40   RECYCLING **Reactive Extrusion**

[VEHICLE ENGINEERING]   [MEDICAL TECHNOLOGY]   [PACKAGING]   [ELECTRICAL & ELECTRONICS]   [CONSTRUCTION]   [CONSUMER GOODS]   [LEISURE & SPORTS]   [OPTIC]

Turning Old into New

A Robust Continuous Process for the Chemical Recycling of Polystyrene

Due to their good feed characteristics and self-cleaning properties, twin-screw extruders enable even contaminated post-consumer polystyrene to be depolymerized continuously and efficiently. This opens up a promising recycling route in terms of industrial implementation via renewed polymer synthesis to produce plastic granules with a quality approaching that of virgin material.
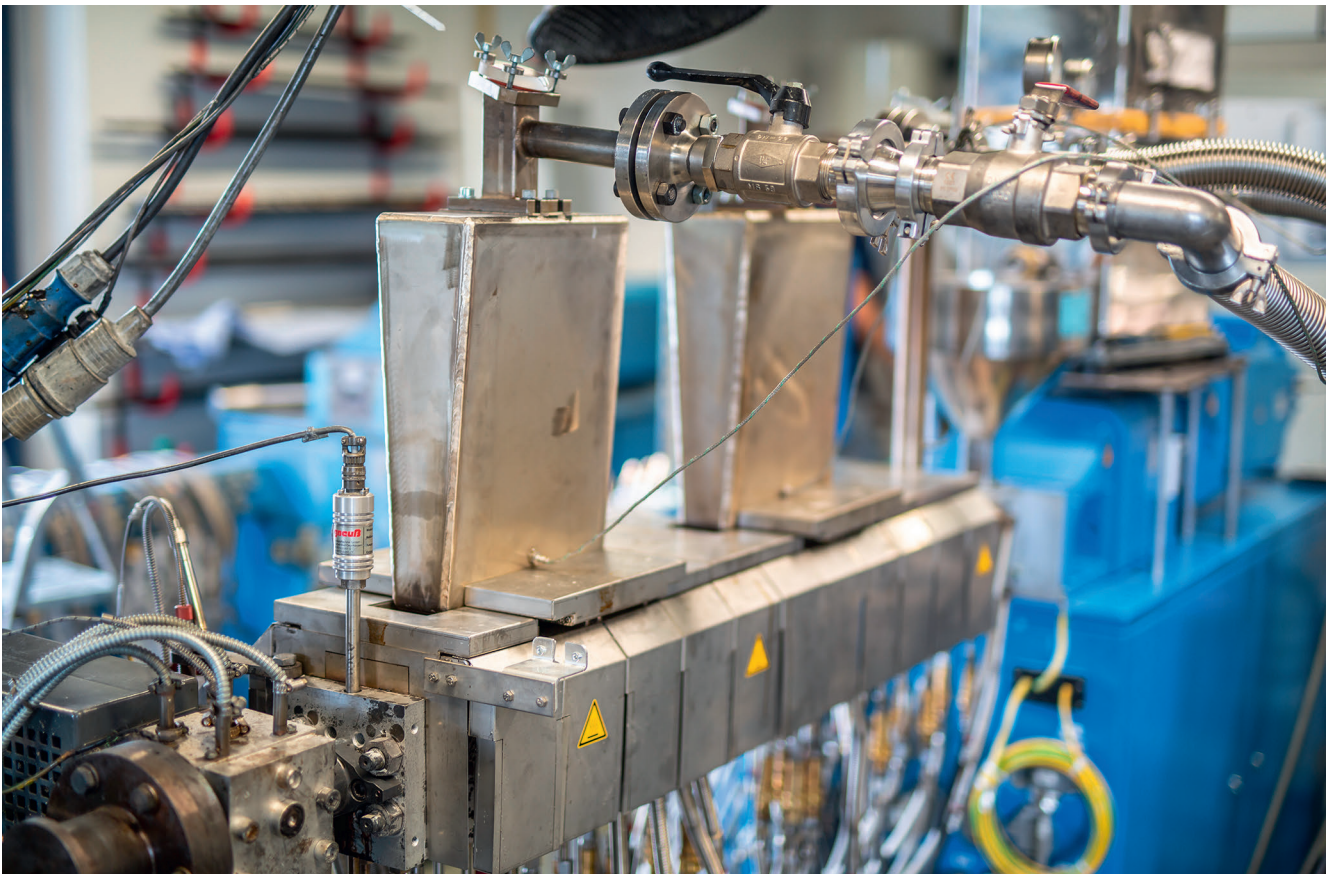
Continuous process in a twin-screw extruder: For industrial implementation of chemical recycling of polystyrene, a reactor technology is required that allows high throughput rates and also processes heavily contaminated post-consumer material continuously with high process stability © IKV

