Secondary Raw Materials of the Future

Recycling Halogen-Free Flame-Retardant Plastics. Example: Polyamide

At present, flame-retardant plastic parts past their service lifetime are predominantly used energetically. The further development of the circular economy makes it necessary to rethink materials recycling. However, this issue becomes increasingly complex wherever such additives as flame retardants, fibers, or fillers are used.

Flame-retardant plastics have to guarantee safe fire protection. Flame-retardant additives either prevent plastics from igniting, or significantly delay the spread of fire. The total annual demand for flame-retardant additives in the European Union amounts to approx. 500 kt/a, and its annual growth rate until 2025 is estimated at 5 to 7 wt. %. For well-known reasons, halogen-free flame-retardants are increasingly relied upon that currently have a market share of 70 wt. % [1].

Their commercially relevant fields of use include electrical and electronic applications as well as building construction and transportation. After their often decade-long duration of use, halogen-free flame-retarded plastic parts mainly find energetic utilization. However, given a market value of some EUR 6.14 billion for the flame retardant component alone, there exists considerable potential for their use as replacements for primary raw materials [2].

Prerequisites for Materials Recycling

For ecological and economic reasons, materials recycling is advantageous if the material flow is sorted and clean. New raw materials are not required when thermoplastics are recycled in a remelting process at minimal energy input. This would create economical replacements for new materials and conserve resources at the same time. Recycled plastics differ fundamentally from new materials. Plastics can become irreversibly altered during processing and application processes [3]. In the case of flame-retardant plastics, the flame inhibiting additives can also be subject to degradation processes and, in some cases, no longer guarantee safe flame protection in long term applications. This risk grows proportionately as the application grows more demanding, and/or the number of previous recyclings increases. Potential raw materials sources include wastes from plastics processing (post-industrial) and from their application (post-consumer). Post-industrial wastes, such as injection residues and faulty batches, are already being recycled and provide a single-variety or defined composition. Post-consumer wastes have to be sorted by suitable processes and be specially prepared. Whether it is worthwhile to sort out and purify these materials has not yet been univocally established.

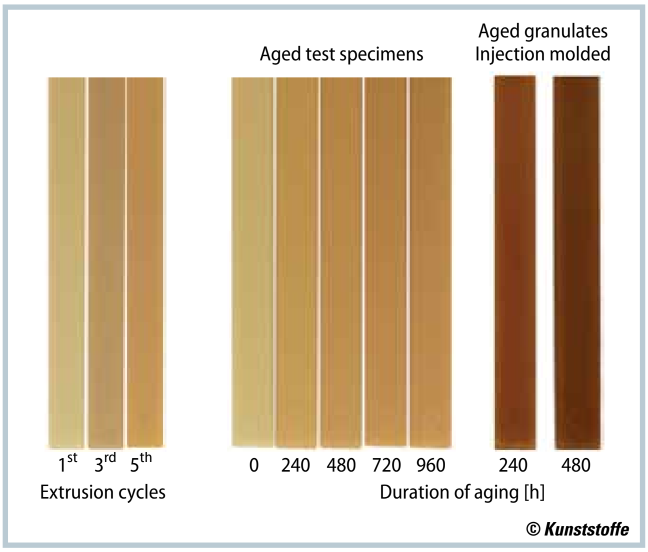

Fig. 1. Discoloration of 1.6 mm thick test specimens for determining fire behavior (UL94) due to influence from multi-extrusion, test specimen aging, and injection molded test specimens from aged granulate (source: Fraunhofer LBF)

Flame Retarded, Glass Fiber-Reinforced Polyamide

In order to find a satisfactory answer to this question, the recycling of such materials was systematically investigated as part of a multi-year project. Market-relevant model formulations were selected from representatives of various classes of polymers (PE, PP, PC/ABS) that were equipped with halogen-free flame-retardants (HFFR) specific to the substrate.

