

O U T L I N E

3.1 Recuperation	95	3.4 Modification of the Chemical Structure	101
3.2 Restabilization	98	3.5 Multiple Processing	101
3.3 Blending Recycled Biopolymers with other Polymers	98	References	102

Reuse is a common practice applied to discarded or used polymer products. Rejected preforms or moldings and used articles are reprocessed as they are, without changing the chemical nature of the polymer; an example of this is the conversion of PET bottles to fibrous material. As a result, most of the applied techniques are similar to those of physical (or mechanical) recycling described in Chapter 5: Physical Recycling. However, there are certain differences. The methods of physical recycling, such as grinding, sorting, compacting, etc., are usually pretreatment processes preceding the reprocessing or recycling of the waste material. Recycling in particular is expensive because the separation of the different polymers is difficult. Reusing polymers is preferable to recycling as it uses less energy and fewer resources. Reuse involves one or more of the following: (1) direct recuperation of scrap material during molding (e.g., feedback of used material); (2) blending of the polymer to be used with other polymers, often in combination with compatibilizers to make new products; (3) mixing with various additives such as antioxidants and/or reinforcing agents; and/or (4) modification of the polymer structure (e.g., by reactive extrusion) to recover its original properties.

3.1 Recuperation

This practice is widely employed for the recycling of industrial scrap, in which these industrial residues

are ground and mixed with virgin material, and directly introduced into the processing machinery. Sources of industrial scrap can be melt lumps, sprues, and defective parts in injection molding, parison waste in blow-molding or, for example, edge trim, cutoffs, and off-spec startup material in film and fiber production processes. The reutilization of these plastics wastes — which exist in considerable quantities in the production or processing of biopolymer products — by direct processing in an extruder is possible only to a very limited extent because of their voluminous nature and poor flow property. Such plastics wastes must first be pretreated appropriately by comminution. The plastics particles which have thereby become flake-like or fleece-like are then agglomerated into highly compacted, free-flowing, and abrasion-resistant granules. During the heat treatment required for the agglomeration, the biopolymers must not be thermally damaged (i.e., they must not be heated above their melting temperature, T_m) since they decompose chemically and release gases that are harmful in most cases, and cause the wastes to become useless for technological reutilization. The granules obtained in this way must have the same quality as the granules of virgin material so that they can be proportionately admixed with the latter. The adjustment of the composition of recycled material in the blend, and the optimization of the processing procedure, are the main technological considerations required to achieve material properties similar to those of the virgin one [1].

Scrap biopolymers generated during molding operations can be viewed as potential resources for the manufacture of new products through recycling processes, with a similar status given to virgin biopolymers. The prospect of reusing scrap polylactide (PLA) as it appears appealing from the aspect of recycling when taking into account the average cost of PLA compared to conventional plastic products. The following are sources of waste PLA: (1) sprues, runners, and selvages left behind during molding and production processes; (2) off-grades of PLA formed by polymerization reaction and not meeting the standard requirements; and (3) used PLA. However, the reprocessing of biopolymer waste is not an easy task. PLA is highly susceptible to thermal deterioration, and reuse of waste PLA is liable to cause coloration, degeneration, and decrease in molecular weight. Other problems such as hygroscopicity, stickiness at high temperatures, and thermal instability of several biopolymers, must also be taken into consideration. Thus, for example, in the reprocessing of PLA, it is important that the material being recycled be as dry as possible in order to prevent a hydrolytic breakdown of the molecular chains during plasticization. However, PLA is hygroscopic, which makes an efficient drying difficult. Furthermore, the low T_g at which the PLA material becomes sticky at higher temperatures, along with a relatively long crystallization time, make it hard to crystallize and/or dry amorphous production wastes (especially residues of deep-drawn films) with conventional crystallization systems and drying systems (WO2008058303 A1, 2008, EREMA). Therefore, unlike general use polymers, it is difficult to reuse PLA. Similarly, plasticized starch is sensitive to hydrolysis during use, and cannot normally be reprocessed for use in the same application. Like PLA, it is not compatible with mainstream plastics used in packaging and cannot be co-recycled into useful secondary products. Additional problems with reprocessing industrial scrap and virgin biopolymers include: (1) inconsistent feeding performance of the production extruder; (2) air inclusions in the melt that lead to defects in the finished products; and (3) difficulty in removing process materials like printing inks and similar materials.