Polystyrene is used to produce a wide variety of food packaging and also for thermal insulation in construction. Especially in the packaging sector, it is often a short-lived disposable product that is disposed of immediately after use. The total amount of polystyrene waste in Europe (EU28+NO/CH) in 2018 was 3.28 million t [1]. This enormous amount of waste makes it necessary to develop efficient recycling methods in order to show alternatives for the utilization of plastic waste for energy. In addition to mechanical recycling, chemical recycling can also be used to return plastic waste to the material cycle [2, 3].

Chemical Recycling of Polystyrene

Besides polymethyl methacrylate (PMMA), polystyrene is one of the polymers that can be depolymerized by splitting the carbon bond, which requires a relatively high activation energy of about 240 kJ/mol [4]. The reaction is affected by exceeding the so-called ceiling temperature, at which polymerization and depolymerization occur at the same rate. A temperature above the ceiling temperature causes the reaction equilibrium to shift in favor of chain degradation. For

polystyrene, this happens at a temperature of 400 °C [5]. With increasing temperature, the reaction speed rises significantly [6]. The reaction also leads to side reactions, so that dimers, trimers, α-methylstyrene and ethylbenzene are formed in addition to styrene (**Fig. 1**). In the absence of oxygen, the reaction starts at a random position along the molecular structure. This produces macro radicals in which the binding energy of the neighboring C-C bonds is reduced, which in turn enables a styrene molecule to be split off from the chain end [7–9].

The chemical recycling of polystyrene can be carried out by several discontinuous processes, for example in a batch reactor. For industrial implementation of the chemical recycling of polystyrene, the achievable throughputs are too low and the sensitivity to contamination of these processes is too high. Therefore, a reactor technology has to be developed which allows high throughputs and at the same time can continuously process highly contaminated postconsumer polystyrene with high process stability [10, 11]. The feasibility of continuous depolymerization of polystyrene in a twin-screw extruder has already been demonstrated [12].

Continuous Depolymerization of Polystyrene in a Twin-Screw Extruder

The continuous depolymerization of polystyrene takes place in a co-rotating, tightly intermeshing twin-screw extruder
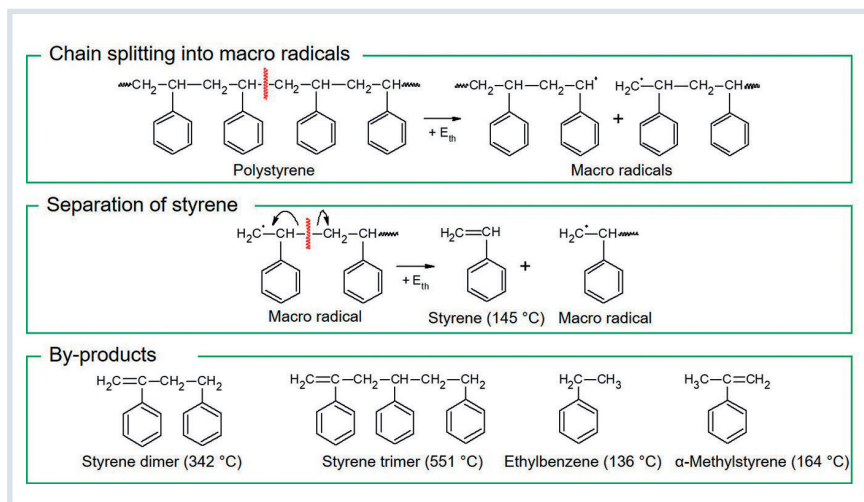