Glass fiber-reinforced polyamide 6 (PA6) and PA66 with flame retardants are used mainly in the electrotechnical/electronics (E&E) as well as the automobile industries [4]. Additives based on metal phosphinates, such as Exolit OP types from Clariant SE of Muttenz, Switzerland, have proven effective in making these materials flame retardant. For the present investigations, an aluminum diethylphosphinate was used in combination with another phosphoric synergist. In case of fire, these materials form a nonflammable, thermally insulating layer »

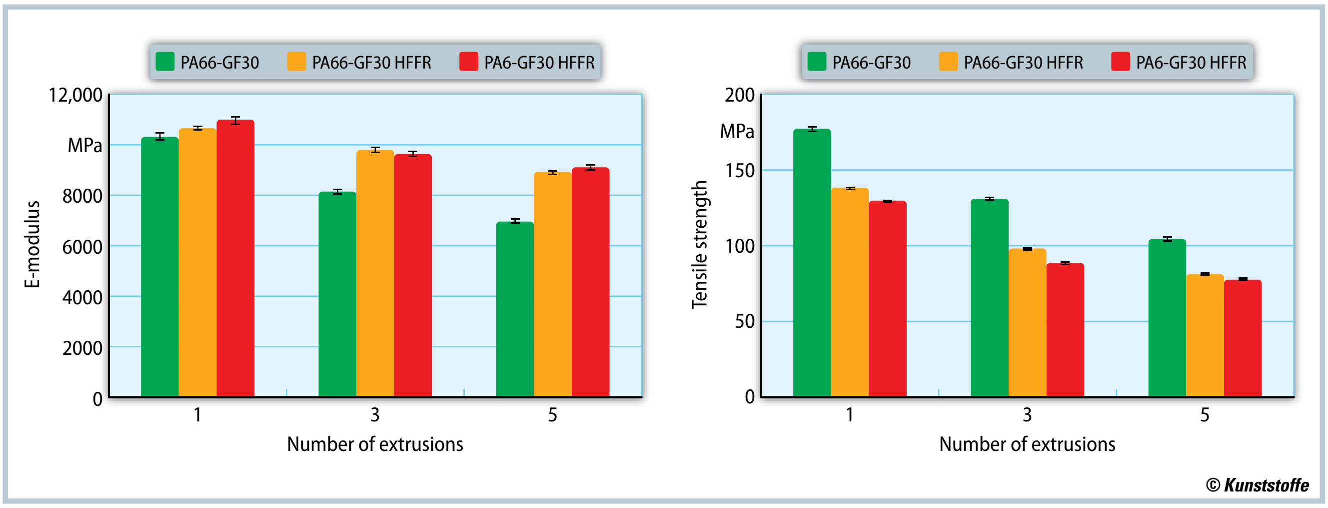

Fig. 2. Influence from multi-extrusion on the mechanical characteristics E-modulus and tensile strength (source: Fraunhofer LBF)

at the surface that acts as barrier against atmospheric oxygen and escaping fumes.

Materials Recycling of Flame-Retardant Polyamides

The investigation of materials recycling of flame-retardant glass fiber-reinforced polyamides involved five extrusion cycles with granulation and intermediate drying of each material as well as the injection molding of test specimens. To investigate the influence of thermo-oxidative degradation processes in actual use, accelerated aging texts were performed under air atmosphere. The results of repeated preparation and use on property profiles were analyzed using capillary rheometry, tensile tests (DIN EN ISO 527) and fire hazard testing (IEC 60695-11-10).

Multiple extrusions were performed on a co-rotating twin-screw extruder with vacuum degassing. The extruder's screw design enables removal of low-molecular residual monomers and degradation products to prevent the accumulation of extrudate. Two different screw configurations were used for the five extrusion cycles. For the compounding process, a screw configuration was used that ensures high mixing effectiveness in order to ensure sufficient dispersion of the additives in the polymer matrix. For subsequent extrusions, a transport screw was used in order to keep the mechanical load on the polymer melt as low as possible.

