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Long chain branching as an innovative up-cycling process of polypropylene post-consumer waste – Possibilities and limitations

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ABSTRACT

Long chain branching (LCB) was used the first time as an innovative tool for value adding to PP from household post-consumer waste. Due to the highly improved melt properties, the possible application profile is extended and not only a "re-cycling" process, even a real "up-cycling" is presented. The used PP was collected from commingled household polyolefin waste, which contained different types of PP and macromolecular impurities such as 10% of polyethylene with high density (PE-HD). In addition, a single PP waste fraction from cleaned beverage and yoghurt cups was manually sorted. The up-cycled PP from single polymer waste, as well as the post-consumer blend, showed pronounced strain hardening and increased melt strength, which was comparable to LCB-PP prepared from virgin PP. However, the up-cycled post-consumer blend showed weaker mechanical performance especially low elongation at break due to PE-HD.

1. Introduction

Polypropylene (PP) with a share of 19.1% on European plastic demand in 2015 is the second most important polymer. Together with polyethylene (PE), these two polyolefins represent 48.5% of the European plastic demand. In case of PP, about one-half of the produced material is used for packaging and therefore for single use. So nearly half of the produced PP ends up after a short period of use as post-consumer waste. 25.8 million tons of plastic waste accrued in Europe in 2014, 30.8% went to landfill, 39.5% were incinerated for energy recovery and 29.7% were mechanically or chemically recycled. Despite increasing recycling rates, incineration or energy recovery still is the preferred option for the treatment of mixed municipal plastics waste especially in Europe (PlasticsEurope, 2016).

Because of the continuously changing composition of the material that has to be sorted, mechanical recycling of post-consumer PP has appeared to be a tough challenge (Cimpan et al., 2015). Most plastics are not miscible and the resulting phase separation influences Young's modulus and other mechanical properties negatively (Goodship, 2007). Several studies have shown that up to 10% of foreign material still remain in recycled PP after sorting by trained personnel (Brandrup, 1996). Sink-float with water as medium is a cost effective standard separation technology for commingled polymer waste. Polyolefin fractions containing PE and PP can be separated from plastics with a specific gravity higher than 1 g/cm^3 (like Polyvinylchloride and Polyethylene terephthalate). However, the polyolefin mixtures are not suitable for high quality products, for this, the content of the main component PP or PE respectively, should be higher than 97% (Bakker et al., 2009). Nonetheless, it is worth noting, that physical processing and sorting technologies have reached a high standard during the last decades (Serranti et al., 2015) which also allows a sorting of single polymer waste by colour (Safavi et al., 2010).

Furthermore, PP undergoes thermo-mechanical, thermo-oxidative and shear-induced degradation during product life and through mechanical recycling. This results in a decrease of the molar mass and a deterioration of the mechanical properties (Incarnato et al., 1999; da Costa et al., 2007), and therefore, results in an economic disadvantage of recycled PP compared to virgin material. The prices for recycling-grade PP granules fluctuate strongly, the average price over the first half year 2017 is about 0.78 ± 0.14 €/kg. Virgin grade PP granules compete with a price of 0.79 ± 0.05 €/kg at the same period (Plasticker, 2017). To improve the mechanical and thermal properties and therefore the competitiveness of recycled PP, additives such as mineral fillers and elastomers can be added (Brachet et al., 2008). Elastomers like ethylene-propylene-rubber (EPR) are also capable to compensate negative side effects of PP-blends with PE impurities (Teh et al.,

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1994). However, HMS-PP (high melt strength PP), a special PP-type for foaming and film blowing is currently traded with a price 0.50 €/kg higher compared to standard linear PP resins. That means that there is some space for modification from the economic point of view.

Long chain branching (LCB) is a well-known industrial post-reactor process to produce PP with high melt strength and strain hardening (HMS-PP). Furthermore, the molar mass is increased and the molar mass distribution is broadened (Gotsis et al., 2004). LCB is a combination of radical induced activation of PP, partial chain scission and recombination. At temperatures below the melting point of PP (solid phase reaction), recombination overwhelms chain scission. This reverses in melt, so the PP macroradical needs to be stabilized with special co-agents. A reaction scheme is given in Fig. 1.

Important studies on the mechanism of LCB formation are reported by (Rätzsch, 1999). Several methods are reported in literature, e.g. LCB-PP can be produced by electron beam irradiation in solid phase (Auhl et al., 2004) – Ampleo™ by Braskem –, by branching in melt with a monomer and peroxide (Zhang et al., 2013) – Daploy™ by Borealis – or by reactive extrusion with peroxydicarbonates (PODIC) with long aliphatic side chains (Lagendijk et al., 2001). Due to its higher melt strength and strain hardening, LCP-PP finds application in film blowing and foaming processes for which linear PP is not suitable (Stange and Münstedt, 2006; Stange et al., 2005).

