

Special Issue: Manufacturing of Advanced Biodegradable Polymeric Components

Guest Editors: Prof. Roberto Pantani (University of Salerno) and
Prof. Lih-Sheng Turng (University of Wisconsin-Madison)

EDITORIAL

Manufacturing of advanced biodegradable polymeric components

R. Pantani and L.-S. Turng, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42889](https://doi.org/10.1002/app.42889)

REVIEWS

Heat resistance of new biobased polymeric materials, focusing on starch, cellulose, PLA, and PHA

N. Peelman, P. Ragaert, K. Ragaert, B. De Meulenaer, F. Devlieghere and Ludwig Cardon, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42305](https://doi.org/10.1002/app.42305)

Recent advances and migration issues in biodegradable polymers from renewable sources for food packaging

P. Scarfato, L. Di Maio and L. Incarnato, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42597](https://doi.org/10.1002/app.42597)

3D bioprinting of photocrosslinkable hydrogel constructs

R. F. Pereira and P. J. Bartolo, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42458](https://doi.org/10.1002/app.42458)

ARTICLES

Largely toughening biodegradable poly(lactic acid)/thermoplastic polyurethane blends by adding MDI

F. Zhao, H.-X. Huang and S.-D. Zhang, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42511](https://doi.org/10.1002/app.42511)

Solubility factors as screening tools of biodegradable toughening agents of polylactide

A. Ruellan, A. Guinault, C. Sollogoub, V. Ducruet and S. Domenek, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42476](https://doi.org/10.1002/app.42476)

Current progress in the production of PLA-ZnO nanocomposites: Beneficial effects of chain extender addition on key properties

M. Murariu, Y. Paint, O. Murariu, J.-M. Raquez, L. Bonnaud and P. Dubois, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42480](https://doi.org/10.1002/app.42480)

Oriented polyvinyl alcohol films using short cellulose nanofibrils as a reinforcement

J. Peng, T. Ellingham, R. Sabo, C. M. Clemons and L.-S. Turng, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42283](https://doi.org/10.1002/app.42283)

Biorenewable polymer composites from tall oil-based polyamide and lignin-cellulose fiber

K. Liu, S. A. Madbouly, J. A. Schrader, M. R. Kessler, D. Grewell and W. R. Graves, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42592](https://doi.org/10.1002/app.42592)

Dual effect of chemical modification and polymer precoating of flax fibers on the properties of the short flax fiber/poly(lactic acid) composites

M. Kodal, Z. D. Topuk and G. Ozkoc, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42564](https://doi.org/10.1002/app.42564)

Effect of processing techniques on the 3D microstructure of poly(L-lactic acid) scaffolds reinforced with wool keratin from different sources

D. Puglia, R. Ceccolini, E. Fortunati, I. Armentano, F. Morena, S. Martino, A. Aluigi, L. Torre and J. M. Kenny, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42890](https://doi.org/10.1002/app.42890)

Batch foaming poly(vinyl alcohol)/microfibrillated cellulose composites with CO₂ and water as co-blowing agents

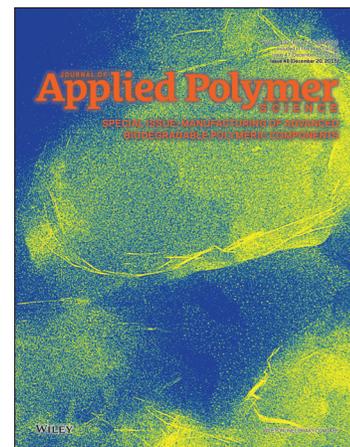
N. Zhao, C. Zhu, L. H. Mark, C. B. Park and Q. Li, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42551](https://doi.org/10.1002/app.42551)

Foaming behavior of biobased blends based on thermoplastic gelatin and poly(butylene succinate)

M. Oliviero, L. Sorrentino, L. Caferio, B. Galzerano, A. Sorrentino and S. Iannace, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42704](https://doi.org/10.1002/app.42704)

Reactive extrusion effects on rheological and mechanical properties of poly(lactic acid)/poly[(butylene succinate)-co-adipate]/epoxy chain extender blends and clay nanocomposites

A. Mirzadeh, H. Ghasemi, F. Mahrous and M. R. Kamal, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42664](https://doi.org/10.1002/app.42664)



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Rotational molding of biodegradable composites obtained with PLA reinforced by the wooden backbone of opuntia ficus indica cladodes

A. Greco and A. Maffezzoli, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42447](https://doi.org/10.1002/app.42447)

Foam injection molding of poly(lactic) acid: Effect of back pressure on morphology and mechanical properties

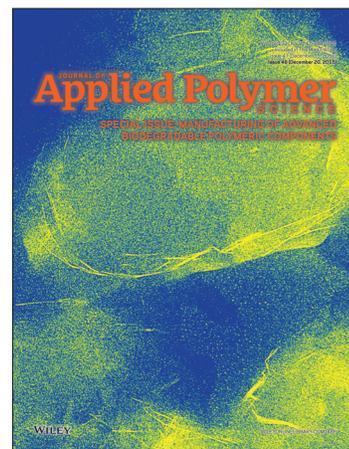
V. Volpe and R. Pantani, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42612](https://doi.org/10.1002/app.42612)

Modification and extrusion coating of polylactic acid films

H.-Y. Cheng, Y.-J. Yang, S.-C. Li, J.-Y. Hong and G.-W. Jang, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42472](https://doi.org/10.1002/app.42472)

Processing and properties of biodegradable compounds based on aliphatic polyesters

M. R. Nobile, P. Cerruti, M. Malinconico and R. Pantani, *J. Appl. Polym. Sci.* 2015, DOI: [10.1002/app.42481](https://doi.org/10.1002/app.42481)



Heat resistance of new biobased polymeric materials, focusing on starch, cellulose, PLA, and PHA

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ABSTRACT: This review provides state of the art information on the heat resistance of biobased thermoplastic materials. It gives an overview of the parameters used to indicate heat resistance, strategies to improve the heat resistance of (biobased) plastic materials and some current “heat resistant” commercially available biobased plastics materials. © 2015 Wiley Periodicals, Inc. *J. Appl. Polym. Sci.* 2015, 132, 42305.

KEYWORDS: biopolymers & renewable polymers; crystallization; differential scanning calorimetry (DSC); packaging; thermal properties

Received 16 February 2015; accepted 8 April 2015

DOI: 10.1002/app.42305

INTRODUCTION

Several reasons explain the growing interest in and the use of biobased plastic materials. The most important one is probably environmental concern/awareness. Since biobased plastic materials are produced from biomass they provide the unique potential of CO₂-neutrality (greenhouse gas). In theory, only the CO₂ which was fixed by the plant during its lifetime, will be released again in the atmosphere after disposal of the plastic (closed loop system), in contrast with conventional plastics which are derived from fossil raw materials. Together with current established measures like reuse and recycling, this aspect can put a closed loop economy in place. However, most currently used biobased plastic materials are not yet CO₂-neutral, because the energy used during the production chain (cultivation of the biomass, transport, processing, ...) is petroleum-based.¹ A second reason in favor of biobased plastic materials is the independence of crude oil. The production of conventional plastics currently needs around 5% of the global crude oil production and this will increase to around 20 to 25% by the end of the century.² Since the growing demand for crude oil will not only come from the plastic industry and the exploitation of crude oil is characterized by fluctuating oil prices, it is feasible to search for alternative resources.² The perception of the consumer towards green products is a third reason for the growing inter-

est in biobased plastic materials. According to a study conducted by Flash Eurobarometer,³ 84% of the European consumers finds the environmental impact of a product important and 77% is willing to pay more for products with a reduced environmental impact. Furthermore, other factors, like compostability as an alternative end-of-life option, legislative drivers (e.g. ban on noncompostable bags) and specific functionality of certain bioplastics (e.g. biocompatibility) contribute to the increasing interest in bioplastics.^{4,5} Furthermore, the transition from a fossil-based economy to a bio-based economy is an important EU 2020 Strategy target.⁶ The implementation of biobased plastics is however currently hindered by several factors such as a higher price compared with conventional crude oil based plastics, uncertainties regarding sufficient available renewable resources and technical limitations. Related to the latter, the heat resistance of most of these biobased plastic materials is insufficient for i.e. use as a packaging material for foods undergoing a heat treatment before or after packaging, for use in the automotive industry or for use as housing of electronic devices. Furthermore, a poor heat resistance can also lead to degradation of the polymer during processing. Different research strategies have been explored to improve the heat resistance of biobased plastic materials, which are described in this review.

Nanou Peelman holds a Master's Degree in Bio-Science engineering (Food Science and Nutrition) from Ghent University (Belgium) and is currently working as a PhD researcher at Ghent University. In the framework of her PhD research, she has worked on a 2-year collective research project titled "Application of bioplastics as food packaging." Currently she is working on the VIS research traject "Sustainable and functional food packaging," in which she investigates the temperature resistance of renewable materials.



Peter Ragaert obtained in 2001 the degree of bioscience engineer chemistry at Ghent University, Belgium. He holds a PhD in the field of microbiological degradation processes on packaged fruits and vegetables. Subsequently, he continued in 2005 in the packaging field as technological advisor of Pack4Food npo, which supports and informs companies in the food packaging sector towards new developments in packaging technology. Besides, since 2010, he is docent packaging technology at Ghent University, focusing on sustainable and functional packaging.



Kim Ragaert obtained her PhD in Polymer Engineering in 2011. She lectures materials science and polymer processing at Ghent University's Faculty of Engineering and Architecture, where she has recently been appointed as assistant professor in the domain of "Sustainable Use and Recycling of Polymers and Composites."



