Improving the Quality of Recycled Materials

An Overview of Suitable Additives

Additives for improving the quality of recycled materials are now established products and a permanent fixture in many a company's product portfolio. With the right additives, such as stabilizers, compatibilizers and reactive additives, recycled materials can attain a level of properties that enables them to compete with virgin materials.

Must not have any smell or taste: food containers made from recycled plastic (figure: MEV-Verlag)

Mechanical recycling is the preferred option for recycling post-consumer plastics. In Europe, some 26 % or 6.6 million t [1] of post-consumer plastics were recycled in this way in 2012. A further increase is inevitable when the EU ban on landfilling plastics comes into force in 2025. Additives for facilitating recycling are key to further boosting mechanical recycling, especially where virgin polymers are to be replaced by recycled materials that have a comparable property profile. The use of recycled materials will become all the more attractive the more cost-effective they are in relation to virgin material, i. e. this means that the additives employed must fit into the available budgetary framework.

With the exception of slightly damaged production scrap, post-consumer plastic is unusable in the form in which it arises or is collected. Usually, and where necessary, it is sorted, cleaned and processed again, e. g. extruded to commercial-grade pellets. In order that a recycled material may possess the necessary quality to ensure sufficient processing and long-term stability for the intended application, reformulation with suitable additives is often necessary (**Fig. 1**). Basically, the entire range of additives available to virgin material is available for this purpose. The most commonly used additives in recycled materials are still [2]

- stabilizers, such as antioxidants and light stabilizers,
- reactive molecules, which are variously described as chain extenders or repair systems, and
- compatibilizers, including impact modifiers.

These have recently been joined by additives to reduce odor in recycled materials.

Restabilization Protects Recycled Material

Restabilization is a key method for improving the quality of recycled material. The stabilizers protect the recycled material against further oxidative (and/or photo-oxidative) damage, just as they do in virgin material. Stabilizer residues from the primary application are naturally beneficial during recycling and further stabilization of recycled material. In addition, the stabilizer consumed in the primary application must be replenished, at the least. The residual level of stabilizer is usually insufficient on its own, especially if re-purposing from the short-term primary application (e. g. packaging) to a long-term application is intended.

Most of the stabilizers for restabilizing recycled materials (except for PVC) in respect of their processing and long-term thermal stability are based on phenolic antioxidants, phosphites or phosphonites in combination with co-stabilizers, e. g. acid scavengers. Light stability is en- »

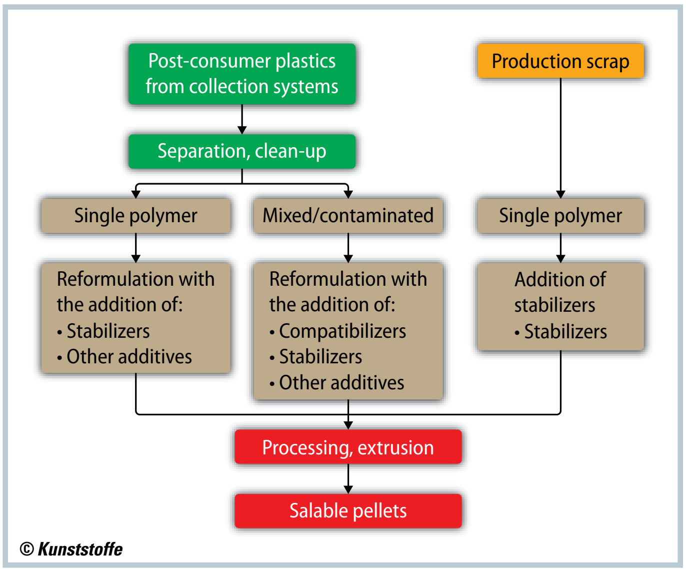

Fig. 1. Flow diagram for the quality improvement in recycled materials (figures 1–4: LBF)