CN101230129 A (2008, SHANGHAI NEW SHANGHUA POLYMER) discloses a recrystallization method for waste PLA that comprises the following steps: recovered PLA with 30 to 400 ppm water content is heat treated and recrystallized

for 5–100 min, preferably 30 min at 20–140°C (30–110°C is preferred), by adopting different temperatures, according to two to eight ascending temperature gradients (preferably two to four), to obtain recrystallized PLA. Waste PLA refers to PLA rim leftovers and discarded products after first processing. The melting enthalpy of the melting peak of PLA crystallization (ΔH_m) is 10 to 30 J/g, the T_m is 140 to 180°C, and the T_g of PLA is 40 to 70°C. Recrystallization of PLA is a simple operation, does not need additional post-processing, requires a relatively short time, and yields recrystallized PLA with satisfactory properties. In addition, the recrystallized PLA can be easily reprocessed.

WO2008058303 A1 (2008, EREMA) discloses a method for the pretreatment, reprocessing, or recycling of thermoplastic material, especially PLA (Figure 3.1). The thermoplastic material is heated in a receiving tank or reactor (1) under constant mixing or movement and/or comminution at a temperature below T_m (preferably over T_g of the thermoplastic, 90 to 110°C). At the same time it is crystallized, dried, and/or purified, especially in a single step. For mixing and heating of the thermoplastic material, at least one comminuting or mixing tool (12) is used. It must be able to turn about a vertical axis (8) and is typically arranged on several levels, one above the other, with working edges that act on the material with a comminuting and/or mixing effect. Heating occurs by applying mechanical energy. The method is best carried out either in a one-stage EREMA PC reactor or in a one- or two-stage VACUREMA reactor.

The mild, constant movement of the polymer material prevents clumping or sticking of the material in the critical temperature range until adequate crystallization of the surface of the particles can prevent individual particles from sticking together. In the treatment tank, the mild and constant movement ensures not only an abeyance of sticking, but at the same time also ensures that the temperature in the tank remains high enough and that each particle remains heated gently to the proper temperature. At the same time, the movement supports a detachment of the migrating molecules from the surface of the particles.

WO2009100473 A1 (2009, EREMA) is a modification of patent WO2008058303. Pretreated thermoplastic material is transferred into a screw injection molding machine (10) having a screw (16) rotating in a housing (17) and being axially

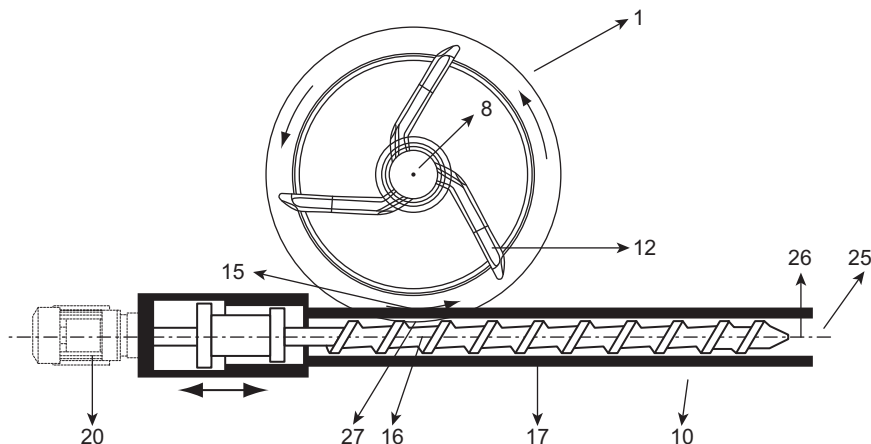


Figure 3.1 Device comprising a reactor or cutter-compactor (1) and a worm-gear injection molding device (10).

1: Reactor or cutter-compactor;
 2: Worm-gear injection molding device; 8: Vertical axis; 10: Injection molding machine; 12: Mixing tool; 15: Removal opening; 16: Screw; 17: Housing; 20: Motor; 25: Nozzle; 26: Worm antechamber; 27: Catchment opening
 (WO2009100473 A1, 2009, EREMA).

displaceable therein and/or acting as a piston, is plasticized in said screw, and molded into a molded part, for example a preform (Figure 3.1).

At the NPE 2009 tradeshow in Chicago, plastics recycling systems provider EREMA demonstrated a recycling system of turning scrap PLA film into near margin quality pellets, using a non-vented Model 906T reclaim extruder for PE film. With a normal non-barrier screw for PE, it processed oriented PLA scrap provided by Biax International, Inc., a large producer of oriented PLA film (OPLA) sheet. Frictional heat generated in the standard cutter/compactor acts like a dryer, removing and venting moisture that makes this material difficult for some systems to reprocess. The use of a short extruder L/D ratio also helps to avoid thermal degradation. EREMA says about 9 million kilograms per year of bioplastic scrap (mostly PLA) is reprocessed on EREMA reclaim extruders in the USA, and about the same amount in Europe (PLA and starch based films for compost bags) [2,3].