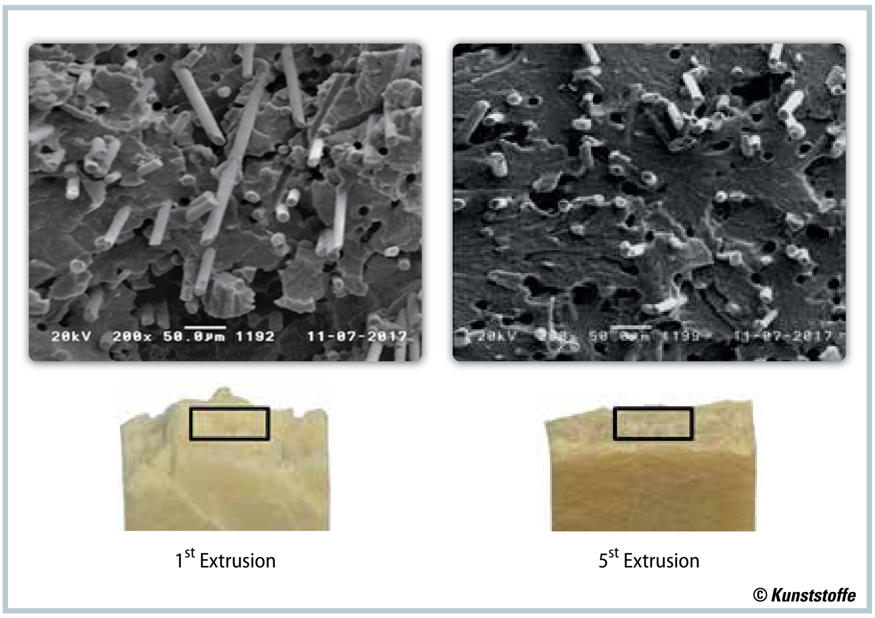

Fig. 3. Fracture surfaces of PA66-GF30 HFFR after the first (left bottom) and fifth extrusion steps (right bottom) under a scanning electron microscope (top) (source: Fraunhofer LBF)

In accelerated aging tests, both granulates and test specimens were subjected to oven storage at 120 °C for up to 1000 h. Aged granulates were also processed to test specimens.

Properties of the Recyclates

Visual checking is the quickest and simplest way to evaluate aging. Functional groups result from processing (**Fig. 1, left**) and oven storage (**Fig. 1, center/right**) that can cause yellowing or browning and thus give indications of the degree of damage.

Mechanical properties were decisively affected as the number of processing cycles increased. After the fifth processing cycle, E-modulus and tensile strength were reduced by 17 % (**Fig. 2, left**) and 40 % (**Fig. 2, right**) respectively. Compared with a glass fiber-reinforced PA66 type without flame retardant, the E-modulus exhibited a strong reduction (39 %) depending on the number of processing cycles, whereas tensile strength remained similar. The flame retardant proved to have no negative influence on mechanical properties from multiple processing.

The macroscopic view of fracture surfaces detected significant differences in the surface structure, as illustrated by PA66-GF30 HFFR after the first and fifth processing cycles in **Figure 3** (**below**). Surface roughness was obviously reduced as the number of processing cycles increased. On closer inspection of the fracture surfaces using a scanning electron microscope (**Fig. 3, top**), it turned out that the glass fibers appearing at the fracture

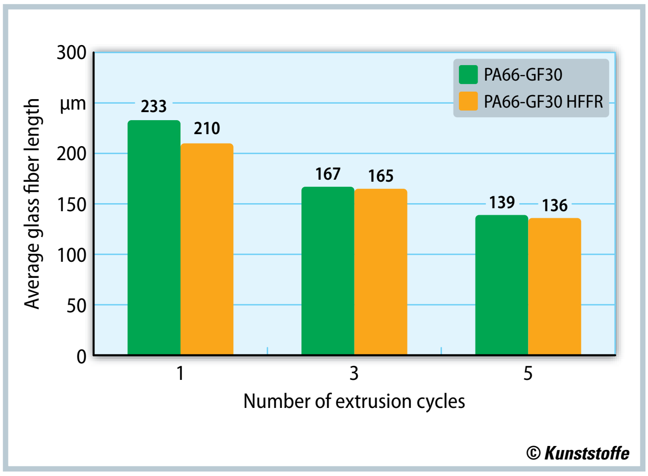

Fig. 4. Influence from multi-extrusion on average glass fiber length (source: Fraunhofer LBF)