Frank Devlieghere is professor in Food Microbiology and Food Preservation, Fish and Meat Technology at the Faculty of Bioscience Engineering since 2003. He is a Bio-science engineer, graduated at Ghent University, finished his PhD in 2000 in the field of predictive microbiology at Ghent University. As a full professor he is now responsible for the research in the field of food preservation.



Bruno De Meulenaer obtained his degree in Bioscience Engineering and his PhD in Applied Biological Sciences in respectively 1994 and 2002, both from Ghent University. Since 2005 he is professor in food chemistry at Ghent University. His research focuses on chemical food safety and stability. In both themes, the role of packaging is important. Migration from food contact materials is studied in addition to protective role of packaging concepts on the impact of oxidation reactions on various food components



Ludwig Cardon is the head of the Centre for Polymer and Material Technologies CPMT at Ghent University. He has a wide experience in the field of Characterization and 3D processing of polymers, including technologies such as injection moulding, (co-)extrusion, blowmoulding, and 3D Printing. Prof. Cardon has more than 80 international publications at peer reviewed journals and conferences. CPMT is (co-)organizer of the biannual international Polymer & Mould Innovations PMI conference.



MATERIALS

According to Robertson⁷ bioplastics can be divided into four categories:

- Category 1: Polymers directly extracted from biomass, e.g. starch and cellulose
- Category 2: Polymers synthesized from bioderived monomers, e.g. polylactic acid (PLA) and bio-polyethylene (bio-PE)
- Category 3: Polymers produced directly by natural or genetically modified organisms, e.g. polyhydroxyalkanoates (PHA)
- Category 4: Polymers produced from petrochemicals, which are biodegradable or compostable, e.g. polybutyrate adipate terephthalate (PBAT) and polycaprolactone (PCL)

Biobased polymers can belong to one of the first three categories, biodegradable polymers can belong to all four different categories. A brief overview of the main biobased plastic materials is described in the following sections.

Drop-in Bioplastics

Drop-in solutions represent the largest market share of the global bioplastics production. These drop-in bioplastics are (partly) biobased, nonbiodegradable polymers which are chemically identical to the corresponding conventional polymer. Therefore, they can be easily used in the existing infrastructure and they can be recycled along their conventional counterparts. The most important drop-ins are bio-polyethylene terephthalate (bio-PET) (e.g. PlantBottleTM, used by Coca Cola and Heinz) and bio-PE (e.g. Actimel bottles from Danone). The monomer ethylene is produced from ethanol, which is fermented from biomass such as sugarcane and sugar beet.^{8–10} The terephthalic acid (PTA) that is polymerized with the biobased ethylene glycol (EG) to produce PET is currently still petroleum based. A more biobased alternative is the use of biobased furandicarboxylic acid (FDCA) instead of PTA to produce polyethylenefuranoate (PEF). PEF, produced by Avantium (Netherlands), has a better gas and water barrier than PET, but is not yet commercially available.^{11,12}

As drop-in bioplastics have a chemically identical structure as their corresponding conventional counterpart, their thermomechanical properties as well as strategies to improve heat resistance are known (e.g. heat-set PET bottles).

New Biobased Plastics

Poly(lactic acid). Poly(lactic acid) (PLA) is a transparent biodegradable/compostable thermoplastic polyester made from sugar rich agricultural products or side-streams (carbohydrate sources, e.g. corn) either chemically or by fermentation. It is nowadays seen as one of the most promising polymers for commercial use as a substitute for low and high-density polyethylene (LDPE and HDPE), PET, and polystyrene (PS). The final properties of the polymer are determined by its stereochemical composition, since lactic acid exist as two optical isomers, L- and D-lactic acid. Poly(L-lactide) (PLLA) and poly(D-lactide)(PDLA) are (semi)crystalline polymers which are hard, while poly(D,L-lactide) (PDLLA) is an amorphous polymer which is brittle. Only when the D- and L-unit sequence is completely alternating with each other, PDLLA can be crystalline. The processing possibil-

ities of this transparent material are very wide, ranging from injection molding and extrusion over cast film extrusion to blow molding and thermoforming.^{13–24}

Polyhydroxyalkanoates. The polyhydroxyalkanoates (PHA) family are biodegradable thermoplastic polymers produced in the microbial cells as an energy reserve through a fermentation process. Since various monomers and substrates can be used for their production and the polymer can be synthesized by various micro-organisms, several types of PHAs with a large diversity in properties exist. More than 100 types of PHA are known, of which polyhydroxybutyrate (PHB) is the most common and best characterized one. The PHAs have potential as a substitute for many conventional polymers, since they possess similar chemical and physical properties.^{12,21,25–34}

Polysaccharides. Starch. Starch is a widely available and easy biodegradable natural resource (energy reserve in plants), which exists out of amylose and amylopectine. High water content or plasticizers (glycerol, sorbitol) are necessary to produce a plastic-like starch-based film. Starch-based thermoplastic materials (TPS) have poor properties, especially at high humidity and are therefore mostly blended with synthetic/biodegradable polymers like PLA, PHB, or PCL. They have been successfully applied on industrial level for foaming, film blowing, injection molding, blow molding, and extrusion applications.^{12,19,21,35–41}

Cellulose. Cellulose is the most widely spread natural polymer and is derived by a delignification from wood pulp or cotton linters. It is a biodegradable polysaccharide which can be dissolved in a mixture of sodium hydroxide and carbon disulphide to obtain cellulose xanthate and then recast into an acid solution (sulfuric acid) to make a cellophane film. Alternatively, cellulose derivatives can be produced by derivatization of cellulose from the solvated state, via esterification (cellulose (di)acetate and cellulose (tri)acetate) or etherification (hydroxypropyl cellulose and methyl cellulose) of hydroxyl groups. Especially cellophane can be used for packaging applications. Since this material is not thermoplastic it is often used with a separate seal layer (e.g. starch).^{12,26,41–43}

Other polysaccharides. Other polysaccharides, like chitin, chitosan, xylans, and mannans (both hemicelluloses) can also be used for the production of biobased plastics. They are extracted from marine and agricultural products and are currently mostly used as edible films or as coatings.^{41,44}

Proteins. Proteins are another raw material that can be used to produce biobased plastics. There are plant-based proteins, like soy proteins, zein and wheat gluten and animal-based proteins, like casein and whey proteins. Despite the many research conducted on these proteins, their use is very limited.^{43,45}

Challenges

The use of bioplastics as food packaging material is subjected to different limitations, restricting at this moment their use. The most important reason for these current limitations of bioplastics compared with conventional plastics is that the latter are a very mature industry, while the bioplastics industry is still in its infancy. Therefore, many opportunities for improvement of these limitations exist. The main problems associated with

renewable biopolymers are threefold: cost, processing and performance.^{2,42}

Besides a higher price level compared with conventional plastics and the concerns on availability as well as on the use of land to produce bioplastics, there are major limitations on the functionality (processing and performance). Chemical companies are not familiar with these new biobased materials (e.g. PLA, PHB), which can create the need for an increase in the R&D department or the implementation of a new production process, since bioplastics can provide difficulties during processing on the current equipment.^{4,46} Furthermore, barrier properties, especially when a very high water barrier is required, moisture sensitivity (change of properties at higher % RH) and heat resistance are still drawbacks hindering the successful market introduction of bioplastics. Strategies to improve gas and water barrier properties of biobased plastics have been described in Peelman *et al.*²¹

HEAT RESISTANCE OF BIOBASED PLASTICS

Polymer Structure and Heat Resistance

The unique semicrystalline nature of most thermoplastic polymers lies at the basis of their (lack of) heat resistance and the variations which can be observed in thermal properties for chemically identical polymer formulations. In brief, most polymer structures consist of crystalline regions, in which the polymer chains are organized into orderly crystalline platelets and amorphous regions, spread out in between the crystalline parts, in which no specific degree of order is observed except for that of a polymer chain to its nearest neighbour. Some polymers are completely amorphous. The potential for crystallinity is largely dependent on the complexity of the polymer chain: the easier the chain can be “folded” into crystalline platelets, the higher the amount of crystals will be. As such, polymers with large side groups, irregular tacticity or dominant branching will be more inclined towards an amorphous structure.

Based on this semicrystalline structure, there are several transformation temperatures which play a significant role in the polymer's structure and therefore its heat resistance. First, the glass transition temperature (T_g) is the temperature above which the amorphous section of the polymer structure will have increased mobility, resulting in a slight sliding and rotating of side groups.⁴⁷ In terms of mechanical properties, T_g signals the transition from a hard and relatively brittle state into a rubberlike state (ISO 11357-2). At temperatures greater than T_g only the crystalline phase warrants the mechanical properties of the material. For some polymers, T_g is below room temperature or even below zero, meaning they are always in the rubberlike state at their temperatures of usage.

Second, the melt temperature (T_m) of a polymer is the temperature at which the ordered crystal structure passes to a viscous liquid. The T_m of a (semicrystalline) material should be higher than the maximum temperature at which the final packaging will be used, but it should also be well below the degradation temperature in order to facilitate the processing.

Third, when considering the cooling of the polymer from the melt, the crystallization temperature T_{cc} is the temperature at which the crystalline regions will begin to form upon cooling.

T_{cc} signals the solidification of a semicrystalline polymer and should theoretically be the same as T_m in value. In practice, however, T_{cc} will always be lower, as a certain amount of supercooling is needed to initiate the crystalline nucleation.

