Long-Chained and High-Viscous

High-Viscosity Recyclates from Cast Polyamide 6

In cast polyamides, the catalyst is retained and remains active, causing the material to degrade during processing in the molten state. To preserve the high-value properties of the material after recycling, specific additives are required. Trials show that it is possible to produce high-viscosity polyamides that can find future use in, for example, thermoforming.

From cuttings to recycled pellets: To enable recycled cast polyamides to retain their robust properties, suitable additives were sought and tested (© IKT)

The most frequently used polyamide is polyamide 6. It is produced from the monomer ε-caprolactam via two different synthesis routes, which are shown in **Figure 1**. In hydrolytic polymerization, water is added to initiate ring opening of the caprolactam to give ε-aminocaproic acid, which then reacts with further lactam to form polyamide. This process is used for mass production. Alternatively, anionic caprolactamates can be employed as a catalyst to effect ring-opening polymerization [1, 2]. Because of the reaction conditions, much higher molecular weights can be achieved with this method.

Characteristics of Cast Polyamide

As a rule, anionic, ring-opening polymerization is not carried out in a synthesis reactor to obtain pellets but takes place directly in a casting mold. Polyamides produced by this method are also known as "cast polyamides". As shown in **Figure 2**, moldings of various dimensions can be made in this way. Cast polyamide 6 possesses very good slip properties, high abrasion and wear resistance, and good machinability, so that it is frequently used for plain bearings or pulleys. In addition, it has good mechanical properties, such as high strength, stiffness, and toughness. The superior property spectrum of cast polyamide 6 as compared with conventionally, i.e. hydrolytically, polymerized polyamides (see above) and various other polycondensates can primarily be attributed to its much higher molecular weight. »

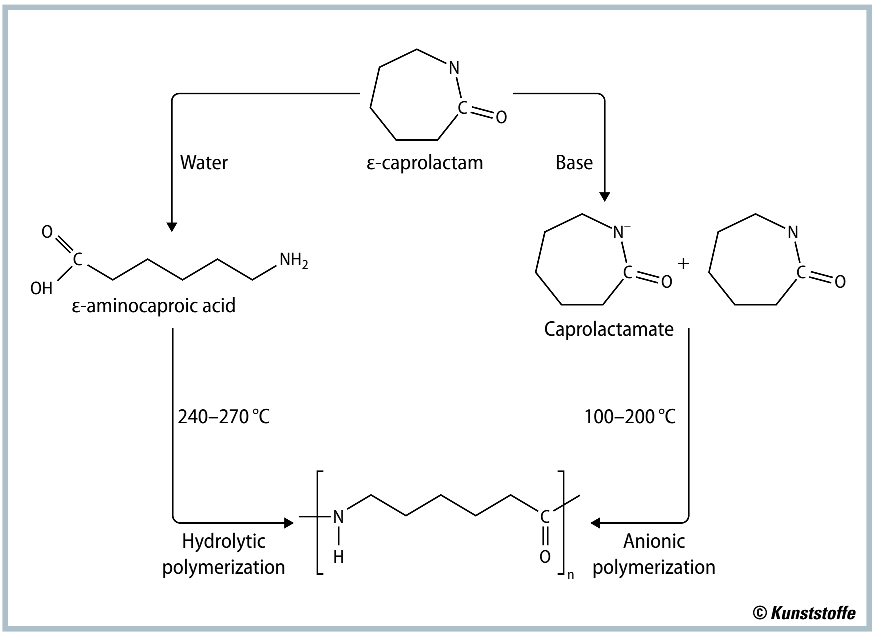

Fig. 1. Synthesis routes for hydrolytic and anionic polymerization of polyamide 6 (source: IKT)

Since the catalyst is retained and remains active in the material, however, cast polyamide degrades during processing in the molten state. This degradation means that recycled cast polyamide has similar mechanical properties to normal commercially available extruded virgin material [2], i.e. reduced values in some areas.

In processing cast polyamide, the amount of scrap (e.g. sprues and runner systems) obtained in the production of components can be up to 10 % of the total production quantity. Due to post-machining and variations in production, the amount of scrap generated can increase to up to 30 % of the material used for a component. Within Europe, this corresponds to a scrap volume of some 5000 t/a.