At the NPE 2012 tradeshow in Milan, recycling equipment maker Tecnova demonstrated the Refil/1 in-line system for reclaiming film scrap. Production rates of the system, which can handle a wide range of materials, including biopolymers, are claimed to be 40–45 kg/hr. The company also showed the Mini 60 line, which is able to process bioplastic, in addition to LDPE/HDPE/PP film. The line is equipped with a special grinder, a die-face cutter, and a cooling system, all specifically designed to be able to handle biopolymers as well as conventional plastics. The regenerated granules can be directly reintroduced into the extrusion process for the production of (biodegradable) film [3].

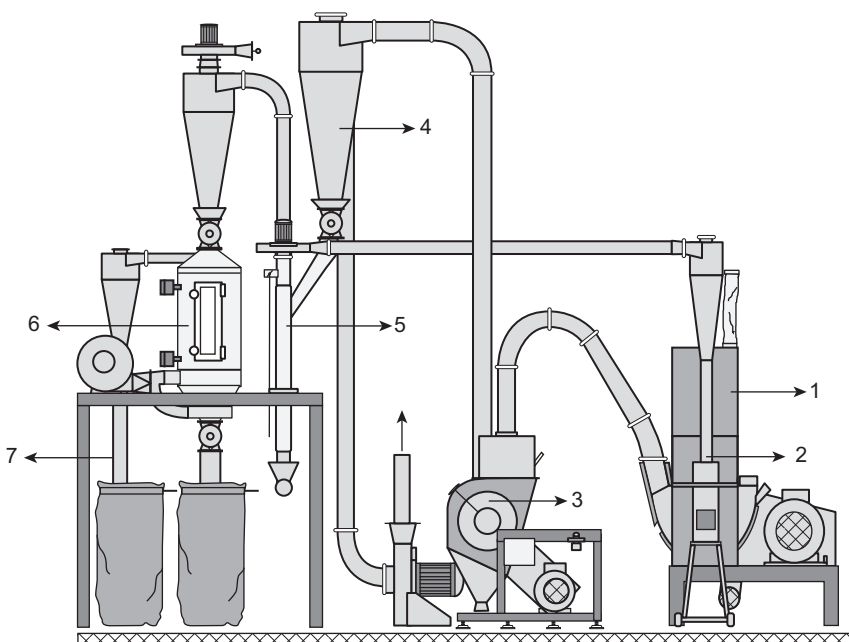
Next Generation Recyclingmaschinen GmbH (NGR) has developed a new technology for bioplastics recycling. NGR's solution uses recycling machines that feed the material to the extruder with an integrated cutter-feeder, which consists of a slow rotating cutter shaft with knives that cut against fixed knives like scissors, and a feeding zone that conveys the material to the extruder without pre-heating it. The NGR cutter-feeder-extruder can reportedly recycle most of the commonly used biopolymers, such as starch or PLA-based products. The screws, vacuum vent and melt filter can all be tailored to the special requirements of biopolymers, such as low heating of the material or the removal of printing inks. This method is also sensitive towards monitoring slight changes in the molecular mass distribution resulting from the inevitable heat stress in any polymer processing step [4].

Pallmann Maschinenfabrik GmbH & Co. has developed a special process for recycling waste generated during the production and processing of PLA foam and film. As shown in Figure 3.2, PLA waste pre-cut into a size smaller than 1/2" is conveyed into the storage bin of the Plast-Agglomerator with a pneumatic conveyor system. From the hopper the feed material is continuously dosed into the agglomeration chamber by a feeding screw. Through mechanical pressure and only frictional heat, the material is evenly sintered through the die holes within fractions of a second. The frictional heat and mechanical pressure can be adjusted in such a way that the sintering is performed below the T_m of each type of plastic to ensure minimal thermal degradation of the product. Waste is generated during the production and processing of PLA foam and film.

Figure 3.2 Plast-Agglomerator, Type PFV

- 1: Hopper; 2: Plast-Agglomerator;
3: Hot-melt granulator; 4: Cyclone;
5: Sifter; 6: Granules cooler;
7: Sacking station

Pallmann Maschinenfabrik GmbH & Co. KG [5].



Valuable virgin material can be saved by recycling this waste, and recycled production waste can be reintroduced into the process for the production of new material.

Suitable apparatus for the continuous regranulation of thermoplastics wastes – in particular, films, fibers, filaments, foam materials and the like – are described in **DE3842072 C1** (1989) and **US2006283340 A1** (2006, **PALLMANN MASCHINENFABRIK GMBH & CO. KG**). These apparatus are mainly used to transform wastes such as polyethylene, polyvinyl chloride, polypropylene, polystyrene, polyamide, mixtures of these wastes, similar thermoplastics, and other organic or inorganic materials, into uniform, free-flowing, and abrasion-resistant granules. This can all be done without thermal damage to the material, as is required for further technological processing in extruders, pressers, or injection-molding machines.