Fig. 1. Depolymerization mechanism of polystyrene to styrene (in brackets: boiling temperatures) © IKV

(DSE). The polystyrene (type: Styrolution PS 156F, manufacturer: Ineos Styrolution Group GmbH, Frankfurt/Main, Germany) is fed into the DSE (type: ZSK 26 Mc, manufacturer: Coperion GmbH, Stuttgart, Germany) by means of a gravimetric screw feeder (manufacturer: Brabender Technologie, Duisburg, Germany). In the melting zone, the plastic is plasticized by the introduction of mechanical energy and by the housing temperature. The residence time depends on the parameters of screw length, mass throughput, screw speed and screw configuration as well as on the input material itself and can therefore be varied over a wide range. Using a vacuum system (manufacturer: Pfeiffer Vacuum, Asslar, and Busch Vacuum Solutions SE, Maulburg, Ger-

many), the gaseous reaction products are removed from the extruder and liquefied in a condenser. Impurities and incompletely degraded polystyrene are discharged from the DSE by the self-cleaning of the screws.

The aim of the depolymerization of polystyrene in the DSE is to process plastic waste with high contamination. After separation and cleaning of the waste according to type, impurities are still present in the plastic stream to be recycled. In addition to foreign matter, these are also fillers and additives that were added to the plastic for customized properties in its original use. Polystyrene is often mixed with stabilizers, antioxidants, flame retardants and colorants [13]. In the packaging industry, fillers »
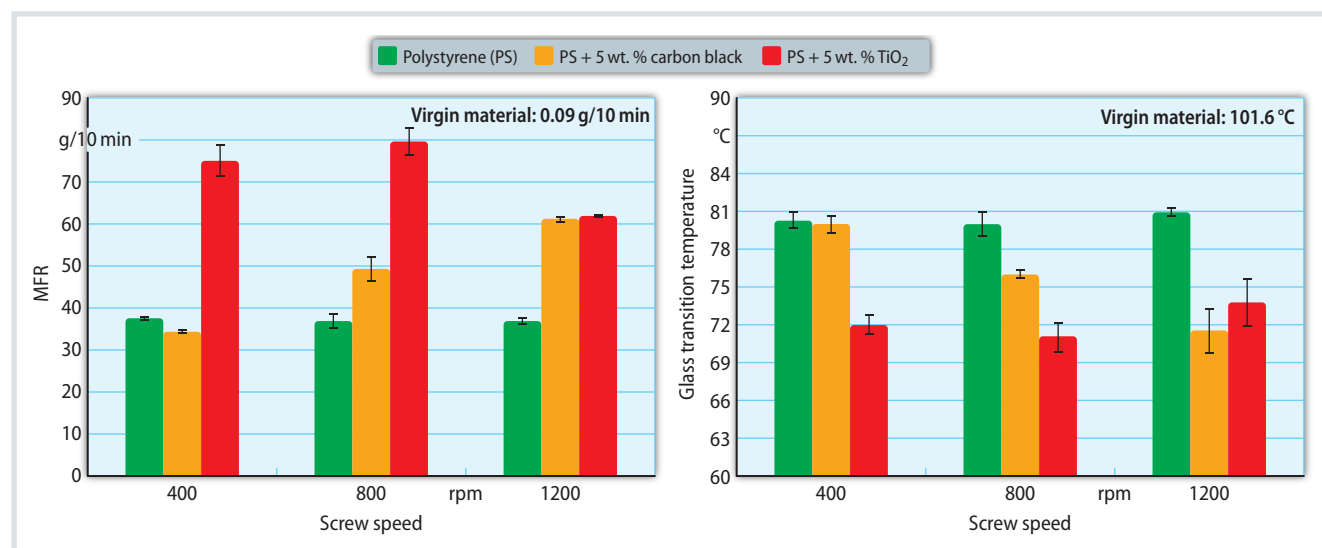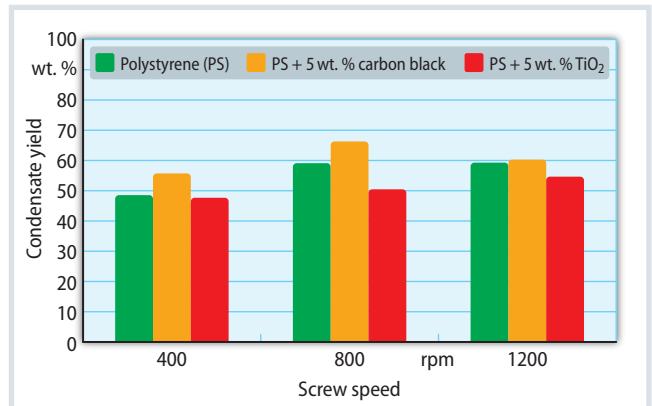