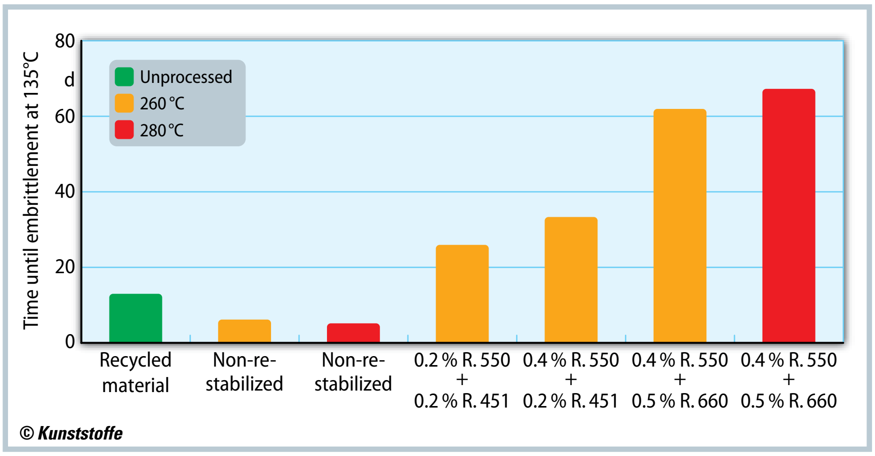

Fig. 2. Aging stability of a $CaCO_3$-filled, recycled PP material from garden chairs at different processing temperatures (R. 451 = Recyclostab 451, R. 550 = Recyclossorb 550, R. 660 = Recycloblend 660)

hanced with hindered amines (HA(L)S), e.g. low- or high-molecular weight, sterically hindered piperidines, and/or UV absorbers, e.g. based on benzophenone or benzotriazole.

The Recyclostab and Recyclossorb series of products from PolyAd Services GmbH, Lampertheim, Germany, have a proven track record as stabilizers for recycled materials. Thus, Recyclostab 411 improves the processing stability of recycled HDPE material and polyolefin films as well as raising compounding throughput. Recyclostab 451 enhances the long-term stability of recycled battery case material, while Recyclossorb 550, which contains light stabilizers in addition to processing and long-term stabilizers, is used for PE pallets, and HDPE applications such as bottle crates and profiles. It has emerged, for example, that a combination of Recyclostab 451 and Recyclossorb 550 can increase the aging resistance of $CaCO_3$-filled recycled PP material obtained from garden chairs to such an extent that it can be re-used in the same application (**Fig. 2**) [3]. Particularly high stability is achieved in this case if long-term stabilization with antioxidants/HALS is augmented with a repair system (Recycloblend 660, see below) to deactivate the filler.

Reactive Molecules and Repair Systems

Stabilizers can generally only retain their existing properties for a certain length of time, albeit an extended one. It is therefore not possible to heal a damaged polymer that, for example, has suffered from molecular weight degradation. However, polycondensation polymers, e.g. polyesters and polyamides, contain end groups (-OH, -COOH, -NH_2), which can be made to react with suitable partners, and to effect molecular-weight buildup. Since the molecular weight also defines the original properties, this affords a way of repairing damage at the same time. Such additives have come to be known as repair additives or repair systems. They are also often referred to simply as chain extenders. They are generally bifunctional reactive molecules because higher functionalities lead to branching and possibly to unwanted crosslinking reactions. The relevant compounds are based on epoxides, oxazolines, oxazolones, oxazines, isocyanates, anhydrides, acyl lactams, maleimides, phosphonites, cyanates, alcohols, carbodiimides and esters [4, 5]. Commercial products include a bisoxazoline sold as Nexamite PBO (from Nexam Chemical, Lund, Sweden), a polymeric carbodiimide sold as Stabilizer 9000 (Raschig GmbH, Ludwigshafen, Germany) and Stabaxol P (Rheinchemie Rheinau GmbH, Mannheim, Germany). Many other chain extenders are available commercially. Often, combinations with branching agents and/or catalysts/activators are offered whose purpose is to accelerate the reaction process.