Finally, crystallization is rarely complete upon cooling of the polymer after processing. Therefore, another transformation temperature is relevant, that of the (post-)crystallization upon (re)heating of the polymer solid. At this temperature T_c further crystallization can occur, until the full potential for crystallinity is reached.

The heat resistance of a material is strongly linked to its crystallinity. A higher degree of crystallinity implies a higher temperature resistance, since the crystalline regions should maintain material stiffness past the glass transition temperature (of the amorphous phase).⁴⁸ Apart from the polymer chain structure, which defines the polymer's potential for crystallinity, the processing of the polymer will affect the degree to which this potential can be realized. This is discussed in more detail further on. The influence of molecular mass (M_w) on heat resistance is a dual one. In general, longer polymer chains will lead to a structurally more sound polymer material, which will have better mechanical and thermal properties. Short polymer chains are too small to form crystalline platelets and will barely contribute to the semicrystalline nature of the polymer. However, very long polymer chains are known to have more difficulty organizing into the crystalline structure, as they are bulkier. As such, an initial degradation of the polymer chains (due to thermal or thermomechanical loading), can in fact be beneficial for the rate of crystallinity in high M_w polymers.

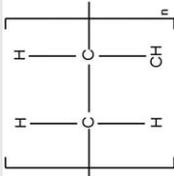
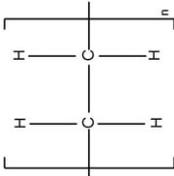
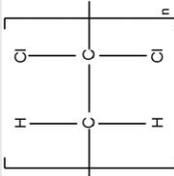
Measuring the Heat Resistance

No clear protocol nor parameter exist to define the heat resistance of a polymer, but several parameters can give an indication of the heat resistance of a material. For an amorphous or low crystalline polymer, T_g can give an indication of the heat resistance, because, to avoid deformation, the T_g should not fall into the temperature range in which the packaging material is to be used.⁴⁸ Furthermore, the crystallization temperatures upon heating (T_c) and upon cooling (T_{cc}) are important. A low T_c or high T_{cc} means that crystallization can start at a low (T_c) or high (T_{cc}) temperature, increasing the temperature window for crystallization, resulting in a more complete crystallization. Determination of these parameters, as well as T_m , can be performed by differential scanning calorimetry (DSC) or by differential thermal analysis (DTA). The degradation temperature is another parameter which is important regarding the heat resistance. It is the temperature at which the polymer chains start to break down into oligomers, monomers, and other small degradation products that can evaporate, resulting in weight loss. The degradation temperature can be determined by thermogravimetric analysis (TGA) and is an important parameter during processing of a material. Furthermore, the heat deflection temperature (HDT), the temperature at which a polymer deforms under a constant load, and the Vicat softening temperature (VST), the temperature at which a needle under constant load can penetrate the polymer 1 mm, also give an indication of the heat resistance. The HDT refers to the maximum temperature at which a polymer can be used as a rigid material.⁴⁹

Table I. Characteristic Parameters of Different (Biobased) Plastics^{1,6,17,30,42,43,50-76}

Material	Chemical structure	T_g (°C)	T_m (°C)	HDT (°C)	VST (°C)	Young's modulus (GPa)	Elongation (%)	Tensile strength (N/mm ²)
(O)PLA		55 to 80	125 to 178 ^a	40 to 135	56	0.3 to 3.8	1.5 to 380	10 to 60
PHB		-10 to 15	153 to 175	- ^b	53 to 148	0.4 to 3.8	6 to 27	15 to 45
	<p>R (PHB) = methyl</p>							
	<p>R (PHBV) = methyl/ethyl methyl R (PHBV) = methyl/ethyl</p>							
PHBV		-10 to 25	145 to 180	105	143	1.2 to 4.6	2.5 to 50	18 to 40
Cellulose		493 to 518	-	-	-	33 to 108	1 to 74	15 to 90
Starch (TPS)		35 to 85	64 to 115	60	53	0.1 to 2.9	1 to 1200	2.1 to 46.8
(O)PS		70 to 115	100 to 240	85 to 95	-	2.3 to 4.1	1 to 4	30 to 100
(O)PP		-17 to 6	160 to 186	60 to 105	-	0.8 to 2.0	100 to 1000	25 to 98

Table I. Continued

Material	Chemical structure	T_g (°C)	T_m (°C)	HDT (°C)	VST (°C)	Young's modulus (GPa)	Elongation (%)	Tensile strength (N/mm ²)
HDPE		-110 to -30	108 to 134	46 to 85	127	0.5 to 1.4	20 to 1000	15 to 40
LDPE		-125 to -30	112 to 136	35 to 50	93	0.1 to 0.4	100 to 900	5 to 25
PET		69 to 115	245 to 265	80 to 115	-	1.7 to 3.5	70 to 180	70 to 177
PVdC		-17.5	170 to 175	54 to 66	-	0.2 to 0.6	10 to 40	25 to 110

^a Crystalline PLA.^b No reliable values found in literature.

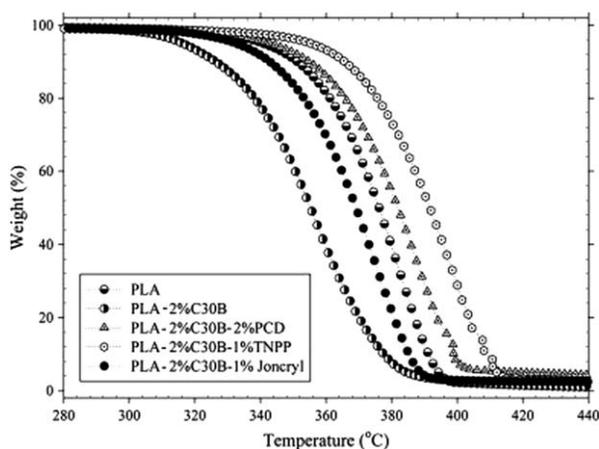


Figure 1. Effect of clay and different chain extenders on thermal degradation of PLA nanocomposites (Reprinted from Ref. 86 with permission from Elsevier).

Molecular mass, and its evolution regarding thermally induced degradation, can be determined by gel permeation chromatography (GPC), a size-exclusion technique which allows immediate calculation of the molecular mass distribution of the polymer. GPC, however, is an expensive and time-consuming technique. As an alternative, inherent viscosity (IV) measurements can be conducted, in which the effluent time of a polymer solution through an Ubbelohde capillary is used as a basis for measurement. It has been found that the evolution (decrease) in IV relates directly to loss of M_w , which can be measured with GPC.¹³

Finally, tensile tests at different temperatures can show to which degree the polymer maintains its mechanical strength at higher temperatures.

Current Heat Resistance of Biopolymers

An overview of some parameters indicating heat resistance, some mechanical properties and the chemical structure of a selection of biobased and conventional plastics are given in Table I. Because crystallization temperatures are not often reported, these were not included in this table. Since heat resistance is closely related to crystallinity, most parameters in this table are also related to the crystallinity of the material. As explained in the previous paragraphs, large variations on these parameters can occur within one and the same material, due to differences in polymer chain morphology or processing temperatures. This makes it difficult to present single values per material type or indeed, to draw straightforward conclusions. But it is clear that, just as for the conventional polymers, the heat resistance of biopolymers depends strongly on the type of material and polymers with lower and higher heat resistance exist. Furthermore, it can be seen that, regarding the biobased materials, especially PLA (amorphous) and starch (crystalline regions) have a poor heat resistance, with respectively a T_g (PLA) and a T_m (starch) within the temperature range of heat treatments used industry. Both materials also show a low HDT and VST.

Improving the Heat Resistance of Biopolymers

A large amount of studies have investigated different strategies to improve the heat resistance of bioplastics. Following

techniques, described in detail in subsequent paragraphs, could be used.

Additives. Additives are substances that are added in small quantities to polymers in order to improve their properties.⁷⁷ Different additives, like plasticizers, chain extenders, nucleating agents, and nanoparticles can have an effect on the heat resistance of biobased materials, mainly by decreasing the T_g and T_m and increasing the degree of crystallinity.

A widely used additive for polymers are plasticizers. The primary role of these additives is to improve the flexibility, ductility and processability of the polymer by decreasing the T_g of the polymer through reducing the intermolecular forces along polymer chains. Regarding heat resistance, this increases the polymer chain mobility which can enhance the crystallization rate by reducing the energy required during crystallization. Plasticizers mainly have an effect in the lower temperature range, where crystallization is limited by the chain mobility with an effect on T_c , extending the crystallization temperature window.^{48,78,79} Several studies have investigated the effect of the addition of plasticizers. Wang *et al.*⁸⁰ found that the addition *N*-octyl lactate (NOL) lowered the T_g with maximum 17.8°C, depending on the NOL content. Furthermore, the T_c and T_m also decreased with increasing plasticizer content. The percentage crystallinity increased with increasing NOL content and was 22.3, 24.5, 31.9, 34.1, 34.4, and 34.3% for respectively 0, 2.5, 5, 7.5, 10, and 12.5% NOL content. Boonfaung *et al.*⁸¹ found that the addition of polypropylene glycol, polyethylene glycol-ran-propylene glycol, dioctyl phthalate, tributyl citrate, and adipic acid lowered the T_g by maximum 15.4°C. Furthermore, these plasticizers also decreased the T_m of PLA. Martin and Averous⁸² reported similar results after the addition of PEG to PLA. T_g was decreased from 58°C to 41 and 30°C for, respectively 10 and 20% PEG (molecular weight = 1500 g/mole) and even further decreased to respectively 30 and 12°C for PEG with a molecular weight of 400 g/mole. They also found an increase in the degree of crystallinity. A lower T_m ensures that the polymer can be processed