Fig. 2. Characterization of polymer degradation based on melt mass flow rate and glass transition temperature as a function of material composition and screw speed Source: IKV; graphic: © Hanser

Fig. 3. Condensate yield as a function of material composition and screw speed

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are frequently used to color the packaging. Titanium dioxide is often used for white coloration due to its low cost and food compatibility. Optically black polystyrene is usually produced by adding carbon black.

In order to analyze the influence of these fillers on depolymerization, one plastic compound is filled with 5 wt. % titanium dioxide and one with 5 wt. % carbon black. These two plastic compounds will be used to clarify whether the fillers have a negative influence on the continuous depolymerization of polystyrene and whether an industrial conversion is basically feasible.

Influence of Screw Speed and Material Composition

The depolymerization process was performed at a housing temperature of 450 °C and a vacuum pressure of 400 mbar. The mass throughput was 10 kg/h, the screw speed was varied (400, 800 and 1200 rpm). This process parameter selection is based on preliminary work [12]. Over a period of 5 min, both the discharged residue and the condensate were weighed. Additional condensate and residue samples were used for material analysis.

The thermally or mechanically induced degradation of polystyrene was estimated by studying the melt flow rate (MFR) and differential scanning calorimetry (DSC). A higher melt flow rate due to depolymerization and the resultant reduced viscosity allows conclusions about degradation. The reason for the change in viscosity is the advancing chain degradation, which can also be observed by a reduced glass transition temperature in DSC. The heating rate in the DSC

measurements was 20 K/min. A triple determination was performed, whereby the test chamber was flushed with nitrogen. The glass transition temperature is determined during the second heating cycle, thus ensuring a comparable thermal history. Furthermore, the condensate yield as well as the chemical composition of the condensate were determined by gas chromatography by Neue Materialien Bayreuth GmbH, Bayreuth, Germany, and evaluated at IKV.

The influence of the fillers on the melt mass flow rate and glass transition temperature is shown in **Figure 2**. The MFR values obtained are between 34.3 and 79.65 g/10 min. In the case of unfilled polystyrene, the MFR in the delivery state is 0.09 g/10 min. In contrast, a clear influence of the screw speed on the MFR can be seen at a carbon black content of 5 wt. %. The MFR value increases from 34.3 g/10 min at a screw speed of 400 rpm to 61.1 g/10 min at 1200 rpm. As a result of the increased surface renewal at increasing screw speed, the polystyrene is degraded more strongly and a higher MFR value is achieved. Titanium dioxide as a filler does not lead to a clear effect. At a low screw speed (400 rpm) a high MFR value of 75 g/10 min is achieved. In contrast to carbon black, a high screw speed leads to a reduced MFR value of 61.85 g/10 min.

