Industry Perspective

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Rheology for Polypropylene Recycling with Organic Peroxides

By Bart Fischer, PhD

Polypropylene (PP) is currently the largest volume thermoplastic polymer globally produced. The installed capacity exceeds 90.000 kton. Polypropylene is a very versatile polymer and is used in a large variety of applications. Each application has its unique requirements with regards to molecular weight and molecular weight distribution. For instance, Biaxially Oriented Polypropylene (BOPP) film requires a Melt Flow Index (MFI) in the range of 2-5, injection molding applications need MFI's around 30, whereas for fibre spinning a narrow molecular weight distribution is required.

There are many different technologies available to produce polypropylene. In each technology various types of catalyst systems can be used. This results in a huge variety of PP types that can be produced. The catalyst system determines to a large extent the molecular weight (MFI) and molecular weight distribution of the polymer produced.

It is claimed by catalyst producers that all grades can be produced as reactor grade through selection of the right catalyst system. In practice, however, only few reactor grades are produced, and special grades are made by post-reactor treatment with organic peroxide, so-called controlled rheology grades. There are two reasons for this. Firstly, some applications, e.g., fibres, require a narrow molecular weight distribution that is difficult to obtain with traditional catalyst systems. Secondly, producing different PP grades by changing the catalysts system is time consuming and results in a loss of production and unit capacity. Moreover, the switch results in substantial amounts of off-spec product. The use of peroxides, on the other hand allows for almost instantaneous switching between grades.

The use of organic peroxides in the production of virgin PP grades is well established and in current practice. The same concept can be used for polypropylene recycling. In this case the goal is different. For virgin polymer organic peroxides help to produce a variety of grades. In recycling the challenge lies more in producing a standardized grade while using raw materials that may vary in MFI and molecular weight distribution. For recyclers it is quite difficult to ensure supply of raw material of constant quality. In practice volumes fluctuate and the quality that is offered differs greatly. At the same time recyclers need to ensure the supply of constant and reproducible product quality. For this reason, a method to adjust MFI and molecular weight distribution is essential. A practical method is blending of material with different MFIs to obtain the target MFI. The use of blending is limited by the availability of raw materials with the right MFI. Lacking that, a different tool, like an organic peroxide, is required. Organic peroxides are applied to adjust MFIs of recycling streams.

Organic peroxides can be used to increase the MFI of PP. This process is generally known as "vis-breaking." Chemically vis-breaking consists of the following steps:

1. The organic peroxide thermally decomposes to generate two free radial species.
2. The free radicals abstract a hydrogen atom from the polymer backbone.
3. At the elevated extrusion temperature, the formed polymer radical is extremely instable and undergoes **ß**-scission, effectively breaking the polymer backbone in two.

One could consider organic peroxides as molecular scissors that cut polymer molecules, thus reducing the molecular weight, and narrowing the molecular weight distribution. The latter effect is obvious since the cutting action is a statistical process in which large molecules have a bigger chance to be cut than smaller molecules.

For the recycling industry this means that product streams with relatively low MFI can be modified to a uniform product with a higher MFI, applying different amounts of peroxide, depending on the MFI of the starting material.

It is less well known that a specific type of organic peroxide can be used to achieve the opposite, to decrease the MFI. This decrease in MFI is a result of the introduction of long chain branches. Chemically, long chain branching is created in the following way. As with vis-breaking, the organic peroxide generates two free radicals that abstract a hydrogen atom. The peroxide used in this case reacts at lower temperatures than vis-breaking peroxides. Polymer radicals formed have a somewhat higher stability at this lower temperature. This allows for the possibility of two polymer radicals (in close proximity) to combine, thus creating a long-chain-branched polymer.

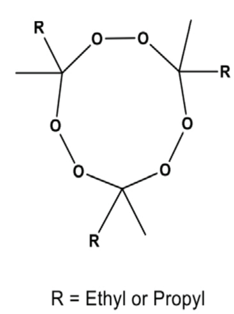
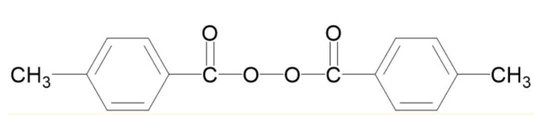


Figure 1. Chemical structure of Trigonox 501-CS40 and Perkadox PM-W75



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The two graphs below show the increase and decrease of MFI as a function of the dosage levels of Trigonox 501-CS40 and Perkadox PM-W75, respectively.