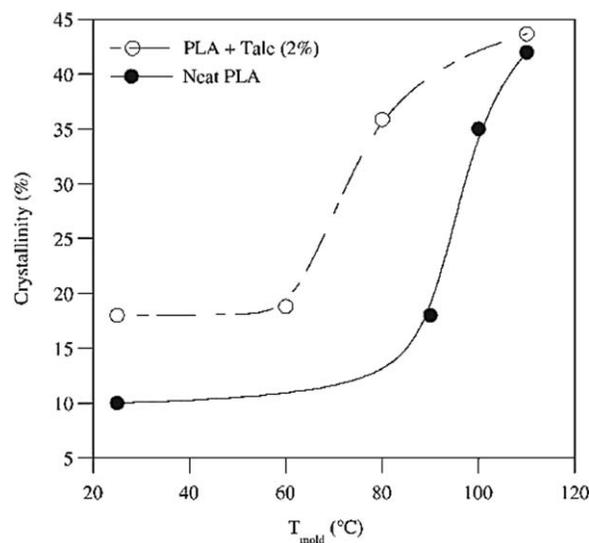


Figure 2. Percentage crystallinity of PLA and PLA + 2% talc dependent on the mold temperature⁹⁵ (©Wiley)

at a temperature well below the degradation temperature (better preservation of the properties), but it was noticed by Arrieta *et al.*⁸³ that plasticizers can also lower the degradation temperature, neutralizing the positive effect. Branciforti *et al.*⁸⁴ also found that the T_g of PHBV decreased with increasing amount of plasticizer. But, addition of plasticizer can also have a negative effect, like a decreased tensile strength and tensile modulus and increased water vapor permeability.^{48,80,81}

Chain extenders can also be used as an additive for polymers. Thermal degradation of polyesters (PLA, PHA) is merely caused by hydrolysis, intermolecular transesterification and back-biting or intramolecular transesterification. Chain extenders are used to prevent this thermal degradation of polymers during production by extending the polymer chain and increasing the molecular weight (by re-coupling of degraded chains) and by decreasing the polymer ends, resulting in a lower chance of back-biting.^{85,86}

Najafi *et al.*⁸⁶ added the chain extenders Joncryl®, a functionalized (epoxide, anhydride, $-\text{COOH}$, $-\text{OH}$) low molecular-weight styrene-acrylate copolymer,⁸⁷ polycarbodiimide (PCDI), a carboxyl-reactive chain extender, and *tris*(nonylphenyl) phosphite (TNPP) to PLA and PLA-based nanocomposites (PLA + Cloisite 30B) and tested the thermal stability by means of a thermogravimetric analysis. The temperature at which thermal degradation started increased after the addition of TNPP and PCDI (2% w/w) as can be seen in Figure 1. This could be explained by the longer polymer chains produced in the PLA-based nanocomposites containing these chain extenders, and hence the reduced number of chain ends per mass. The addition of Joncryl® was not as effective at increasing the onset of degradation of the PLA-based nanocomposites as compared with the other two chain extenders. This might be attributed to a significantly branched structure, having an increased number of ends per chain.

The viscosity of PLA and PLA/PBAT with Joncryl® remained constant in time, indicating a lower thermal degradation.⁸⁸ Addition of Joncryl® (epoxy-functionalized) to PHBV induced a lower crystallization temperature and crystallinity. This is caused by a lower mobility and rate of crystallization because of the longer chains.⁸⁹ Di *et al.*⁹⁰ found that the addition of 1,4-butanediol and 1,4-butane diisocyanate to PLA increased the T_g slightly, because of the higher molecular weight and the cross-linking of the chains. Furthermore, a lower T_m was observed (more than 10°C), caused by defects in the lamellar crystals by cross-linking of the chains.

A third type of additives are nucleating agents. Because of the long chain character and the high viscosity, nucleation is often a critical step during the crystallization of a polymer. Most of the times, this primary crystallization takes place at temperatures much lower than the T_m of the polymer, meaning a high degree of undercooling is necessary to initiate nucleation. Nucleating agents can increase the degree of crystallinity by lowering the surface free energy barrier towards nucleation and thus initiating heterogeneous crystallization at higher temperature upon cooling. So, as for plasticizers, addition of nucleating agents broadens the crystallization temperature window (during

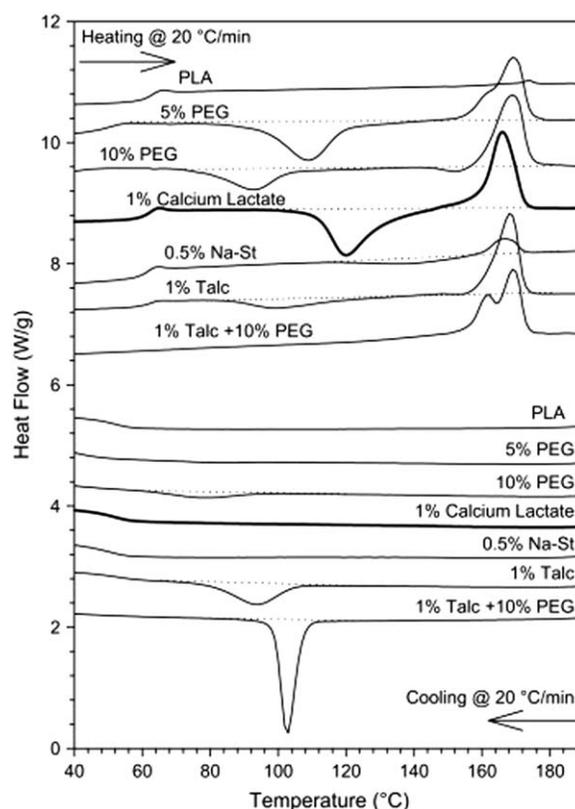


Figure 3. DSC thermograms for PLA and PLA formulations cooled at 20°C/min and subsequently heated at 20°C/min (Reprinted from Ref. 48 with permission from Elsevier).

cooling), causing a more complete crystallization and reducing re-crystallization during heating. This will result in more consistent mechanical properties upon heating.^{50,91–93} Nucleating agents have to be compatible and dispersible in the polymer and they have to be present in a solid state at the temperature at which nucleation takes place.⁹² Kolstad⁹⁴ found that the addition of 1% talc to PLA reduced the crystallization half time ($t_{1/2}$) from around 40 min to 90 s. Addition of 5% plasticizer could even further reduce $t_{1/2}$ to 70 s (acetyl triethyl citrate) and 60 s (polyethylene glycol). Harris and Lee⁹⁵ found that the addition of 2% talc to PLA induced a higher crystallinity compared with pure PLA (Figure 2). Furthermore, organic compounds like *N,N*-ethylenebis (12-hydroxy-searamide), benzoylhydrazide compounds or calcium lactate have been reported as effective nucleating agents for PLA.^{96–98} The brittleness of PHB, which is caused by big crystal structures that can re-crystallize during storage and induce microcracks, can be reduced by nucleating agents. They ensure the formation of smaller and more consistent spherulites, avoiding re-crystallization.⁹⁹ Furthermore, PHB can also act as a nucleating agent in PLA/PHB blends⁸³ and the addition of PDLA to PLA can increase T_m and HDT.^{43,100}

Furthermore, Li and Huneault⁴⁸ found that the simultaneous use of a nucleating agent and a plasticizer had a synergistic effect on the crystallinity of PLA (Figure 3). DSC curves showed a much sharper crystallization peak upon cooling (20°C/min) for PLA with 1% talc and 10% PEG compared with PLA with only 1% talc or 10% PEG. Furthermore, the crystallization peak

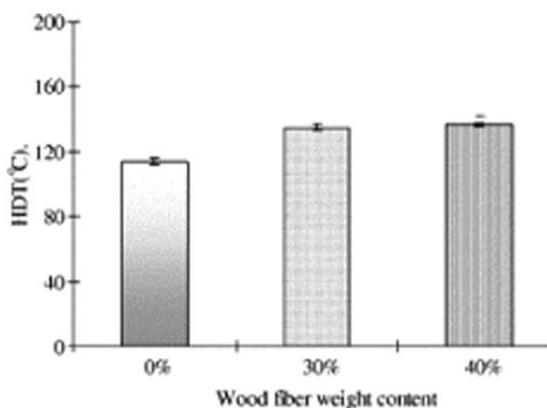


Figure 4. Effect of wood fiber content on heat deflection temperature (HDT) of PLA (Reprinted from Ref. 119 with permission from Elsevier).

was shifted to a higher temperature, expanding the crystallization window. This can be explained by the increasing chain mobility in the lower temperature range (caused by the plasticizer) and the increasing nucleation rate in the upper temperature window (caused by the nucleating agent). Addition of 1% talc and 10% PEG allowed the PLA to reach its maximal crystallization (40%)

Blends and Copolymers

Blending with another (bio)polymer is also a technique to improve the thermal and mechanical properties of a biobased plastic material.^{22,43} When blending materials, compatibility is very important. Essentially, polymers are immiscible in the melt. This will induce a phase segregation, which in turn will lead to reduced mechanical properties. The larger the difference in chemical nature of the polymer chains, the higher the surface tension between the two will be and the more immiscible they will turn out to be.¹⁰¹ Several techniques, like the introduction of a reactive functional group, chemical modification or cross-linking, can improve this compatibility.^{51,102,103}

PLA/PHB blends are a typical biopolymer blend combining the best properties of both polymers. The crystallinity of PLA can be increased because of the much more crystalline PHB,