One example is a polyethylene terephthalate (PET) composed of different grades (virgin material, production scrap, post-consumer waste) that was made to react with increasing concentrations of pyromellitic acid dianhydride (and small amounts of pentaerythritol as moderator and a phosphonate as catalyst) (**Fig. 3**) [6]. It transpires that the properties of virgin material can be replicated provided that the concentration of incorporated additive is carefully adjusted.

In particular, polymeric repair systems can serve not only to increase molecular weight, but also to render polyamides or polyesters compatible with polymeric contaminants. The outcome is an increase in typical molecular weight-dependent properties, such as mechanical characteristics, tensile strength and elongation, heat resistance and impact strength. Typical applications include PET bottle material and recycled polyamide (PA) carpet. Commercial products include alternating copolymers of maleic anhydride-ethylene (ZeMac from Vertellus Specialties, Indianapolis, Indiana, USA; sales: C.H. Erbslöh GmbH & Co. KG, Krefeld, Germany), Joncryl (polystyrene polyacrylate polyglycidyl copolymers from BTC Europe GmbH, Monheim, Germany), styrene-maleic anhydride copolymers (e.g. SMA 9000P from Total Cray Valley, Paris, France) as well as products from PolyAd Services, such as PolyAd PET stabilizer technology and PolyAd solution.

Products also recommended for enhancing polyamides contaminated with polyolefins are Fusabond P353 and Fusabond P613 (maleic anhydride-grafted polypropylene (PP) with varying degrees of grafting from DuPont Packaging & Industrial Polymers, Geneva, Switzerland) while polyesters can be enhanced with Elvaloy PTW (polyethylene-butyl acrylate-glycidyl methacrylate copolymer) or Elvaloy AC (polyethylene-butyl acrylate copolymer from DuPont Packaging & Industrial Polymers).

Whereas efforts to improve the properties of polycondensation polymers, such as polyamides and polyesters, usually take the form of molecular weight building, the corresponding emphasis in the case of polypropylene or PP/HDPE recycled materials is on controlled molecular weight decrease/increased flow. Molecular-weight-reducing products based on free-radical generators are sold under the trade names Irgatec CR 76 (BASF SE, Ludwigshafen, Germany) and Struktol RP 11 (Struktol Company of America, Stow, Ohio, USA).

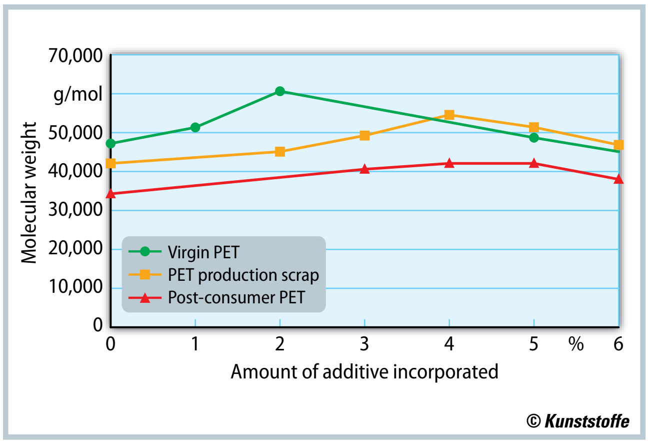

Fig. 3. Molecular weight buildup of PET through addition of dianhydride

Compatibilizers Enhance Properties

Polymers that differ in structure are immiscible with one another for thermodynamic reasons and so do not form homogeneous blends. The polymer which is present in the higher concentration will generally form the continuous phase, and the polymer present in lower concentration will be dispersed in it. As there is relatively little adhesion between the continuous and the dispersed phase, these blends possess poor mechanical properties. Compatibilizers are therefore frequently added to boost the mechanical properties of polymer blends and recycled materials obtained from polymer mixtures. By lowering the interfacial tension between the polymers, stabilizing the dispersed phase against agglomeration, increasing adhesion between the interfaces and reducing phase separation, they help to prevent delamination in the solid. From a structural point of view, compatibilizers are often related to impact modifiers.