surface were severely shortened after the fifth extrusion. Further conclusions as to the loss of glass fiber length were supplied by micro X-ray computed tomography (micro CT), thus enabling precise measurement of average glass fiber length. The reduction in average glass fiber length (**Fig. 4**) correlates directly with the mechanical characteristics E-modulus and tensile strength as determined by the number of processing cycles. Damage to the polymer could be excluded by a determination of molecular weight distribution.

The shorter glass fibers have no negative influence on fire behavior (**Table 1**, **Fig. 5**). The flame retardant polyamides achieved a V-0 classification despite the number of processing cycles. The mechanical characteristics from tensile strain tests subsequent to oven storage show that storage duration has no significant influence on E-modulus (**Fig. 6**, **left**) and tensile strength (**Fig. 6**, **right**). This posi- »

PA66	UL94-test specimen made from PA66-GF30 HFFR (1.6 mm thickness)		UL94-test specimen made from PA66-GF30 HFFR (0.8 mm thickness)	
Extr.	Σt1+t2 [s]	Classification	Σt1+t2 [s]	Classification
1st	9.5	V-0	26.0	V-0
3rd	8.2	V-0	24.9	V-0
5th	8.1	V-0	13.6	V-0
PA6	**UL94-test specimen made from PA6-GF30 HFFR (1.6 mm thickness)**		**UL94-test specimen made from PA6-GF30 HFFR (0.8 mm thickness)**	
Extr.	Σt1+t2 [s]	Classification	Σt1+t2 [s]	Classification
1st	9.3	V-0	26.9	V-0
3rd	4.5	V-0	21.9	V-0
5th	9.8	V-0	12.7	V-0

Table 1. Post fire test: Influence from multi-extrusion on the fire behavior of PA66-GF30 HFFR (top) and PA6-GF30 HFFR (bottom). The indicated total number of times (Σt1+t2) corresponds to the sum of five tested specimens (source: Fraunhofer LBF)

PA66-GF30 HFFR		UL94-test specimen (1.6 mm thickness)		UL94-test specimen (0.8 mm thickness	
	Duration of aging [h]	Σt1+t2 [s]	Classification	Σt1+t2 [s]	Classification
Test specimen aging	0	5.5	V-0	26.0	V-0
	240	23.8	V-0	14.1	V-0
	480	8.6	V-0	28.0	V-0
	720	10.3	V-0	42.3	V-0
	960	7.6	V-0	14.8	V-0
Granulate aging	240	6.2	V-0	23.7	V-0
	480	11.6	V-0	21.2	V-0

Table 2. Influence from oven aging on fire behavior (UL94). The indicated total number of times (Σt1+t2) corresponds to the sum of five tested specimens (source: Fraunhofer LBF)

The Authors

Christoph Schultheis, M. Sc., is a scientific assistant in the group Additivation; christoph.schultheis@lbf.fraunhofer.de
Dr. Elke Metzsch-Zilligen heads the group Additivation at the Fraunhofer LBF; elke.metzsch-zilligen@lbf.fraunhofer.de
Dr. Rudolf Pfaendner heads the plastics division at the Fraunhofer LBF; rudolf.pfaendner@lbf.fraunhofer.de

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German Version

- Read the German version of the article in our magazine *Kunststoffe* or at *www.kunststoffe.de* tive trend continued with respect to fire behavior. Taking the entire duration of storage into consideration, the flame retardant properties remained the same. It should be emphasized that the test specimens injection molded from aged granulates also achieved a V-0 classification (**Table 2**).

Text specimens manufactured from aged granulates exhibited more intense browning than aged test specimens (**Fig. 1**). Due to higher surface-to-volume ratio, the granulate underwent material oxidation more rapidly than the test specimens.