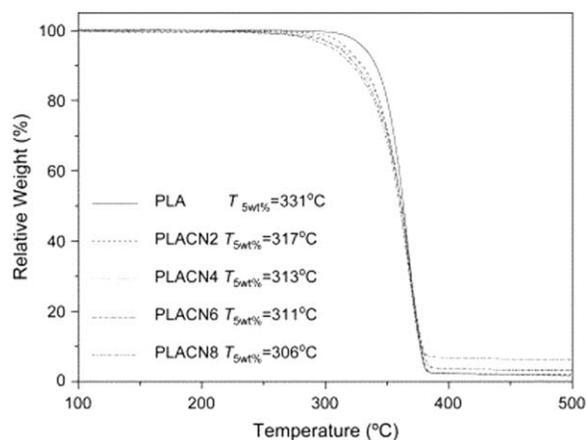


Figure 5. TG curves for the pure PLA and PLA + clay (2, 4, 6, and 8 wt %) samples (Reprinted from Ref. 123 with permission from Elsevier).

increasing the HDT of pure PLA.^{104,105} Furthermore, a blend of 75/25 PLA/PHB improved the mechanical properties of both pure polymers.¹⁰⁵ Blending of PBAT and PLA had a positive effect on the elongation and strength of PLA and resulted in a more constant viscosity, inducing a broader processing temperature window.^{106,107}

The creation of copolymers can also ameliorate the heat resistance of a polymer. The copolymer PHBV (11 mol % HV into PHB) decreases T_m from 175 to 157°C and T_g from 9 to 2°C.⁵¹ The lower T_m means that the processing can be performed at temperatures further away from the degradation temperature than for pure PHB, but T_m is still high enough to not compromise its use as a packaging material (temperatures up to 120°C).

Because of the chirality of lactic acid (L and D-lactic acid), several copolymers of PLA can be formed. The (thermal) properties of PLA depend on the ratio of L- and D-lactic acid present in the polymer. An increasing quantity of D-isomer esterified in the chain makes the polymer less crystalline, decreases the crystallization rate and lowers the T_m of PLA.^{4,16,108} It was shown that the T_m of PLA changed from 178 (100/0 L/D,L) to 125°C (80/20 L/D,L) with decreasing amount of L-isomer.^{109–111} Furthermore, Dorgan *et al.*¹¹² found that the T_g of PLA with 100% L-lactic acid was 60.2°C, while the T_g of PLA with 50% L-lactic acid was 54.6°C.

The melt temperature, crystallinity, and heat deflection temperature of PLA can be improved by the creation of stereocomplex PLA (sc-PLA) and stereoblock PLA (sb-PLA). Sc-PLA is formed by melt-blending of PLLA and PDLA (1 : 1) when PDLA segments interact inter- and intramolecular with PLLA segments. Sb-PLA is formed similarly between block copolymers of PLLA and PDLA. The melt temperature for both polymers is around 200 to 240°C and 180 to 230°C for respectively sc-PLA and sb-PLA. The HDT of amorphous PLA and stereocomplex PLA is respectively 55 to 60°C and 160 to 200°C. An increased crystallinity can only be accomplished if the cooling rate is slow. Because of the high production rates (e.g. injection molding) this is sometimes difficult. This can be overcome by the use of nucleating agents.^{43,113–115} Furthermore, also the mechanical properties of sc-PLA are better than those of PLLA and PDLA.¹¹⁶

Biocomposites

A composite is a multiphase system in which a filler (discontinuous phase) is embedded in a matrix (continuous phase). The efficiency depends on the adhesion between the components.⁵¹ Although the filler is not added to improve the heat resistance, it can have a positive effect. Especially the introduction of natural fibers (e.g. flax) is a technique to improve the heat resistance of (bio)polymers.^{117,118} The HDT of PHBV with bamboo fiber increased with from 114°C to 120°C and 123°C for respectively 30 and 40 wt % fiber and the HDT of PHBV with wood fiber also increased (Figure 4). The main reason of HDT improvement is the fiber reinforcement which has higher HDT than the matrix, but as well a higher degree of crystallinity, due to the nucleating properties of the fiber surface.^{117,119} Furthermore, the degradation temperature of the PHBV/bamboo fiber

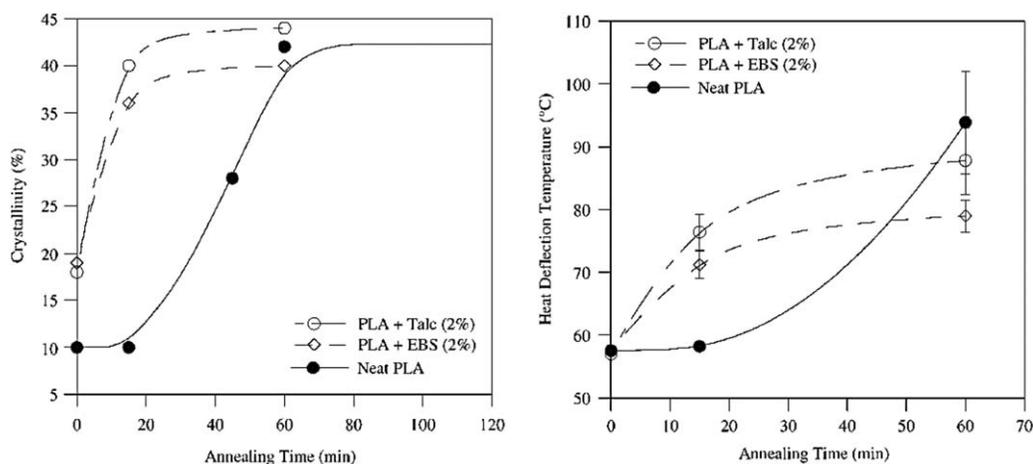


Figure 6. Crystallinity (left) and HDT (right) of pure PLA, PLA + EBS (ethylene *bis*-stearamide) and PLA + talc in function of the annealing time at 80°C⁹⁵ (©Wiley).

composite was higher than the one of pure PHBV.¹¹⁹ A PLA/bamboo fiber composite increased the degree of crystallinity with 8% compared with pure PLA, probably because the surface roughness of the bamboo fiber initiated the growth of crystals.¹²⁰ Du *et al.*¹²¹ also found a clear increase in HDT of cellulose fiber reinforced PLA (160.8°C) compared with neat PLA (79°C).

Nanocomposites

The development of (bio)nanocomposites is a new strategy to improve the physical properties of biopolymers. Although the effect of the use of nanoparticles on barrier properties of bioplastics is clear and consistent, their influence on the heat resistance of biobased plastic materials is not always clear.

The addition of organomodified montmorillonite clay (MMT) to PLA accelerates the degradation temperature of PLA. This is believed to be associated with the organomodifier bonded on the silicate layer surface (clay).¹²² Strongly exfoliated structures resulted in a decreased onset temperature for thermal degradation up to 25°C (Figure 5).^{86,123}

Arrieta *et al.*¹²⁴ also found a lower degradation temperature for PLA with synthesized cellulose nanocrystals or surfactant modified cellulose nanocrystals. On the other hand, Martino *et al.*¹²⁵ found that the addition of 3 wt % of MMT (Cloisite-30B) increased the initial decomposition temperature with 10°C and Arrieta *et al.*¹²⁴ showed that the degradation temperature of a PLA/PHB blend with synthesized cellulose nanocrystals or surfactant modified cellulose nanocrystals improved. This can be explained by the fact that clay may act as heat barrier at the beginning of the thermal decomposition giving rise to the slight improvement in degradation temperature. But at higher temperatures the silicate layers could accumulate heat and then promote the degradation process.¹²⁵

Also changes in T_g and T_m are not always clear and depend on the type of nanoparticle used, the nanoparticle loading and dispersion. A small increase in T_g was noticed by Azeredo *et al.*¹²⁶ when cellulose nanofibers were added to a mango puree film. Anglès and Dufresne³⁵ also found an increase in T_g and

T_m after addition of cellulose nanofibers to TPS, as well as Alemдар and Sain¹²⁷ who found an increase of 30 to 40°C of T_g for TPS films with addition of cellulose nanofibers, starting from 2 wt % of fiber. Krishnamachari *et al.*¹²⁸ noticed that the T_g of PLA rinsed with 6°C after addition of 1% organically modified montmorillonite (OMMT) (Cloisite 30B, m/m) and with 8% after addition of 2% OMMT. Higher percentages did not increase the T_g more, indicating an optimum. The T_g of PLA/nanofiber, PHB/clay and PLA/clay nanocomposites did not significantly improve.^{123,129–131}

The addition of 4% OMMT (m/m) to PLA resulted in an increase in HDT from 76 to 93°C.¹⁹ A gradual increase in HDT from 75 to 111°C depending on the amount of OMMT added was shown by Sinha Ray *et al.*¹³²

Furthermore, the addition of nanoclay to PHB and PHBV increased the cold crystallization temperature (T_{cc}) and the crystallization rate. Also cellulose nanoparticles had a positive effect on the crystallinity of PLA and PLA/PHB. In these cases the nanoparticles had a nucleating effect and the better the particles were diffused into the polymer matrix, the greater the effect. But, regarding clay particles, big clay platelets can hinder a thorough crystal growth.^{123,131,133}

Processing Parameters

Polymers can be processed making use of different techniques, like extrusion, injection molding, and thermoforming. Depending on the used technique and the applied heat profiles, the exerted thermomechanical loading on the polymer can vary, resulting in different material properties. Heat resistance can be influenced by the processing parameters, e.g. by thermal degradation during processing, by the crystallinity which is affected by the cooling rate and by the maximum processable molecular weight.