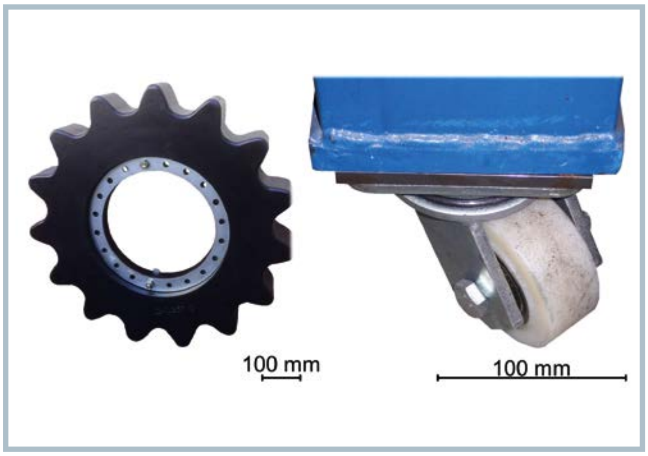

Fig. 2. Gearwheels and pulleys are typical applications for cast polyamide (source: IKT)

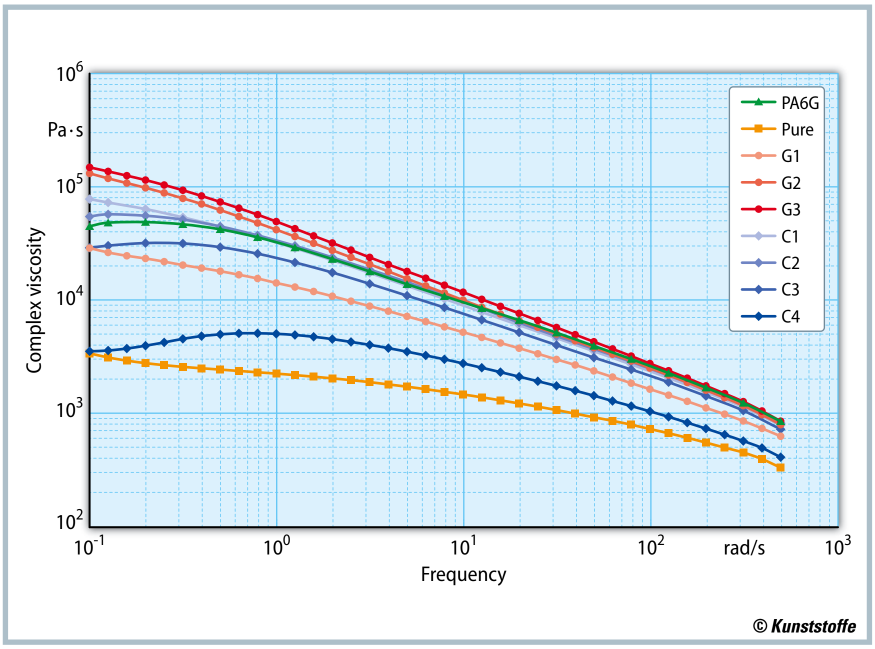

Fig. 3. The viscosities of cast polyamide recyclates with polyester-modified wax (G) and carboxylic acid (C) at 270 °C, partly according to [3] (source: IKT)

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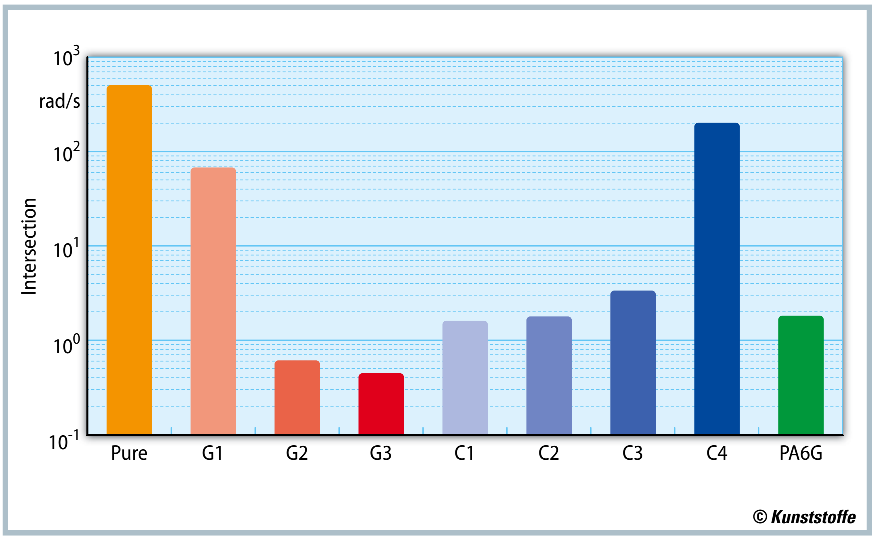

Fig. 4. The intersection of the storage and loss modulus curves of a thermoplastic permits analysis of its average molecular weight. Just small quantities of carboxylic acid achieve a molecular weight similar to the original weight, while larger amounts of wax produce even higher average molecular weights (source: IKT)

Due to their high molecular weight, cast polyamides inherently have a high viscosity, which is reduced during recycling, as the comparison between the cast polyamide PA6G and the "pure" recyclate in **Figure 3** shows. To retain this high viscosity, it is necessary either to prevent molecular weight degradation or to increase molecular weight by incorporating suitable additives.