3.2 Restabilization

The reprocessing of waste polymers leads to materials with generally worse properties than those of the original materials. This is due to changes in the chemical structure caused by previous degradation processes. Restabilization is a well-known practice for protecting recycled materials from thermo-mechanical degradation during reprocessing, and for

enhancing long-term stability throughout reuse. Restabilization does not effectively recover the degraded material, but it does prevent further degradation processes that may be catalyzed by the oxidative moieties present in its structure or by moisture. Several processing and light stabilizers, including combinations of hindered phenols and hindered amine stabilizers, have been employed for the restabilization of recycled biopolymers. Without restabilization, these biopolymers can interfere in the auto-oxidation cycle by neutralizing peroxide radicals and decomposing hydroperoxides [1]. Some additives, such as catalyst deactivators, have been reported to stabilize PLAs in the melt. Such additives include benzoyl peroxide [6,7], 1,4-diaminoanthraquinone [8,9], 2-hydroxy-2,4,6-cycloheptatrienone (tropolone) [10], natural, and biodegradable acid [11]. Additives such as carbodiimide compounds are used to retard the hydrolysis of biopolymers. Compatibilizers are also added to improve the performance of waste biopolymers (see also Chapter 7: Degradation on Demand; Section 7.2: Suppression of (Bio)degradability).

3.3 Blending Recycled Biopolymers with other Polymers

Blending recycled polymers with virgin materials is one of the most common and well-established

procedures for upgrading the properties of single-stream waste polymeric materials.

Sharp has developed recycling technology for repeatedly recovering plastic from used consumer electronics and reusing it in parts in new consumer electronics. In 2010, the volume of plastic that was derived from this closed-loop recycling technology and reused in new products increased to 1300 tons. Sharp has disclosed a number of patents for related methods and apparatus for recovering and reusing biodegradable aliphatic polyesters such as PLA and PHB. The methods are used for the recovery and recycling of bio-based thermoplastics from discarded domestic electrical appliances such as air conditioners, televisions, refrigerators, and washing machines, as well as from electronic office equipment and electrical-electronic components.

JP2007284495 A (2007, SHARP KK) discloses a method for the separation, recovery, and reuse of thermoplastic resin (A) from waste material comprised of a thermoplastic resin derived from renewable resources, and a thermoplastic resin derived from fossil resources. Thermoplastic resin (B) is then added to thermoplastic resin (A), and mixed and molded. The method further involves a resin collection process and a gravity-separation process. In the resin collection process, thermoplastic resin is separated and recovered from a waste material using water that has a specific gravity difference. Similarly, the thermoplastic resin (B) is recovered from the waste material. The gravity-separation process involves separating and recovering other thermoplastic resin from crushed material containing plastic. The thermoplastic resin composition derived from renewable resources contained in thermoplastic resin (A) is PLA consisting of L-lactic acid and/or D-lactic acid units. The thermoplastic resin composition derived from fossil fuel resources contained in thermoplastic resin (A) is polyolefin composition or polystyrene composition. While mixing thermoplastic resin (A) with thermoplastic resin (B), additive (which assigns hydrolysis resistance), a compatibilizing agent and/or antioxidant, and a compatibilizing agent having reactive functional group(s) on a side chain, are added. The quantity of additive, compatibilizing agent, and antioxidant with respect to 100 parts by weight of thermoplastic resin (A) and thermoplastic resin (B) are 0.01–10, 0.01–30 and 0.01–5 parts by weight, respectively. The preferred additive is carbodiimide compound, the thermoplastic resin

component is a polyolefin-type resin composition, and the compatibilizing agent is a block copolymer containing PLA as a main component. The compatibilizing agent with reactive functional group(s) in its side chain is a copolymer (a) containing an olefin-type thermoplastic resin component and a styrene-type thermoplastic resin component, or is a modified polymer (b) with a structural unit containing a carboxylic acid group or its derivative(s) group in the principal chain or side chain of the olefin-type thermoplastic resin. The content of copolymer (a) and modified polymer (b) are 0.1–20 and 0.1–10 parts by weight, respectively. The preferred antioxidant is a phenolic antioxidant and/or a phosphorus-type antioxidant.

JP2009161655 A (2009, SHARP KK) discloses a method for recycling a bio-based thermoplastic resin waste by mixing the bio-based thermoplastic resin waste with at least one polymer selected from a styrene-based resin (A), an aliphatic polyester resin (B), and a vinyl-based polymer (C), and heating and melting the mixture. The bio-based thermoplastic resin waste material contains acrylonitrile butadiene-styrene copolymer (ABS), and PLA having L-lactic acid and/or D-lactic acid. The styrene resin (A) is acrylonitrile butadiene-styrene copolymer (ABS). The aliphatic polyester resin (B) is PLA that consists of L-lactic acid and/or D-lactic acid units. The vinyl polymer (C) contains polymer of (meth)acrylic ester, and has hydroxyl and/or functional groups that have carboxyl group reactivity. The thermoplastic resin composition further contains (in weight parts) rubber-containing copolymer (D) (0.1–50), phenolic antioxidant and/or phosphorus-type antioxidant (E) (0.01–5), and hydrolysis-proof stabilizer (F) (0.01–10). The rubber-containing copolymer (D) is silicone acrylic-type and/or core shell-type acrylic-type copolymer.