High processing temperatures can cause thermal degradation of a (bio)polymer, resulting in lower glass transition, melt and degradation temperatures of the finished product (after processing) compared with the pellets (before processing). Al-Itry *et al.*⁸⁸ found that the degradation of processed PLA started

Table II. Overview of Commercially Available Biobased Heat Resistant Materials (Sources: Company Websites)

Company	Product	Application/resistance	MFI (g/10 min- 190°C-2.16 kg)	VST (°C)	T _g (°C)	T _m (°C)	HDT (°C)	Base
Films/trays								
Innovia	Natureflex™NVS/NVR	Oven (200°C/30 min) +	NA	-	-	-	-	Cellulose
	Natureflex™NE/DNE	Microwave (1000 W/5 min)	NA	-	-	-	-	Cellulose
	Natureflex™HK1	-	NA	-	-	-	-	Cellulose
	CelloTherm™ (T & P)	Ovenable/microwaveable	NA	-	-	-	-	Cellulose
	Cellophane™p32	For higher temperature use	NA	-	-	-	-	Cellulose
Innovia/Corbion	Cellophane/PLA laminate	-	-	-	-	-	-	Cellulose/PLA
Moonen Packaging	Roots BioPack	Microwave/oven	NA	-	-	-	-	Sugar cane
Plantic	eco Plastic™/eco Plastic™ R	-	NA	130	-	-	-	Starch
Safta/Novamont	Naturene	For higher temperature use	NA	-	-	-	-	Starch
Materials								
Beologic	-	-	-	-	-	-	-	PLA + Wood Plastic Composite
FKuR	BioFlex®F6611	135°C	2-3.5	>130	-	150-170	-	PLA
NaturePlast	NaturePlast PLI 013	High temperature	6	-	-	-	123	PLA
NatureWorks	Ingeo 3801X	120°C	8	-	45	155-170	65	PLA
Purac/Corbion	Synterra® IM	can withstand boiling water	6	100-160	-	-	123	PLA
	Synterra® PLLA & PDLA	-	8 to 12	-	55-60	175-180	-	PLA
	PLA compoundend blends	≈ PS, PP, ABS	3 to 30	-	-	190-220	95-120	PLA
SK Chemicals	Ecoplan Dura	-	-	-	-	-	100-120	PLA
Supla Co. Ltd.	SUPLA™ (diff. grades)	100-150°C	-	-	-	-	>100	PLA blend
Sukano	Sukano®bio-loy	improved thermal resistance	-	-	-	-	-	PLA
Teijin	Biofront™	Highly heat resistant	-	-	-	210	-	sc-PLA
Toray Industries	Ecodear®V751 X52	Heat resistant	-	-	-	-	81	PLA + 30% glass fiber
Unitika	Terramac®	Heat resisting grades	-	-	-	170	110-140	PLA
FKuR	Biograde®C9550	-	11 to 15 (230°C-5 kg)	118	-	>180	-	Cellulose
	Biograde®C7500	Heat resistant	-	110	-	>180	-	Cellulose

Table II. Continued

Company	Product	Application/resistance	MFI (g/10 min- 190°C-2.16 kg)	VST (°C)	T _g (°C)	T _m (°C)	HDT (°C)	Base
			17 to 21 (230°C-5 kg)					
	Biograde®C6509CL	-	38 to 42 (230°C-5 kg)	104	-	180-190	-	Cellulose
Biomer	UP4924	-	-	-	-	-	-	PHB
Kaneka	Aonilex®	Strongly resistant to heat	-	103-129	0-2	126-145	92-121	PHA
Metabolix	Mirel® F1006	Microwave/boiling water	-	-	-	-	-	PHB
DSM	Arnitel Eco	From freezer to oven	-	-	-	200	-	Rapeseed oil
Braskem/FKuR	Bio-PE	-	-	-	-	-	-	Sugar cane
	Bio-PP	-	-	-	-	-	-	Sugars

30°C earlier than the (nonprocessed) pellets. It is therefore important to perform the processing at temperatures below the degradation temperature to preserve the heat resistance of the original material (pellets).

An enhanced crystallinity of PLA and other biopolymers had a positive effect on certain mechanical and thermal properties (higher HDT).^{95,111} Crystallinity of the final polymer product can be affected by adapting the cooling rate (during injection molding). Fast cooling will increase crystalline nucleation, but effectively disrupt crystalline growth, which can cause the formation of less perfect crystals and lower overall crystalline fraction, resulting in a lower T_m . Effectively quenching the polymer will even lead to a fully amorphous structure. A slower cooling rate, induced by a higher mold temperature, will allow the crystals to form more completely, increasing the crystallinity and the size and stability of the crystals. Harris and Lee⁹⁵ found that the crystallinity of PLA (with or without talc) that was injected into a heated mold during 3 min increased as the mold temperature increased. Li and Huneault⁴⁸ found similar results. The percentage crystallinity of PLA increased exponentially when the mold temperature rose from 20 to 80°C. At 80°C the maximal crystallization of PLA (with 5% ATC and 1% talc) was reached. Also the orientation of the polymer chain, the remaining of unreacted monomer or a heat setting treatment can influence the crystallinity and thermal stability.¹¹⁰ Furthermore, annealing of the polymer can lead to a better formation of crystals and an increase in crystallinity. The optimum crystallization temperature for PLA was between 105 and 115°C.⁹⁴ According to Harris and Lee⁹⁵ the degree of crystallization and the HDT increased with increasing annealing time (Figure 6).

Tokoro *et al.*¹²⁰ also found annealing at 110°C during 5 h increased the degree of crystallinity from 25 to 42% for pure PLA and from 31 to 50% for PLA/bamboo fibers.

A higher mold temperature can increase the crystallization, but it can also effect the mechanical properties. Vadori *et al.*¹³⁴ showed that the elongation at break decreased from 243 to 22% with increasing mold temperatures from 30 to 90°C. Furthermore, the crystallization influences the optical properties.¹⁷

Also the application of the polymer is important and affects the choice of polymer grade to be used (extrusion grade for films, thermoform grade for trays, and injection mold grade for beakers, ...). Extrusion and thermoform machines can handle polymers with a high viscosity (high molecular weight). A higher molecular weight affects the thermal degradation temperature (higher) and the crystallization (lower) of a polymer. This means that the heat resistance of an extrusion grade of a polymer can differ from the injection mold grade of that same polymer.

In general it can be stated that the processing parameters, especially a higher mold temperature, have an influence on the heat resistance of biopolymers. Mainly the prevention of degradation and the control of crystallinity can be adjusted.

Furthermore, the eventual application of the material is important to select the optimal process parameters.

Available Heat Resistant Biopolymers

An overview of heat resistant biopolymers or biopolymers that claim a “higher heat resistance” that are already commercially available are listed in Table II. Some of these materials applied one of the above-described technique to increase the heat resistance of the biopolymer. Several finished products (films and trays) that can be used for food products undergoing a heat treatment (e.g. microwave, oven) are already commercially available. Furthermore, various other materials that can be processed into heat resistant packaging material can be found on the market, especially PLA-based. Since PLA has a very poor heat resistant, it is not surprising that many research regarding the improvement of heat resistance has focused on this biopolymer.

CONCLUSIONS

Many techniques to overcome the poor heat resistance of biopolymers, have been proven successful. The use of nucleating agents (in combination with the use of plasticizers) and a high mold temperature, inducing a slower cooling rate seem the best solution to obtain a higher crystallinity and therefore a higher heat resistance of the processed material. Specific for PLA, stereocomplexation is a very promising technique to create heat resistant products. Chain extenders on the other hand seem the best technique to reduce the thermal degradation during processing. Although several biopolymers with an enhanced heat resistance are already commercially available, they are currently not often commercially used. Nevertheless, the information of the material producers indicate a much broader applicability of biobased plastics that need a certain heat resistance. However, processing tests and tests in industrial environments are needed to evaluate the performance of these materials.

These results were obtained in the framework of a Flemish Innovation Partnership (VIS-traject) supported by the Institute for the Promotion of Innovation by Science and Technology in Flanders, Belgium (IWT), and by 69 participating companies in close collaboration with four research institutes (Ghent University, Packaging Centre, Belgian Packaging Institute and KULeuven).