The choice of compatibilizers depends on the molecular structures of the polymers to be blended and they will generally contain structural elements contained by those components. As a result, a universal compatibilizer for all conceivable polymer blends is scarcely feasible. Accordingly, suitable compatibilizers in adjusted compositions and amounts are described for specific mixtures of recycled materials. In order to produce a significant effect, the concentrations of compatibilizers usually need to be above 5%.

Compatibilizers offered for recycled materials are chiefly aimed at the following areas of application: polyolefin blends of PE and PP, polyolefins contaminated with low levels of polar polymers such as PA and EVOH (e.g. from plastic films) and polyamides and/or polyesters contaminated with (low amounts of) polyolefins.

A number of different products are available as compatibilizers for polyolefin blends. Specifically for this purpose, polymer manufacturers offer polyolefin copolymers and elastomers, e.g. Engage 8100 (ethylene-octene copolymer, Dow Europe, Horgen, Switzerland), Infuse 9500 (polyolefin block copolymer, Dow Europe) and Entira EP (DuPont Packaging & Industrial Polymers). Further suitable alternatives are the Kraton grades (Kraton Performance Polymers, Amsterdam, Netherlands), Recycloblend 720 (PolyAd Services) and, for mixtures from bottle caps (1:1 PP/PE), PolyAd Bottlecap Stabilizer (PolyAd Services) along with Ken-React KPR Rezyk-1240 (from Kenrich Petrochemicals Inc, St. Bayonne, New Jersey, USA; sales: Farrl GmbH, Neu-Isenburg, Germany). For example, the addition of copolymers such as Entira EP 1754 can significantly boost the notched-impact strength of polyolefin blends (**Fig. 4**).

A very wide range exists for the compatibilization of polar polymers in polyolefins. The method of choice utilizes polymers with reactive groups (see also repair additives above). The most commonly employed here are maleic anhydride-grafted polyolefins. Relevant providers are DuPont Packaging & Industrial Polymers with Fusabond E 226 (polyethylene), P 353 (polypropylene), and M 603 (Random PP/PE copolymer), Dow Europe with Amplify GR 205 (HDPE base) and GR 216 (polyolefin elastomer), ExxonMobil Chemical Central Europe GmbH, Cologne, Germany, with Exxelor PO 1020 (PP homopolymer) and Exxelor VA 1803 (amorphous polyethylene copoly- »

Addition of SEBS-g-MA [%]	Elongation at break [%]	Impact strength [J/m]	Mean diameter of PET particles [µm]
0	5	27	7.5
2.5	140	54	4.5
5.0	250	88	3.2
7.5	285	108	2.9
10.0	320	123	2.7

Table 1. Effect of compatibilizers as illustrated by a PP/PET blend

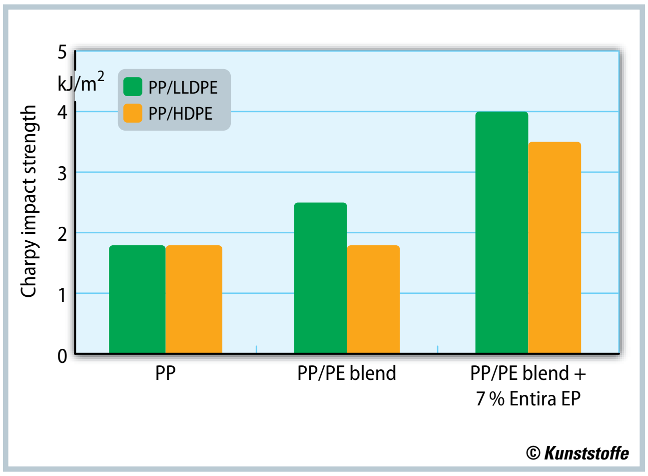

Fig. 4. Improvement in the mechanical properties of plastic blends (PP homopolymer with LLDPE and/or HDPE) due to the addition of a compatibilizer based on ethylene copolymer (EP Entira 1754; data: DuPont Packaging & Industrial Polymers)