With this purpose in mind, the Institut für Kunststofftechnik (IKT, Institute of Polymer Technology) at the University of Stuttgart, Germany, is experimenting for the first time with the use of a polyester-modified wax (Ceralene 694, manufacturer: EuroCeras Sp., Kędzierzyn-Koźle, Poland), which is used as a lubricant for polyamides, and a dicarboxylic acid (terephthalic acid, supplier: Merck, Darm- »

Cast polyamide scrap has so far often been thermally recycled, i.e. incinerated for energy and heat recovery. However, because of its high-value properties as described above, cast polyamide 6 offers great potential for material recycling, particularly if its high molecular weight can be retained.

Recycling Cast Polyamide Scrap

The starting material for recycling cast polyamide scrap should be sorted/segregated clean waste, since contaminants can have an adverse effect on subsequent material properties. This is also extremely important for high reproducibility of recyclate properties, especially for technical applications.

Before recycling cast polyamides (both cuttings and sprues) on a twin-screw extruder, the waste material should be pre-ground for better feedability. This is followed by washing to remove smaller-sized contaminants and, in particular, cooling emulsions left over from machining or traces of oil. For recycling, it is also important for the polyamide to be dry when processed and for a degassing zone to be provided in the plant configuration. In the present case, processing was carried out on a co-rotating twin-screw extruder (type: ZSK 26, manufacturer: Coperion GmbH, Stuttgart, Germany) with an L/D ratio of 41.

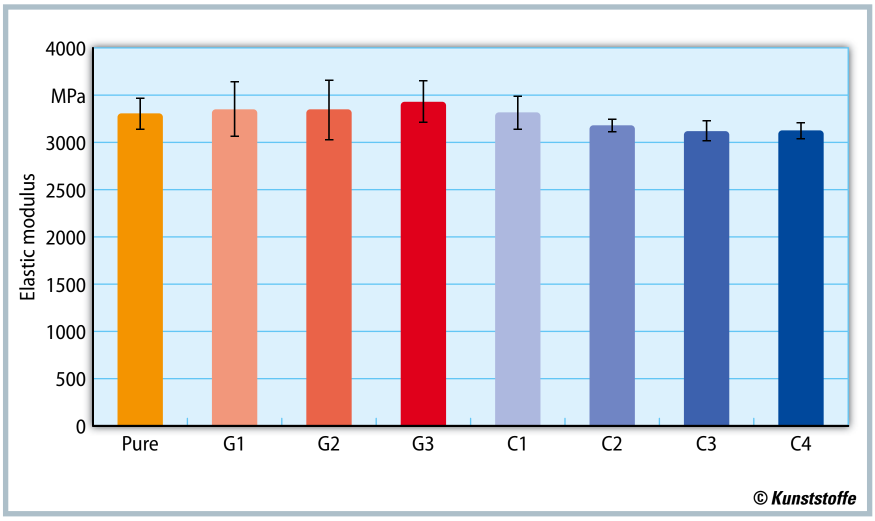

Fig. 5. The elastic modulus of the high-viscosity cast polyamide recyclates, partly according to [3], remains virtually the same, despite different additives (source: IKT)

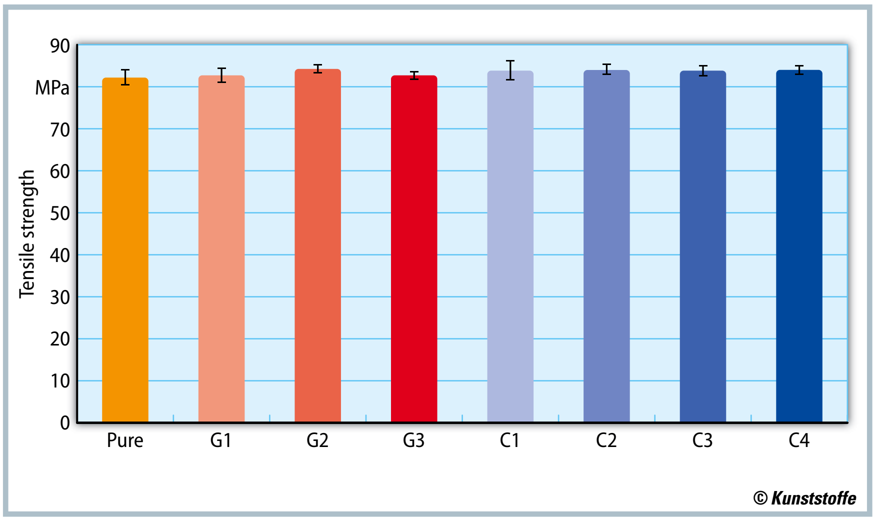

Fig. 6. The tensile strength values of the cast polyamides, partly according to [3], are not influenced by the additives (source: IKT)