JP2010005948 A (2010, SHARP CORP) discloses a method for reusing a biodegradable polymer waste. It is comprised of the following two processes: (1) mixing the biodegradable polymer waste, which is composed mainly of an acrylic resin (e.g., PMMA), and at least one biopolymer selected from the group consisting of L-lactic acid and D-lactic acid units, with polymers containing a styrene-based resin (e.g., ABS), preferably in combination with at least one antioxidant and a hydrolysis-proof stabilizer. This mixture is then thermally melted to obtain a raw material as resource; and (2) manufacturing a biodegradable molded article from the recycled

material. The biodegradable polymer waste is selected from domestic electrical appliances, electronic office equipment, electrical and electronic components, and the like.

JP2008100413 A (2008, SHARP CORP) discloses a method for recycling waste plastic material having a paint film formed from a bio-based coating. It includes the following steps: (1) crushing the waste plastic material having the paint film; (2) heating/melting the crushed waste plastic material; (3) producing a plastic raw material using it; and (4) producing a plastic molding. The recycling method does not adversely affect the environment, while preventing the lowering of the physical properties of a regenerated plastic material even when the waste plastic material having a paint film, without removing the paint film, is mixed with a plastic material to be coated to be recycled.

JP2002226623 A (2002, KANEBO LTD) discloses a method of reclaiming a foam molding from a biodegradable aliphatic polyester (e.g., PLA or PBS) by grinding and molding the foam again. Furthermore, a reclaimed molded article is obtained by mixing the ground foam with unused PLA-based foam beads (primary foam) of 70% or more and then molding the mixture. The reclaimed foam is used for shock-absorbing materials and for packing.

EP1241231 A1 (2002, CANON KK) discloses in one of its embodiments the recycling of molded articles obtained from a biodegradable polymer composition, comprising a biodegradable biopolymer (A) and a biodegradable liquid crystalline biopolymer (B). The source material for the biodegradable biopolymer or liquid crystalline biopolymer can be waste paper. Molded articles include ink tanks of ink-jet printers, toner containers of electrophotography apparatus, packing materials, casings of printers and cameras, transparency sheets, and so forth. In one example, a transparent sheet prepared from butyl ester of hydroxyethylcellulose (B) and PLA (A) was melted and pressed again to mold a transparency sheet. This sheet was found to be usable as a transparency sheet without causing problems in light transmissivity and other properties. In another example, the transparency sheet was melted, pelletized, and then molded into a casing of an ink-jet printer casing by an injection machine. The casing was formed with no problem in molding (see also Chapter 6: Chemical Recycling; Section 6.3: Hydrothermal Depolymerization).

WO2011146562 A2 (2011, DU PONT) discloses a method for making a fiber containing from 0.1 to 99.9 wt.% (preferably 5 to 10 wt.%) with recycled poly(trimethylene terephthalate) (PTT). It is comprised from the following steps: (1) providing carpet yarns containing recycled PTT (Sorona®); (2) melt-pelletizing the yarns; (3) combining the recycled PTT with virgin PTT to form a blend; and (4) spinning the blend to form a fiber. In some preferred embodiments, the PTT being reclaimed and recycled and/or virgin PTT with which the PTT is combined are bio-derived; i.e., the PTT can be prepared from 1,3-propanediol that has been produced using a biological method such as fermentation (see also Chapter 1: Introduction to Biopolymers; Section 1.3.2.3: Aromatic Polyesters (Bio-Based)). The use of bio-derived starting materials in virgin PTT, and preferably also in the PTT in the carpet being used for the recycled polymer, provides a sustainable and more environmentally friendly consumer product than processes using only fossil fuel-based raw materials.