mer), and Kraton Performance Polymers Inc. with FG1901 or FG1924 (SEBS with 30 % or 13 % styrene fraction). Polyamide-polyethylene blends can be compatibilized with products from the Apolhya series (Arkema GmbH, Düsseldorf, Germany). These are polyolefin-grafted PA6. Compatibilizer variants containing further reactive polar groups are ethylene-glycidyl methacrylate copolymers, e.g. Lotader AX8840, Lotader AX 8900 (Arkema GmbH) and Joncryl ADR (BTC Europe GmbH). A further variant is maleic anhydride-grafted ethylene-butyl acrylate copolymers such as Lucofin 1494H (Lucobit AG, Wesseling, Germany). As with all reactive compatibilizers, relatively high quantities (about 10 %) must be added in order that a significant improvement may be achieved in the impact strength of an inhomogeneous blend, whereas it only takes lesser amounts to elicit significant improvements in elongation [7].

A major effect of the compatibilizer in incompatible blends is to improve the mechanical characteristics to the extent that it can become a ductile material. These correlate well with the reduced particle sizes of the dispersed phase, as illustrated by SEBS-g-MAH in a PP/PET blend (**Table 1**) [8].

Also on the market are compatibilizers for other, more unusual mixtures of recycled materials. For example, Resalloy 165 and Resalloy 109 (Resirene SA, Tlaxcala, Mexico), which are based on polystyrene-epoxy copolymers, offer compatibilization of HIPS/PC and HIPS/PET, while Resalloy 285, a maleic anhydride-functionalized ABS, can compatibilize PA+ABS and PC+ABS. In all cases, there is a marked improvement in the impact strength, elongation at break and ease of processing of the blends.

Enhancing and Eliminating Odors

Due to prior applications, such as food packaging, but also as a result of degradation, some recycled materials contain contaminants which, even when present only in traces, give rise to an unpleasant, intolerable odor during processing and in the subsequent application. A number of additives for masking, eliminating or at least mitigating these unwanted odors are commercially available. Odors can be eliminated with odor absorbers, such as zeolites, which can sequester the molecules inside their cage structure. A longer-lasting effect is provided by reactive additives, which enter into a chemical reaction with the functional groups of the compounds responsible for the odor (often sulfurous components or amines) and convert them into non-volatile compounds that no longer smell. This is the approach underpinning the action of zinc ricinoleate (Tego Sorb PY 88; Evonik Industries AG, Essen, Germany), which can initiate a reaction with hydrogen sulfide, mercaptans, thioethers and amines. Struktol RP 17 (Struktol Company of America) offers a combination of lubrication and deodorization. Generally, all reactive compounds can contribute to odor minimization, e.g. Recycloblend 660 (PolyAd Services), which contains oxirane groups that enter into reaction with, e.g., acids and amines.

Outlook

The use of recycled plastics in high-quality applications is no longer wishful thinking, but a reality nowadays. Additives such as customized stabilizer systems and polymeric additives in the form of reactive and non-reactive compatibilizers are making great contributions here. The number of possible recycled additives and providers has increased significantly in recent years, with the result that the challenge now is to develop the best technical and economical solution for the desired property profile. In this regard, the Plastics Division of the Fraunhofer LBF, Darmstadt, acts as a neutral development partner that continually undertakes projects aimed at expanding the corpus of knowledge of recycled materials. ■

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