h					
Drying temperature prior to molding	60 °C					

Table 9	
Extruder Conditions	
Extruder Type	Prism 16mm Counter-Rotating Twin Screw Extruder
Order of Addition	All ingredients mixed together and fed into the extruder hopper.
	20-25
All Zones and Die (°C)	220°C
RPM	250

Table 10	
Molding Conditions	
88 ton Nissei molding machine	
Examples	20-25
Drying Conditions:	
Temperature (°C)	60
Time (h)	48
Temperatures:	
Nozzle (°F)	428

Table 10	
Molding Conditions	
88 ton Nissei molding machine	
Examples	20-25
All Zones	428°F (220°C)
Mold (°F)	100°F (37.8°C)
Oil Temp (°F)	100°F (37.8°C)
Speeds:	
Screw RPM (%)	65
% Shot - Inj Vel Stg 1	60
% Shot - Inj Vel Stg 2	50
% Shot - Inj Vel Stg 3	40
% Shot - Inj Vel Stg 4	35
% Shot - Inj Vel Stg 5	30
Pressures:	
Hold Stg 1 (PSI) - Time(sec)	300 7
Hold Stg 2 (PSI) - Time(sec)	240 7
Timers:	
Injection Hold (sec)	7
Cooling Time (sec)	25
Operation Settings:	
Shot Size (mm)	50
Cushion (mm)	1.0

Table 11						
Deflection Temperature in °C Under Flexural Load of 66 psi						
according to ASTM D648						
	20	21	22	23	24	25
Ratio	1.5:1.0	1.5:1.0	1.5:1.0	1.0:1.0	1.0:1.0	0.67:1.0
% Moisture	Essentially Dried Before Shaping					
HDT #1	76.9	82.5	78.8	76.8	88.7	79.9
HDT #2	81.3	80.3	79.7	73.5	85.3	82.8
HDT #3	79.5	82.0	77.8	76.2	86.1	--
HDT #4	82.7	80.5	80.1	74.0	88.2	--
Average	80.1	81.3	79.1	75.1	87.1	81.4
Std. Dev.	2.5	1.1	1.0	1.6	1.6	1.2

[00078] Examples 20-25, when compared with Example 5, which represents use of SMAC from the first set of SMAC candidates, show nearly equal or even better HDT properties are possible while using the second set of candidates. Example 23 is less than the other Examples of this set because Dylark 2500 is an impact grade of SMAC. But combining some of Xiran SZ26080 with Dylark 2500 as seen in Example 24 yields the best of this set of Examples for purposes of HDT.

[00079] The invention is not limited to the above embodiments. The claims follow.

What is claimed is:

1. A heat resistant polylactic acid compound, comprising: a blend of
(a) polylactic acid and
(b) styrene maleic anhydride copolymer;
wherein the compound has polylactic acid as a significant component;
wherein polylactic acid and styrene maleic anhydride copolymer have a weight ratio of 2.3:1.0 or less; and
wherein if the blended compound is essentially dried before shaping into a plastic article, then the blended compound after shaping into the plastic article has a heat deflection temperature increase of at least 5°C more than the heat deflection temperature of the polylactic acid alone, when both are measured at 66 pounds per square inch using the protocol of ASTM D648.
2. The compound of Claim 1, wherein if the blended compound is essentially dried before shaping into a plastic article, then the blended compound after shaping into the plastic article has a heat deflection temperature of at least 65°C at 66 pounds per square inch using the protocol of ASTM D648.
3. The compound of Claim 1 or Claim 2 further comprising a compatibilizer of a poly (meth)acrylate.
4. The compound of Claim 1 or Claim 2, wherein the polylactic acid and the styrene maleic anhydride copolymer are dried before or during being blended together.
5. The compound of Claim 1 or Claim 2 or Claim 3, further comprising an impact modifier.

6. The compound of Claim 1 or Claim 2, further comprising calcium carbonate.
7. The compound of Claim 1 or Claim 2, wherein the amount of styrene maleic anhydride copolymer ranges from about 7 to about 54 weight percent of the total compound and wherein polylactic acid and styrene maleic anhydride copolymer have a weight ratio of 1.9:1.0 or less.
8. The compound of any of Claims 3-6, wherein the amount of styrene maleic anhydride copolymer ranges from about 7 to about 54 weight percent of the total compound and wherein polylactic acid and styrene maleic anhydride copolymer have a weight ratio of 1.9:1.0 or less.
9. The compound of Claim 1 or Claim 2, wherein the blended compound after being essentially dried has a moisture content of less than 0.1% and wherein the polylactic acid is the principal component of the compound.
10. The compound of any of Claims 3-7, wherein the blended compound after being essentially dried has a moisture content of less than 0.1% and wherein the polylactic acid is the principal component of the compound.
11. A plastic article shaped from a blended compound of Claim 1 or Claim 2.
12. The article of Claim 11, wherein the article is molded or extruded and wherein the article is shaped for use in transportation, appliance, electronics, building and construction, packaging, or consumer markets.
13. A plastic article shaped from a blended compound any of Claims 3-10, wherein the plastic article has a heat deflection temperature increase of at least

5°C more than the heat deflection temperature of a plastic article made of polylactic acid alone, when both are measured at 66 pounds per square inch using the protocol of ASTM D648.

14. The article of Claim 13, wherein the article is molded or extruded and wherein the article is shaped for use in transportation, appliance, electronics, building and construction, packaging, or consumer markets.

15. A method of making the compound of any of Claim 1 or Claim 2, comprising the steps of

(a) gathering ingredients including polylactic acid and styrene maleic anhydride copolymer and

(b) blending them into a compound for subsequent molding or extruding into a plastic article shaped for use in transportation, appliance, electronics, building and construction, packaging, or consumer markets.

16. The method of making the compound of Claim 15, further comprising the steps of

(c) drying the blended compound to a moisture content of less than 0.1% and

(d) shaping the blended compound into a plastic article for use in transportation, appliance, electronics, building and construction, packaging, or consumer markets.