CN101275009 A, US2008237910 A1 (2008, FUJI XEROX CO LTD; FUJIFILM CORP), and **CN101130627 A** (2008, FUJI XEROX CO LTD) disclose methods of recycling biodegradable polymer compacts used mainly as exterior parts of a printer, a copying machine, a facsimile and the like. In CN101275009 A and US2008237910 A1 (2008, FUJI XEROX CO LTD; FUJIFILM CORP) the biodegradable polymer composition comprises 21 to 70% of an aliphatic polyester (e.g., PLA), 35–65% of a second polymer having a glass transition temperature (T_g) higher than the T_g of the aliphatic polyester (e.g., polycarbonate) and 1–20 mass percent of an aluminum phosphate as flame retardant. In CN101130627 A (2008, FUJI XEROX CO LTD) the composition comprises an aliphatic polyester and a lignophenol. The general recycling method comprises freeze-grinding, heating the obtained ground product at a temperature lower than the T_m of the aliphatic polyester, and injection molding the ground product to obtain a biodegradable polymer compact (see also Chapter 5: Physical Recycling; Section 5.2: Grinding). Examples of the aliphatic polyesters include PLA, poly(3-hydroxybutyrate) (PHB), poly(butylene succinate) (PBS), and poly(butylene adipate) (PBA). Of those, the commercially available PLA and PHB are preferred, with PLA being particularly preferred. The use of lignophenol endows the polyester with oxidation resistance, heat resistance, surface hardness, abrasion resistance,

weather resistance, and recycling efficiency (see also Chapter 7: Degradability on Demand; Section 7.2.3: Functional Group-Capping Agents and Catalyst-Deactivation Agents).

3.4 Modification of the Chemical Structure

Chemical modification of the structure of the recyclates is another way to upgrade effectively the properties of recycled products. The use of certain compounds such as radical generators, compounds with reactive functional groups, or chain extenders can be effective in inducing branching and/or cross-linking reactions, or increasing the molecular weight of the degraded polymeric chains from waste materials during melt reprocessing (reactive extrusion). This procedure increases the molecular weight of the polymer chains and improves rheological and mechanical properties [1]. Chemical modification has been successfully applied to upgrade degraded bio-based aromatic polyesters.

US2011071235 A1 (2011, SABIC INNOVATIVE PLASTICS US LLC) discloses a method of making an *in situ* biodegradable composition containing an aliphatic-aromatic copolyester from used aromatic polyesters. In one of its embodiments the aromatic polyester is recycled polyethylene terephthalate (PET) or poly(trimethylene terephthalate) (PTT) derived from renewable resources. The biodegradable copolyester can be prepared by two methods. The first entails reacting the recycled aromatic polyester with a dihydric alcohol selected from the group consisting of ethylene glycol, propylene glycol, butylene glycol, 1,4-butanediol tetramethyl cyclobutanediol, isosorbide, cyclohexanedimethanol, bio-derived alcohols, hexylene glycol, and an aliphatic dicarboxylic acid of the formula $(\text{CH}_2)_m(\text{COOH})_2$, where m is 4–10, at a temperature from 160°C to 250°C in the presence of a transition metal catalyst (e.g., a titanium alkoxide catalyst to form a first mixture). The second method requires subjecting the first mixture to vacuum distillation at a pressure of less than 2 Torr and a temperature of 220°C to 260°C to form a molten aliphatic-aromatic copolyester.

Chain extenders are reactive additives that, when added during melt processing, enhance the mechanical properties of polyesters, such as PET, and polyesters derived from renewable resources

such as PLA and polyhydroxybutyrate (PHB). Chain extenders can be classified according to the polyester functional groups with which they react: carboxyl-end or hydroxyl-end chain extenders. Common chain extenders are dianhydrides, bis(oxazolines), bis-(hydrooxazine), carbodiimides, diepoxides, and diisocyanates. The chain extension process depends fundamentally on the chain extender concentration and the processing parameters; it is critical to adjust the concentration of the chain extender to successfully achieve chain extension and avoid undesired extensive branching and cross-linking reactions.

BASF's Joncryl[®] ADR chain extenders are reactive polymers that can be used to upgrade the mechanical properties of degraded aliphatic polyesters such as PLA and PHB. The usage of Joncryl[®] functional additives typically requires good compounding and feeding techniques to ensure that the additive is evenly dispersed into the polymer matrix and performs its function, be it chain extension or flow enhancement [12].

3.5 Multiple Processing

When polymer materials are subjected to the elevated temperatures and pressures typically applied in the referenced molding processes, the polymers can be prone to molecular degradation, unwanted polymerization, and unwanted reaction with other materials that may be present in the polymer material. This is particularly true in polymer materials that have been processed once and are processed a second time at elevated temperature. This means they are subjected to a second melting and processing cycle as is typical in reuse of scrap or recycled polymer preforms or bottles as the raw polymer material for new preforms and bottles. Such polymer reaction processes can cause the polymer material to acquire undesirable coloring, yellowing, blackening, haze, or other degradation of transparency. These processes may also cause a reduction in melt strength or intrinsic viscosity, or may otherwise deleteriously affect their processability or layer compatibility during subsequent molding into a shaped article, or the physical or aesthetic properties of such article during use.