Usefulness and Conclusion

The investigation results show that halogen-free flame-retardant glass fiber-reinforced polyamides offer unusually great potential for materials recycling. Given appropriate processing, the recyclates can provide a genuine alternative to new material.

In general, it can be said that professional recycling enables optimum use of a material. That is why plastics recycling has been gaining in importance for decades. Deteriorated materials properties can be compensated by targeted stabilizer systems, chain extenders, and compatibilizers that significantly improve recyclate quality. Therein lies the challenge to develop a technical and economical solution for the desired property profile. The goup Additivation at the Fraunhofer Institute for Structural Durability and System Reliability (LBF) has gained extensive expertise in the additivizing of plastics wastes for materials recycling. ■

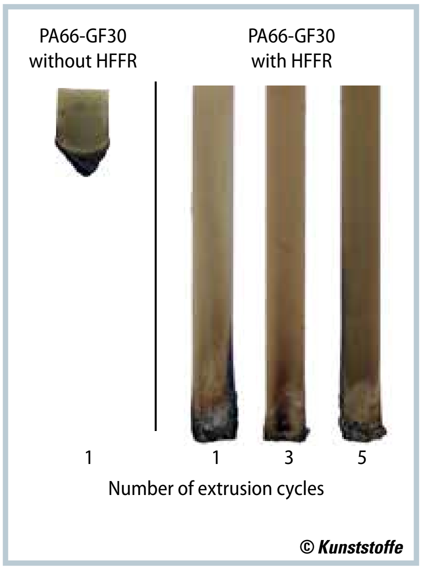

Fig. 5. Multi-extrusion: test specimen after passing the fire test with and without addition of flame-retardant (source: Fraunhofer LBF)

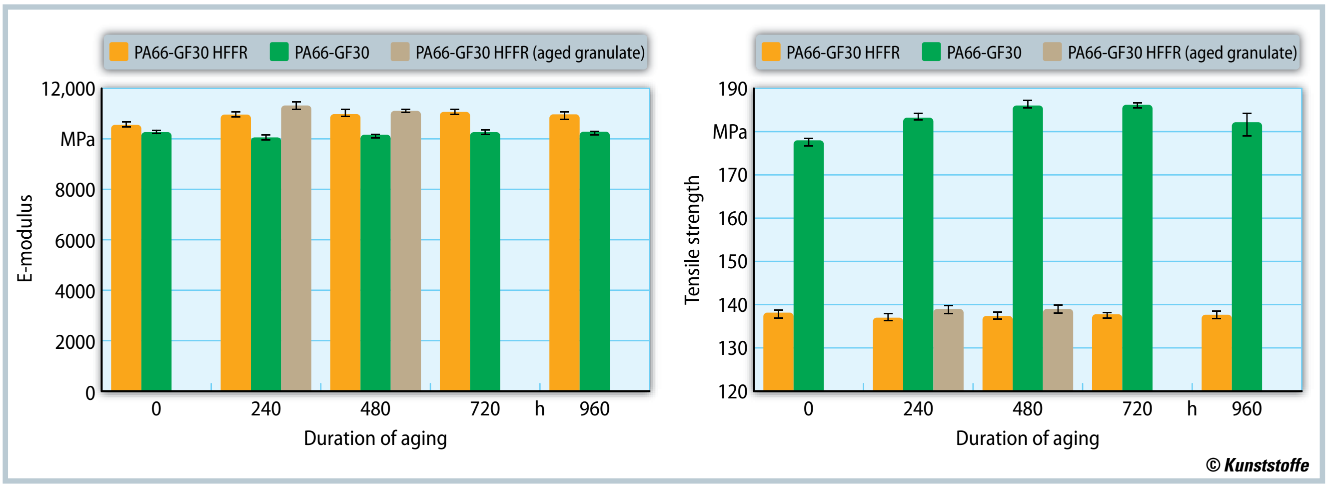

Fig. 6. Influence from oven aging on mechanical characteristics (source: Fraunhofer LBF)