In our previous work (Kamleitner et al., 2017) model mixtures from PP and PP containing 10% PE-HD as impurity (both from virgin film grade material; the viscosity ratio of dispersed PE in matrix PP ≈ 1:6 at 180 °C) were long chain branched according to (Wong and Baker, 1997) and (Lagendijk et al., 2001) respectively. Each modified sample showed strain hardening behaviour and mechanical properties increased significantly, despite the PE-HD impurities.

LCB offers the possibility to extend the application profile of recycled material to higher value applications like blow moulded films and foams and has high potential to become an innovative recycling process, which contains a value adding to PP. Consequently, if "down-cycling" is used for low value application of recycled material, one can speak of "up-cycling" in the case of LCB of PP post-consumer waste, which is emphasised in Fig. 2.

The results from our previous work shall be used to apply our "up-cycling"- concept on PP from post-consumer household waste and discuss challenges that occur from a recycled feedstock. Especially 10% impurities, a recycled system is likely to contain of, from different PE-HD packaging material and the resulting limitations will be one focus of our study. Dynamic and elongational rheology (the most convenient tools for LCB detection) will be used to discuss the changes of the molecular structure. Tensile and impact tensile tests shall complete the data set.

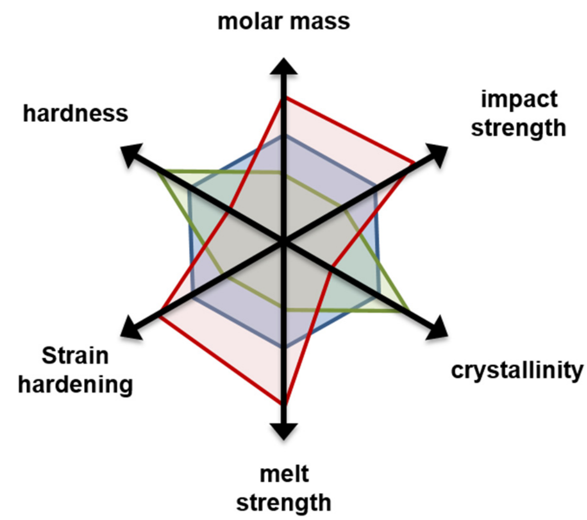

Fig. 2. Proposed improvements of PP properties (blue) by LCB (red) compared to mechanical Recycling (green). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

2. Materials and methods

2.1. Materials

PP was collected from household post-consumer waste containing yoghurt, vegetable and beverage cups (thermoformed PP), boxes for rigid packaging (injection-moulded PP), bottle caps (injection-moulded PE-HD), and chewing gum containers and milk bottles (extrusion blow-moulded PE-HD). The material feedstock contained of 30% thermoformed PP, 60% injection moulded PP and 5% injection moulded PE-HD and 5% extrusion blow moulded PE-HD (rBlend). Furthermore, a single polymer waste fraction was sorted manually from thermoformed cups (rPP-cups). Complex viscosity and dynamic moduli of the raw materials are given in Fig. 3. As can be seen, the rheology data are in accordance with

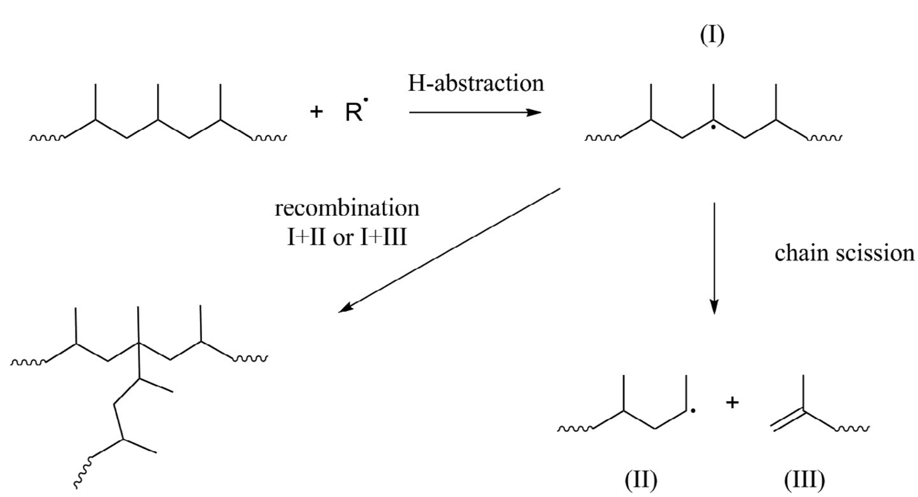

Fig. 1. General reaction scheme of the LCB formation.

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