Multiple processing is used to assess the recyclability of polymeric materials and to study the thermo-mechanical degradation during processing and mechanical recycling. The analysis of structural and morphological changes induced by consecutive

processing steps offers useful information for the optimization of processing conditions during mechanical recycling in order to avoid further degradation. One example is the choice of processing conditions and the further addition of stabilizers and other additives. Vilaplana and Karlsson [1] reviewed the factors that affect the final properties of reprocessed polymers: condition of incoming waste material (degradation state, presence of impurities, degree of branching, residual presence of additives, constituent copolymers), and reprocessing conditions (temperature profiles, screw type, presence of residual oxygen in the extruder). The structural and macroscopic properties of polymers are therefore modified during multiple processing. Chain scission is responsible for a decrease in the molecular weight of the polymeric chains, which leads to an increase in the degree of crystallinity in semicrystalline polymers, a decrease in viscosity, and a modification of the mechanical properties. This results in a progressive embrittlement of the reprocessed material [1].

Several research papers have analyzed the effects of multiple processing on the structural, rheological, and mechanical properties of the most common biopolymer, PLA.

The effect of seven injection cycles on the rheological and mechanical properties of PLA on a pilot scale was studied by Pillin et al. [13]. The viscosity of PLA decreased strongly (from 3960 to 713 Pa s) after only one injection cycle, and after four cycles PLA's viscosity became nearly 150 Pa s. Most of the mechanical performances of PLA also rapidly became rapidly too weak for an industrial application of the polymer. This decrease could be explained by the strong degradation of PLA during processing, which yields large chain scission as evidenced by rheological experiments and molecular weight measurements. Reprocessing of PLA induced an increase of crystallization during cooling with the thermo-mechanical cycles. This can be explained by higher chain mobility due to chain scission during injection. The addition of stabilizers suppressed this crystallization during cooling. Quinone was found to be an efficient stabilizer for trapping free radicals and maintaining PLA chain length with time at the processing temperatures. On the basis of these results, it was concluded that the main phenomenon of the degradation of PLA is driven by free radicals and not by hydrolysis due to moisture. These results indicate that PLA industrial waste can support moderate recycling, which is

a significant improvement on the environmental impact of this polymer.

The effect of multiple (up to 10 times) extrusions of PLA on its physical and mechanical properties was also studied by Żenkiewicz [14]. By raising the number of extrusion cycles, the tensile strength diminished slightly and the impact strength clearly decreased. The melt flow rate (MFI) and water vapor and oxygen transmission rates steadily increased. Variation of the number of extrusion cycles did not affect T_g , whereas it did cause a lowering of the cold crystallization temperature and slightly diminished the T_m . The results indicate that PLA industrial waste is suitable for reuse as an additive to a virgin polymer.

The effect of multiple extrusions and injections on the rheological and mechanical properties of a 50/50 polylactide/polystyrene blend (PLA/PS) was studied by Hamad et al. [15]. The viscosity of the blend decreased when increasing the processing cycle number, which was attributed to the reduction of the molecular weights with the processing cycle. The mechanical properties of the blend worsened with an increasing processing cycle number, and the tensile strength and elongation at break of the blend decreased sharply after two processing cycles. The least change was observed for Young's modulus (reduction by a factor of 0.26 after four processing cycles). The results indicate that PLA/PS waste is suitable for reuse as an additive during compounding of PLA/PS blends or as the raw polymers, PLA and PS.

References

- [1] Vilaplana F, Karlsson S. Quality concepts for the improved use of recycled polymeric materials. A review. *Macromolecular Materials and Engineering* 2008;293:274–97.
- [2] *Plastics Technology*, <http://www.ptonline.com/products/pe-film-reclaim-system-works-for-pla-too>.
- [3] Laird K. *PlasticsToday.com*, <http://www.plasticstoday.com/articles/recycling-made-simple-erema-ngr-052220125>; 21.05.2012.
- [4] eppm -NEWS. NGR Develops Effective Solution for Bioplastic Recycling (6 14), <http://www.eppm.com/x/guideArchiveArticle.html?gname=&&browse=p&bid=21&id=35453>; 2012.