REFERENCES

1. European Bioplastics. Available at: <http://en.european-bioplastics.org/>. Last accessed November 12, 2014.
2. Philp, J. *Ind. Biotechnol.* **2014**, *10*, 19.
3. TNS Political & Social. Flash Eurobarometer; Report December 2012, European Commission, Directorate-General for Environment, Brussels, Belgium, **2013**.
4. Barker, M.; Safford, R. Industrial uses for crops: markets for bioplastics. Project report 450, HGCA, London, **2009**. Available at: http://publications.hgca.com/publications/documents/cropresearch/PR450_Final_Project_Report.pdf. Last accessed January 13, 2015.
5. NanoMarketsBlog. Regulatory Drivers for the Bio-plastics Market. Website NanoMarkets, **2013**. Available at: http://nanomarkets.net/blog/article/regulatory_drivers_for_the_bio-plastics_market. Last accessed January 13, 2015.
6. European Bioplastics. Bioplastics packaging - Combining performance with sustainability - Materials and market development in the packaging segment. Fact sheet, European Bioplastics, Berlin, Germany, **2014c**. Available at: http://en.european-bioplastics.org/wp-content/uploads/2011/04/fs/Packaging_eng.pdf. Last accessed August 6, 2014.
7. Robertson, G. L. In *Food Packaging: Principles and Practice*; Robertson, G. L., Ed.; CRC Press: Boca Raton, FL, **2013**; Vol. 3, Chapter 3, p 49.
8. European Bioplastics. What are bioplastics? Fact sheet, European Bioplastics, Berlin, Germany. Available at: http://en.european-bioplastics.org/wp-content/uploads/2011/04/fs/Bioplastics_eng.pdf. Last accessed August 6, 2014.
9. European Bioplastics. Bioplastics, facts and figures, European Bioplastics, Berlin, Germany, **2014a**. Available at: http://en.european-bioplastics.org/wp-content/uploads/publications/EuBP_FactsFigures_bioplastics_2013.pdf. Last accessed August 6, 2014.
10. Tullo, A. H. *Chem. Eng. News* **2008**, *86*, 21.
11. Gotro, J. Polyethylene Furanoate (PEF): 100% Biobased Polymer to Compete with PET?, **2013a**. Available at: <http://polymerinnovationblog.com/polyethylene-furanoate-pef-100-biobased-polymer-to-compete-with-pet/>. Last accessed December 17, 2014.
12. Molenveld, K.; Van Den Oever, M. Catalogus Biobased Verpakkingen; Wageningen UR: The Netherlands, **2014**.
13. Ragaert, K.; Dekeyser, A.; Cardon, L.; Degrieck, J. *J. Appl. Polym. Sci.* **2011**, *120*, 2872.
14. Yu, L.; Dean, K.; Li, L. *Prog. Polym. Sci.* **2006**, *31*, 576.
15. Bogaert, J. C.; Coszach, P. *Macromol. Symp.* **2000**, *153*, 287.
16. Drumright, R. E.; Gruber, P. R.; Henton, D. E. *Adv. Mater.* **2000**, *12*, 1841.
17. Jamshidian, M.; Tehrani, E. A.; Imran, M.; Jacquot, M.; Desobry, S. *Compr. Rev. Food Sci. Food Saf.* **2010**, *9*, 552.
18. John, R. P.; Nampoothiri, K. M.; Pandey, A. *Appl. Microbiol. Biotechnol.* **2007**, *74*, 524.
19. Joshi, S. *J. Ind. Ecol.* **2008**, *12*, 474.
20. Liu, L. Bioplastics in food packaging: Innovative Technologies for Biodegradable Packaging, **2006**. Available at: <http://www.iopp.org/files/public/SanJoseLiuCompetitionFeb06.pdf>. Last accessed October 10, 2012.
21. Peelman, N.; Ragaert, P.; De Meulenaer, B.; Adons, D.; Peeters, R.; Cardon, L.; Van Impe, F.; Devlieghere, F. *Trends Food Sci. Technol.* **2013**, *32*, 128.
22. Rasal, R. M.; Janorkar, A. V.; Hirt, D. E. *Prog. Polym. Sci.* **2010**, *35*, 338.
23. Siracusa, V.; Rocculi, P.; Romani, S.; Dalla Rosa, M. *Trends Food Sci. Technol.* **2008**, *19*, 634.
24. Södergard, A.; Stolt, M. *Prog. Polym. Sci.* **2002**, *27*, 1123.
25. Berger, E.; Ramsay, B. A.; Ramsay, J. A.; Chaverie, C.; Brauneegg, G. *Biotechnol. Technol.* **1989**, *3*, 227.

26. Cyras, V. P.; Soledad, C. M.; Analia, V. *Polymer* **2009**, *50*, 6274.
27. De Koning, G. J.; Witholt, B. *Bioprocess Eng.* **1997**, *17*, 7.
28. Farinha, I. d. S. Optimization of bioplastics production from cheese whey, **2009**. Available at: <http://hdl.handle.net/10362/2377>. Last accessed January 14, 2015.
29. Lunt, J. *Bioplast. Mag.* **2009**, *3*, 36.
30. Madison, L. L.; Huisman, G. W. *Microbiol. Mol. Biol. Rev.* **1999**, *63*, 21.
31. Ramsay, J. A.; Berger, E.; Ramsay, B. A.; Chavarie, C. *Bio-technol. Technol.* **1990**, *4*, 221.
32. Reddy, C. S. K.; Ghai, R.; Rashmi; Kalia, V. C. *Bioresour. Technol.* **2003**, *87*, 137.
33. Sanchez-Garcia, M. D.; Gimenez, E.; Lagaron, J. M. *Carbo-hydr. Polym.* **2008**, *71*, 235.
34. Singh, R. *Org. Process Res. Dev.* **2011**, *15*, 175.
35. Anglès, M.; Dufresne, A. *Macromolecules* **2000**, *33*, 8344.
36. Avella, M.; De Vlieger, J. J.; Errico, M. E.; Fischer, S.; Vacca, P.; Volpe, M. G. *Food Chem.* **2005**, *93*, 467.
37. Bastioli, C. *Polym. Degrad. Stab.* **1998**, *59*, 263.
38. Chivrac, F.; Pollet, E.; Avérous, L. *Mater. Sci. Eng. R Rep* **2009**, *67*, 1.
39. Gotro, J. Thermoplastic Starch: A Renewable, Biodegradable Bioplastic, **2013b**. Available at: <http://polymerinnovation-blog.com/thermoplastic-starch-a-renewable-biodegrad-able-bioplastic/>. Last accessed January 12, 2015.
40. Mensitieri, G.; Di Maio, E.; Buonocore, G. G.; Nedi, I.; Oliviero, M.; Sansone, L. *Trends Food Sci. Technol.* **2011**, *22*, 72.
41. Weber, C. J.; Haugaard, V.; Festersen, R.; Bertelsen, G. *Food Addit. Contam.* **2000**, *19*, 172.
42. Petersen, K.; Nielsen, P. V.; Bertelsen, G.; Lawther, M.; Olsen, M. B.; Nilsson, N. H. *Trends Food Sci. Technol.* **1999**, *10*, 52.
43. Shen, L.; Haufe, J.; Patel, M. K. Product overview and market projection of emerging bio-based plastics, **2009**. Available at: <http://en.European-bioplastics.org/wpcontent/uploads/>. Last accessed July 31, 2014.
44. Mikkonen, K. S.; Tenkanen, M. *Trends Food Sci. Technol.* **2012**, *28*, 90.
45. Krochta, J. M. Protein-Based Films and Coatings; CRC Press: Boca Raton, FL, **2002**, p 1.
46. Iles, A.; Martin, A. N. *J. Clean. Prod.* **2013**, *45*, 38.
47. Sperling, L. H. Introduction to Physical Polymer Science; John Wiley and Sons: Hoboken, NY, **2005**, p 355.
48. Li, H.; Huneault, M. A. *Polymer* **2007**, *48*, 6855.
49. Tumalla, P.; Liu, W.; Drzal, L. T.; Mohanty, A. K.; Misra, M. *Ind. Eng. Chem. Res.* **2006**, *45*, 7491.
50. Auras, R. A.; Sing, P. S.; Singh, J. J. *Packag. Technol. Sci.* **2005**, *18*, 207.
51. Avella, M.; Martuscelli, E.; Raimo, M. *J. Mater. Sci.* **2000**, *35*, 523.
52. Ayranci, E.; Tunc, S. *Food Chem.* **2001**, *72*, 231.
53. Bastarrachea, L.; Dhawan, S.; Sablani, S. S. *Food Eng. Rev.* **2011**, *3*, 79.
54. Avérous, L. In Monomers, Polymers and Composites from Renewable Resources; Belgacem, M. N., Gandini, A., Eds.; Elsevier: Oxford, **2008**; Vol. 1, Chapter 21, p 433.
55. Bio-Plastics. Bioplastic types: starch blends and derivatives, **2013**. Available at: <http://www.bio-plastics.org/en/information--knowledge-a-market-know-how/bioplastic-types/starch-blends-a-derivates>. Last accessed May 18, 2014.
56. Clarinval, A.; Halleux, J. *Biodegrad. Polym. Ind. Appl.* **2005**, *3*.
57. Corre, Y. M.; Bruzard, S.; Audic, J. L.; Grohens, Y. *Polym. Test.* **2012**, *31*, 226.
58. Diacel. Available at: http://www.daicel.com/cell_ac/en/. Last accessed January 1, 2015.
59. Efunfa. Available at: http://www.efunda.com/materials/polymers/properties/polymer_sheet.cfm?MajorID=PVD&MinorID=2. Last accessed May 22, 2014.
60. Goodfellow. Available at: <http://www.goodfellow.com/E/Cellulose-Acetate.html>. Last accessed October 9, 2014.
61. Hoka. Available at: <http://www.hoka.de/en/company/materials.html>. Last accessed January 13, 2015.
62. Matbase. Available at: <http://www.matbase.com/material-categories/natural-and-synthetic-polymers>. Last accessed January 9, 2015.
63. MatWeb. Available at: <http://www.matweb.com/reference/deflection-temperature.aspx>. Last accessed January 9, 2015.
64. Middleton, J. C.; Tipton, J. A. *Biomaterials* **2000**, *21*, 2335.
65. Mo, C.; Yuan, W.; Lei, W.; Shijiu, Y. *J. Appl. Packaging Res.* **2014**, *6*, 40.
66. Nakamura, H.; Shirakawa, Y.; Kitamura, H.; Sato, N.; Shinji, O.; Saito, K.; Takahashi, S. *Sci. Rep.* **2013**, *3*, 2502.
67. Nampoothiri, K. M.; Nimisha, R. N.; Rojan, P. J. *Bioresour. Technol.* **2010**, *101*, 8493.
68. Plastics News. Current Resin Pricing, Commodity thermoplastics. Available at: <https://www.plasticnews.com/resin/commodity-thermoplastics/current-pricing>. Last accessed March 10, 2014.
69. Platt, D. Prices rise in January. Available at: <http://www.europeanplasticsnews.com/subscriber/newscat2.html?cat=14&channel=400&id=4062>. Last accessed March 10, 2014.
70. Orient HDPE. Properties compare for LDPE and HDPE. Available at: <http://www.polymer-insulators.com/list1.asp?id=309>. Last accessed March 10, 2014.
71. Rodríguez, M.; Osés, J.; Ziani, K.; Matè, J. I. *Food Res. Int.* **2006**, *39*, 840.
72. Rossa, L. V.; Scienza, L. C.; Zattera, A. J. *Polym. Compos.* **2013**, *34*, 450.
73. Shogren, R. J. *Environ. Polym. Degrad.* **1997**, *5*, 91.
74. Sudesh, K.; Abe, H.; Doi, Y. *Progr. Polym. Sci.* **2000**, *25*, 1503.
75. Talja, R. A.; Helén, H.; Roos, Y. H.; Jouppila, K. *Carbohydr. Polym.* **2007**, *67*, 288.
76. Tharanathan, R. N. *Trends Food Sci. Technol.* **2003**, *14*, 71.
77. Work, W. J.; Horie, J.; Hess, M.; Stepto, R. F. T. *Pure Appl. Chem.* **2004**, *76*, 1985.