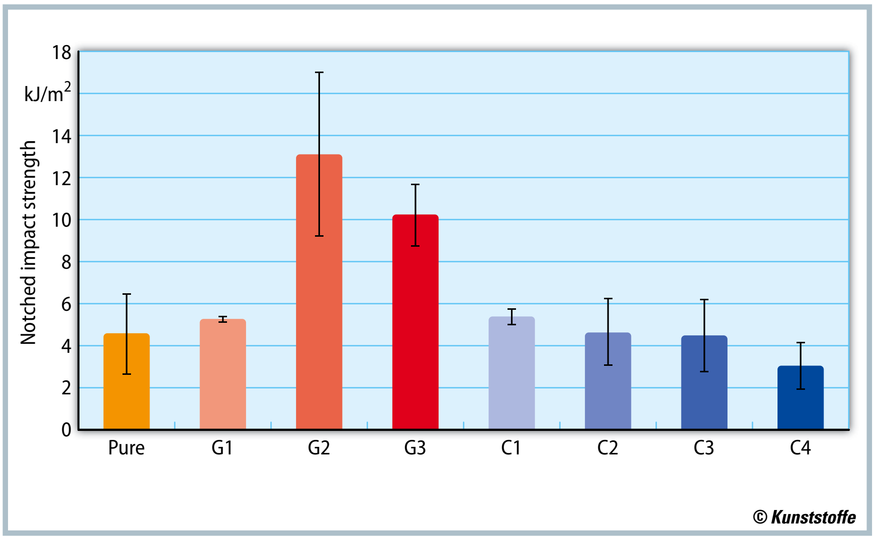

Fig. 7. In their effect on the notched impact strength values of the cast polyamide recyclates, partly according to [3], wax and carboxylic acid show different trends (source: IKT)

stadt, Germany). The cast polyamide is dry mixed before processing with different quantities of additives.

Properties of the Recyclate

As can be seen from the complex viscosity curves (**Fig. 3**), viscosity increases significantly with increasing content of polyester-modified wax (G1–3). It is even possible to achieve higher viscosities than those of the original cast polyamide. However, because of the lubricant effect of the polyester-modified wax, processability is retained.

On addition of small quantities of the dicarboxylic acid (C1–2), similar viscosities to those of the original cast polyamide are achieved. On the other hand, a higher content (C3–4) reduces viscosity again.

In rotational rheological measurements, the storage and loss modulus curves were determined. The crossover point of these curves (**Fig. 4**) pemits comparative analysis of the average molecular weight. An intersection at lower frequencies is equated with a higher average molecular weight [4].

The crossover points of the two curves for cast polyamide 6 occurs at much lower values than for the "pure" recyclate. In the latter case, the crossover point is even outside the measuring range. This indicates the molecular weight degradation already noted in the literature and is consistent with the flow behavior shown.

The crossover points for the additive-modified recyclates and average molecular weights derived from them behave in accordance with the complex viscosity curves in **Figure 3**. It should be pointed out that even small amounts of the carboxylic acid permit an average molecular weight to be obtained similar to that of the original cast polyamide, while larger amounts of the wax give rise to even higher average molecular weights.

Additional studies show that the wax leads to (wide-meshed) crosslinking but the melt is still processable. When carboxylic acid is used, on the other hand, no detectable crosslinking takes place. Examination of mechanical properties (**Figs. 5 to 7**) shows that neither the elastic modulus nor tensile strength is influenced by the additives.

On the other hand, the results of the Charpy notched impact test (**Fig. 7**) are striking. Here two different trends can be shown for the two additives. With carboxylic acid addition, notched impact strength decreases with increasing additive content. The reason for this probably lies in the acid itself. Along with the possibility of chain lengthening, the acid group can also attack the amide groups of the polyamide and so cause chain scission. This is also evident from the reduction in viscosity and average molecular weight described above. With higher additions of the wax, on the other hand, notched impact strength is increased significantly. This fits with the high viscosities and average molecuar weights, as well as the detectable crosslinking.

Conclusion

The trials have shown that the very good properties of cast polyamides can be retained in material recycling. With suitable additives, it is even possible to further increase average molecular weight, while still ensuring processability.

With recyclates of anionically polymerized cast polyamide, chain length and viscosity can be adjusted to suit requirements. High viscosities can be offered, in particular. This opens up the possibility of polyamide formulations that are suitable for thermoforming and blow molding. ■