- [5] Pallmann Maschinenfabrik GmbH & Co. KG. Recycling of PLA (Polylactic Acid) Foam and Film Waste with The Plast-Agglomerator, Type PFV. http://www.pallmannindustries.com/pla_foam_waste_recycling.htm.
- [6] Södergård A, Näsman JH. Stabilization of poly-(L-lactide) in the melt. *Polymer Degradation and Stability* 1994;46:25–30.
- [7] Södergård A, Näsman JH. Melt stability study of various types of poly(L-lactide). *Industrial & Engineering Chemistry Research* 1996;35:732–5.
- [8] McNeill I, Leiper H. Degradation studies of some polyesters and polycarbonates—1. Polylactide: General features of the degradation under programmed heating conditions. *Polymer Degradation and Stability* 1985;11:267–85.
- [9] McNeill I, Leiper H. Degradation studies of some polyesters and polycarbonates—2. Polylactide: Degradation under isothermal conditions, thermal degradation mechanism and photolysis of the polymer. *Polymer Degradation and Stability* 1985;11:309–26.
- [10] Wachsen O, Platkowski K, Reichert KH. Thermal degradation of poly-L-lactide—studies on kinetics, modelling and melt stabilisation. *Polymer Degradation and Stability* 1997;57: 87–94.
- [11] Hartmann M. Advance in the commercialization of poly(lactic acid). *Polymer Preprints* 1999;40: 570–1.
- [12] BASF-News Release. New life for recycled plastics and bioplastics in packaging applications, http://www2.basf.us/corporate/news_2009/news_release_2009_00073.htm; 19 March 2009.
- [13] Pillin I, Montrelay N, Bourmaud A, Grohens Y. Effect of thermo-mechanical cycles on the physico-chemical properties of poly(lactic acid). *Polymer Degradation and Stability* 2008;93: 321–8.
- [14] Żenkiewicz M, Richert J, Rytlewski P, Moraczewski K, Stepczyńska M, Karasiewicz T. Characterisation of multi-extruded poly(lactic acid). *Polymer Testing* 2009;28:412–8.
- [15] Hamad K, Kaseem M, Deri F. Effect of recycling on rheological and mechanical properties of poly(lactic acid)/polystyrene polymer blend. *Journal of Materials Science* 2011;46: 3013–9.

Patents

Patent	Pub. date	Family members	Applicant
CN101130627 A	20080227	US2008048365 A1 20080228; JP2008050446 A 20080306; US7598305 B2 20091006; CN101130627 B 20120502	FUJI XEROX CO LTD
CN101230129 A	20080730		SHANGHAI NEW SHANGHUA POLYMER
CN101275009 A	20081001	JP2008274222 A 20081113; CN101275009 B 20120222	FUJI XEROX CO LTD; FUJIFILM CORP
DE3842072 C1	19891228	EP0373372 A2 19900620; JPH02202403 A 19900810; US5009586 A 19910423; EP0373372 A3 19910502; EP0373372 B1 19930908; JP6013176 B 19940223	PALLMANN MASCHINENFABRIK GMBH & CO KG
EP1241231 A1	20020918	US2002130436 A1 20020919; JP2002275379 A 20020925; US2006035860 A1 20060216; US7064113 B2 20060620; JP3902916 B2 20070411; US7608593 B2 20091027	CANON KK

(Continued)

Patents (Continued)			
Patent	Pub. date	Family members	Applicant
JP2002226623 A	20020814		KANEBO LTD
JP2007284495 A	20071101		SHARP CORP
JP2008100413 A	20080501		SHARP CORP
JP2009161655 A	20090723		SHARP CORP
JP2010005948 A	20100114		SHARP CORP
US2006283340 A1	20061221	DE102005027861 A1 20061228; DE102005027861 B4 20120802; US7467585 B2 20081223	PALLMANN MASCHINENFABRIK GMBH & CO KG
US2008237910 A1	20081002	US7767744 B2 20100803	FUJI XEROX CO LTD; FUJIFILM CORP
US2011071235 A1	20110324	WO2011038071 A1 20110331; CN102498151 A 20120613; EP2480589 A1 20120801; KR20120099384 A 20120910	SABIC INNOVATIVE PLASTICS US LLC
WO2008058303 A1	20080522	CA2668902 A1 20080522; AU2007321746 A1 20080522; MX2009004892 A 20090521; KR20090092806 A 20090901; EP2101974 A1 20090923; CN101535018 A 20090916; AT505462 A1 20090115; JP2010509413 A 20100325; US2010216902 A1 20100826; KR20110007259 A 20110121; RU2009122359 A 20101220; RU2412804 C1 20110227; EP2295218 A1 20110316; AU2007321746B B2 20110818; CN102357943 A 20120222; JP2012066588 A 20120405; AT552958 T 20120415; ES2385105 T3 20120718; DK2101974 T3 20120723	EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT MBH
WO2009100473 A1	20090820	AU2009214810 A1 20090820; CA2715048 A1 20090820; AT506489 A1 20090915; CN101945743 A 20110112; EP2252440 A1 20101124; KR20100120212 A 20101112; MX2010008248 A 20100823; AT506489 B1 20101215;	EREMA ENGINEERING RECYCLING MASCHINEN UND ANLAGEN GESELLSCHAFT MBH

(Continued)

Patents (*Continued*)

Patent	Pub. date	Family members	Applicant
		US2011049763 A1 20110303; JP2011514850 A 20110512; RU2010137909 A 20120320	
WO2011146562 A2	20111124	WO2011146562 A3 20120518; US2012128924 A1 20120524	DU PONT

This page intentionally left blank