These trends are also confirmed by observing the glass transition temperature. The glass transition temperature drops from 80.0 °C at 400 rpm to 71.5 °C at 1200 rpm with a carbon black content of 5 wt. %. and indicates an increasing molecular degradation with increasing speed. Titanium dioxide achieves a higher molecular degradation at 400 and 800 rpm compared to carbon black and
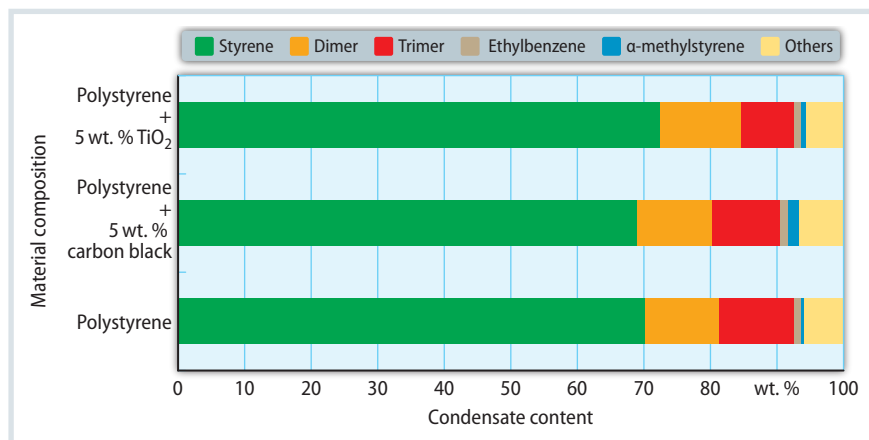
Fig. 4. Composition of the condensates depending on the input materials Source: IKV; graphic: © Hanser

unfilled PS (higher MFR value; lower glass transition temperature). In contrast, a high screw speed of 1200 rpm leads to a higher glass transition temperature for titanium dioxide. One possible reason is that the reaction products of depolymerization cannot be removed fast enough via the vacuum system and the reaction is inhibited.

Figure 3 shows the dependence of the condensate yield for the test materials as a function of the screw speed. The yield is generally in the range of 47.4 to 66 wt.%. The maximum yield of 66 wt.% is achieved by polystyrene with a carbon black content of 5 wt.% at a screw speed of 800 rpm. PS with 5 wt.% carbon black achieves the highest condensate yield for each screw speed. The increase in speed also tends to lead to higher yields. One explanation for this is that the increased speed increases surface renewal and thus the reaction products can be removed more quickly. In addition, a higher speed also reduces the dwell time of the materi-

al in the twin-screw extruder, so that an optimum is achieved for the material. For the carbon black-filled material, the optimum is 800 rpm, while for titanium-filled and unfilled PS it is 1200 rpm. In general, however, the tests show that the condensate yield for carbon black and titanium dioxide is at the same level or higher than for unfilled polystyrene and therefore has no negative influence on the process in this respect.

Figure 4 shows the condensate composition for the test materials determined by gas chromatography measurements at a screw speed of 1200 rpm. The styrene content in the condensate is highest for titanium dioxide at 72.5 wt.%. The compound with 5 wt.%. carbon black achieves the lowest styrene content of 69 wt.%. Unfilled PS showed a styrene content of 70.4 wt.%. Based on the tests, there seems to be a small influence of the fillers on the side reactions, so that the sum of the corresponding products has a higher proportion for carbon black

and a lower proportion for titanium dioxide. However, the styrene fractions are very similar, so that no significant negative influence due to the presence of fillers was found.

Overall, for an input mass flow of 10 kg/h and the respective optimum screw speeds, the results of condensate yield and composition result in a calculated styrene yield of 4.1 kg/h for titanium dioxide, 4.3 kg/h for carbon black and 4.3 kg/h for pure polystyrene. Therefore, contamination with the fillers carbon black and titanium dioxide in the test chamber under consideration does not have a negative effect on depolymerization.

Conclusion

The addition of carbon black and titanium dioxide influences the reaction equilibrium of the depolymerization and the associated styrene content in the condensate. Especially when processing plastic waste, the results of depolymerization cannot be estimated due to different fillers. Compared to pure polystyrene, plastic compounds filled with carbon black achieve a higher condensate yield of up to 7 wt.%. The condensate composition is only slightly influenced by the addition of carbon black or titanium dioxide. Nevertheless, the depolymerization of polystyrene with carbon black and titanium dioxide achieves a comparable styrene yield in condensate of 4.1 to 4.3 kg/h. The depolymerization of polystyrene in a twin-screw extruder thus represents a robust process for the chemical recycling of polystyrene. ∎