Figure 2. MFI as function of dosage level of Trigonox 501-CS40 (extrusion temperature 210°C)

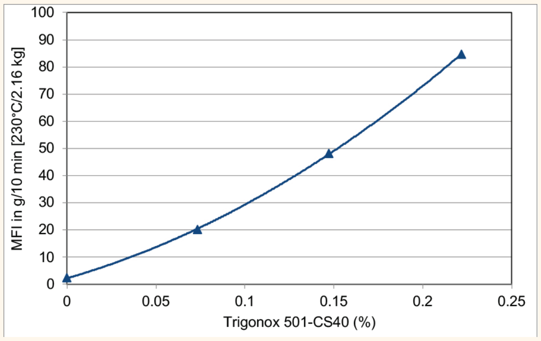
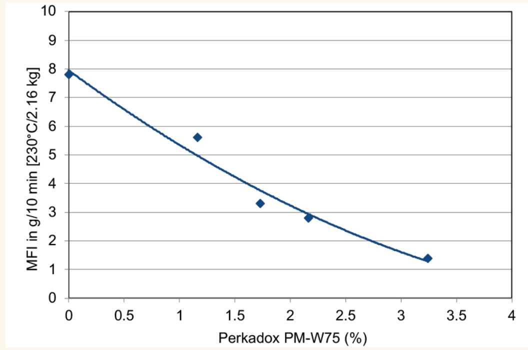


Figure 3. MFI as function of dosage level of Perkadox PM-W75 (extrusion temperature 210°C)



For vis-breaking of PP different peroxides are commercially available. For PP recycling Trigonox 501-CS40 is especially advised. It has important advantages over the alternatives. Firstly, of all available peroxides for vis-breaking Trigonox 501-CS40 has the lowest level of volatile organic compounds (VOCs) generated as decomposition product of the peroxide. This is highly beneficial for reducing odour of the recycled PP. Secondly, Trigonox 501-CS40 can be stored at ambient conditions and does not need temperature control in winter as it will not solidify or crystalize. Additionally, it needs no cooling during the summer months.

Perkadox PM-W75 is currently the only peroxide available that can be used for decreasing the MFI of recycle PP.

The creation of long chain branches has the additional beneficial effect that it increases melt strength. The combined effect of MFI decrease and meltstrength increase is shown in **Figure 4**.

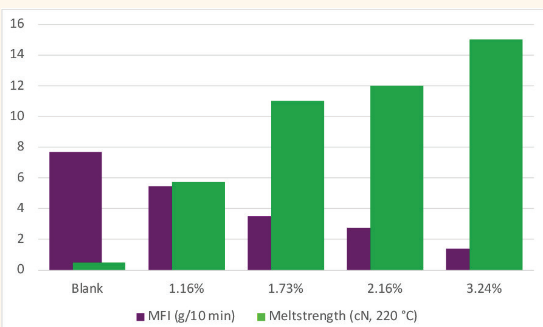


Figure 4. MFI and melt strength as a function of dosage level of Perkadox PM-W75

Meltstrength increase is a good example of "up-cycling" of recyclate. Use of Perkadox PM-W75 gives the recycled PP superior properties to the original product, especially for those applications where (higher) meltstrength is required.

PP modifications were carried out using a Haake PolyLab Rheodrive 7 system fitted with a Haake Rheomex OS PTW16 twin screw extruder (from Therma Scientific), under nitrogen atmosphere. The melt strength was measured with a Göttfert Rheotens 71.97 in combination with a Göttfert Rheograph 20 high pressure Capillary Rheometer at 220°C. The MFI was measured by means of a Göttfert model MI-3 Melt Indexer (230°C, 2.16 kg). Reactor grade PP homopolymer powders with different start MFI were used. Irganox® B225, 0.2 phr and Calsium stearate 0.05 phr were used as stabilizer.

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About the Author

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