78. Jerez, A.; Partal, P.; Martínez, I.; Gallegos, C.; Guerrero, A. *Biochem. Eng. J.* **2005**, *26*, 131.
79. Vieira, M. G. A.; Altenhofen da Silva, M.; Oliveira dos Santos, L.; Beppu, M. M. *Eur. Polym. J.* **2011**, *47*, 254.
80. Wang, Y.; Qin, Y.; Zhang, Y.; Yuan, M.; Li, H.; Yuan, M. *Int. J. Biol. Macromol.* **2014**, *67*, 58.
81. Boonfaung, P.; Wasutchanon, P.; Somwangthanaroj, A. In *Pure and Applied Chemistry International Conference; Bangkok, Thailand, 2011; Vol. 2011*, p 621.
82. Martin, O.; Averous, L. *Polymer* **2001**, *42*, 6209.
83. Arrieta, M. P.; López, J.; Hernández, A.; Rayón, E. *Eur. Polym. J.* **2014**, *50*, 255.
84. Branciforti, M.; CvCorrêa, M. C. S.; Pollet, E.; Agnelli, J. A. M.; Nascente, P. A. D. P.; Avérous, L. *Polym. Test.* **2013**, *32*, 1253.
85. Kopinke, F.; Mackenzie, K. *J. Anal. Appl. Pyrol.* **1997**, *40*, 43.
86. Najafi, N.; Heuzey, M.; Carreau, P.; Wood-Adams, P. M. *Polym. Degrad. Stab.* **2012**, *97*, 554.
87. BASF. Performance Chemicals – Joncryl Functional Additives; Presentation Ghent University: Ghent, Belgium, **2013**.
88. Al-Itry, R.; Lamnawar, K.; Maazouz, A. *Polym. Degrad. Stab.* **2012**, *97*, 1898.
89. Duangphet, S.; Szegda, D.; Song, J.; Tarverdi, K. *J. Polym. Environ.* **2013**, *22*, 1.
90. Di, Y.; Iannace, S.; Di Maio, E.; Nicolais, L. *Macromol. Mater. Eng.* **2005**, *290*, 1083.
91. Battegazzore (2011). *Exp. Polym. Lett.* **2011**, *5*, 849.
92. Bernland, K. M. Nucleating and clarifying polymers. Available at: <http://dx.doi.org/10.3929/ethz-a-006371353>. Last accessed November 24, 2012.
93. Kai, W.; He, Y.; Inoue, Y. *Polym. Int.* **2005**, *54*, 780.
94. Kolstad, J. J. *J. Appl. Polym. Sci.* **1996**, *62*, 1079.
95. Harris, A. M.; Lee, E. C. *J. Appl. Polym. Sci.* **2007**, *107*, 2246.
96. Bigg, D. M. In *Conference Proceedings ANTEC: Society of Plastics Engineers – Annual Technical Conference, Nashville, TN; 2003*, p 2816.
97. Nam, J. Y.; Okamoto, M.; Okamoto, H.; Nakano, M.; Usuki, A.; Matsuda, M. *Polymer* **2006**, *47*, 1340.
98. Kawamoto, N.; Sakai, A.; Horikoshi, T.; Urushihara, T.; Tobita, E. *J. Appl. Polym. Sci.* **2007**, *103*, 198.
99. El-Hadi, A.; Schnabel, R.; Straube, E.; Müller, G.; Henning, S. *Polym. Test.* **2002**, *21*, 665.
100. Yamane, H.; Sasai, K. *Polymer* **2003**, *44*, 2569.
101. Wu, S. *Polym. Eng. Sci.* **1987**, *27*, 335.
102. Bordes, P.; Pollet, E.; Averous, L. *Prog. Polym. Sci.* **2009**, *34*, 125.
103. Thiebaud, S.; Aburto, J.; Alric, I.; Borredon, E.; Bikiaris, D.; Prinos, J. *J. Appl. Polym. Sci.* **1997**, *65*, 705.
104. Furukawa, T.; Sato, H.; Murakami, R. *Macromolecules* **2005**, *38*, 6445.
105. Zhang, M. I. N.; Thomas, N. L. *Adv. Polym. Technol.* **2010**, *30*, 67.
106. Gu, S. Y.; Zhang, K.; Ren, J.; Zhan, H. *Carbohydr. Polymer* **2008**, *74*, 79.
107. Jiang, L.; Wolcott, M. P.; Zhang, J. *Biomacromolecules* **2006**, *7*, 199.
108. Bolck, C.; Ravenstijn, J.; Molenveld, K.; Harmsen, P. *Bio-based Plastics; Wageningen University, Propress: Wageningen; 2012*, p 67.
109. Baratian, S.; Hall, E. S.; Lin, J. S.; Xu, R.; Hunt, J. *Macromolecules* **2001**, *34*, 4857.
110. Bigg, D. M. *Adv. Polym. Technol.* **2005**, *24*, 69.
111. Lim, L. T.; Auras, R.; Rubino, M. *Prog. Polym. Sci.* **2007**, *33*, 820.
112. Dorgan, J.; Janzen, J.; Clayton, M.; Hait, S.; Knaus, D. J. *Rheol.* **2005**, *49*, 607.
113. Fukushima, K.; Kimura, Y. *Polym. Int.* **2006**, *55*, 626.
114. Ikada, Y.; Tsuji, H. *Macromol. Rapid Commun.* **2000**, *21*, 117.
115. Tsuji, H. *Macromol. Biosci.* **2005**, *5*, 569.
116. Tsuji, H.; Ikada, Y. *Polymer* **1999**, *40*, 6699.
117. Singh, S.; Mohanty, A. K.; Sugie, T.; Takai, Y.; Hamada, H. *Compos. Appl. Sci. Manuf.* **2008**, *39*, 875.
118. Yu, J.; Yang, J.; Liu, B.; Ma, X. *Bioresour. Technol.* **2009**, *100*, 2832.
119. Singh, S.; Mohanty, A. *Compos. Sci. Technol.* **2007**, *67*, 1753.
120. Tokoro, R.; Vu, D. M.; Okubo, K.; Tanaka, T.; Fujii, T.; Fujiura, T. *J. Mater. Sci.* **2008**, *43*, 775.
121. Du, Y.; Yang, N.; Kortschot, M. T. *J. Mater. Sci.* **2014**, *2630–2693*.
122. Meng, Q.; Heuzey, M. C.; Carreau, P. *J. Polym. Degrad. Stab.* **2012**, *97*, 2010.
123. Wu, D.; Wu, L.; Wu, L.; Zhang, M. *Polym. Degrad. Stab.* **2006**, *91*, 3149.
124. Arrieta, M. P.; Fortunati, E.; Dominici, F.; Rayón, E.; López, J.; Kenny, J. *Carbohydr. Polym.* **2014**, *107*, 16.
125. Martino, V. P.; Jiménez, A.; Ruseckaite, R. A.; Avérous, L. *Polym. Adv. Technol.* **2011**, *22*, 2206.
126. Azeredo, H. M. C.; Mattoso, L. H. C.; Wood, D.; Williams, T. G.; Avena-Bustillos, R. J.; McHugh, T. H. *J. Food Sci.* **2009**, *74*, 31.
127. Alemdar, A.; Sain, M. *Compos. Sci. Technol.* **2008**, *68*, 557.
128. Krishnamachari, P.; Zhang, J.; Lou, J.; Yan, J.; Uitenham, L. *Int. J. Polym. Anal. Char.* **2009**, *14*, 336.
129. Abdulkhani, A.; Hoseinzadeh, J.; Ahori, A.; Dadashi, S.; Takzare, Z. *Polym. Test.* **2014**, *35*, 73.
130. Araújo, A.; Botelho, G.; Oliveira, M.; Machado, A. *Appl. Clay Sci.* **2014**, *88*, 144.
131. Bordes, P.; Pollet, E.; Bourbigot, S.; Avérous, L. *Macromol. Chem. Phys.* **2008**, *209*, 1473.
132. Sinha Ray, S.; Yamada, K.; Okamoto, M.; Ueda, K. *Polymer* **2003**, *44*, 857.
133. Zhao, H.; Cui, Z.; Wang, X.; Turng, L. S.; Peng, X. *Compos. B Eng.* **2013**, *51*, 79.
134. Vadori, R.; Mohanty, A. K.; Misra, M. *Macromol. Mater. Eng.* **2013**, *298*, 981.