## **Peroxides in polypropylene**

# Molecular weight adjustment of polypropylene after polymerization is today intensively practiced by producers in order to offer a wide range of grades to customers and rationalise polymerization operations. This operation, commonly called "vis-breaking" or "controlled rheology", is generally performed at the finishing step into an extruder by addition of peroxide.

#### Part I. Viscosity breaking of PP (vis-breaking)

Molecular weight adjustment of polypropylene after polymerization is today intensively practiced by producers in order to offer a wide range of grades to customers and rationalise polymerization operations. This operation, commonly called "visbreaking" or "controlled rheology", is generally performed at the finishing step into an extruder by addition of peroxide. Viscosity reduction is controlled by the amount of peroxide introduced.

Figure 1 shows impact of peroxide on MFI of PP at 230C.



Figure 1 : MFI versus peroxide(DHBP) content after extrusion at 230C

This approach is not only used by PP producers but also by converters particularly where high fluidity is required like :

- PP Non wovens by melt blown
- PP composites , Glass Mat Thermoplastic (GMT)
- PP recycling to adjust viscosities

#### Mechanism

1) The first step is the thermal decomposition of peroxide generating free radicals.

2) These free radicals are able to abstract randomly hydrogen atoms from the polymer backbone to generate ternary macroradicals.

3) The unstable macroradicals produced stabilize themself by a reaction named " b-scission " breaking polymeric chain and driving down viscosity.

The mechanism of degradation is described below :



Key parameters in PP decomposition are the active oxygen content and the half-life time (t1/2) of the peroxide. t1/2 represents the time needed to decompose half of the peroxide. Temperature accelerate decomposition of peroxide (cf table1), however in industrial compounding conditions, temperature doesn't appear so critical but as many external parameters may disturb the process, resin producers generally use on-line rheometer for an accurate control of MFI.

Figure 2 shows a typical extrusion line configuration for vis-breaking.



Figure 2 : Example of line configuration for vis-breaking, peroxide can be injected in the feed-hoper

#### Peroxides used

Among the large range of peroxides commercially available, these three are often mentionned for PP vis-breaking :



Indicative Half-life time versus temperature of these peroxides are given in Table1.

DCUP	58	17	4-5
DHBP	95	23	9-10
DTBP	110	24	6-7

Table 1: t1/2 measured in chlorobenzene, t1/2 are only indicative because decomposition is strongly influenced by the media

DHBP is one of the most used. Due to his high molecular weight the volatility is limited and flash point is reasonably high. Organoleptic properties are better than DCUP. Ditertiobutyl peroxyde is also efficient, much cheaper than DHBP and also used industrially by some producers. However, DTBP has higher volatility and lower flashpoint. As a result, the handling of this product is constraining and the usage is limited to resin producers.

### **Physical form**

Liquid peroxides are generally introduced in small quantities in PP. Moreover, liquids are not easy to handle particularly for converters. This is the reason why different solid forms are also commercially available.

#### Peroxide in mineral filler

Most of the producers propose peroxides absorbed at 40-45% in mineral filler like CaCO3, Chalk, Silica. The carrier used is cheap and the quantities remaining small. This may cause problems of dosing accuracy in some cases. Moreover, the product is in powder form and "fluffy". Some users (particularly converters) want to avoid it. Absorbed peroxide is phlegmatized and product more stable. Dispersion of the filler may also appear as a problem particularly on combination with monomers.

#### Peroxide absorbed in porous PP particules

Peroxides absorbed in PP porous powder are also commercially available and also called "dry peroxide". This approach is also used for silane. Porous particules coming from sheripol process and up to 20% of peroxide can be added maintaining good flowability. The carrier is more expensive but the product is less "fluffy" and mineral free (optical properties). Dosing accuracy is higher in this case. Some "ultraporous" PE and PP powder are also available. Peroxide concentration can go up to 50%. However, this product is very expensive compared to the two first options.

#### Peroxide masterbatch

Only few suppliers/masterbatchers propose this solution. The carrier has to be extruded at very low temperature to avoid decomposition. The solution is more expensive than absorbed products and peroxide concentration can go up 10%. However, masterbatches offer lots of benefits like :

- Product in pellet shape ; the product can be premixed with pellets without segregation
- Possibility of powder free process (excellent for converters)
- Good homogeneity because the product is predispersed.
- Excellent dosing accuracy.

Morever, below 10% of peroxide the product is not classified anymore as dangerous and the constraining legislation not required (storage, special equipment).

#### Impact on properties

#### Interactions with additives

b-scission reaction generates double bonds reducing thermal and color stability of PP. This is why an efficient stabilisation is required. As peroxides are used as radical initiator, they can interfer with stabilisers protecting the polymers from free radical attacks. This is the reason why in vis-breaking process it is strongly recommended to incorporate the additives in a second step when most of the peroxide has reacted (cf figure 2). If not, efficiency of peroxide and quality of stabilisation may decrease. These effects are illustrated on figure 3 showing impact of peroxide on melt stability and effect of a phenolic antioxydant on vis-breaking efficiency. Some studies have shown that bellow 0.5% of peroxide in PP, activity of phosphites is not affected. In some cases, significant efficiency reduction of nucleating agents has been observed when peroxides are added.



#### Effect of residuals

Product of decomposition of peroxides may have negative impact of final properties and particularly for long term ageing and organoleptic critical in food applications (table 2).

Peroxide	Residuals		
DCUP	benzophenone, cumylalcohol, cumylmethyl ether, methane		
DTBP	t-butylalcohol, methane, acetone		
DTAP	t-amylalcohol, ethane, acetone		
Table 2 : main residuals and decomposition products of different peroxides			

For example cumyloxy radicals, coming from decomposition of DCUP, lead to the formation of methyl radicals and acetophenone, a molecule with an unpleasant odor. Remaining methyl radicals are able to abstract hydrogen (methane generation) or recombine.



Tertiobutoxy radicals, coming from decomposition of DHBP or DTBP, also lead to the formation of methyl radicals and acetone, destroying organoleptic properties and FDA approvals.



Some producers, claim they obtain better organoleptic properties when using ditertioamylperoxyde (DTAP) generating more stable tertioamyloxy radicals. This product seems to offer an interesting solution for FDA applications and lower odor products. Comparison between DTAP and DHBP is shown on table 3. Color stability seems better also.

Product	MFI	Odor intensity @ 20°C
PP non extruded	12	25
PP extruded	-	45
PP + 400 ppm DHBP	36	110
PP + 500 ppm DTAP	33	80
PP + 700 ppm DHBP	49	150
PP + 1200 ppm DTAP	55	170
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Table 3 : Effect of different peroxides on odor



#### DTAP

#### Conclusion

It is possible to control PP viscosity by addition of peroxide during conversion process. Many peroxides in different physical forms are commercially available. Every user has to find his best compromise between facility of operations, safety and cost. However, addition of peroxide can also impact negatively long term stability of PP and destroy completely organoleptics properties.

This is the reason why it is recommended to start with a resin having a MFI as close as possible of the target and have an efficient devolatization in order to :

- Reduce cost by reducing amount of peroxide needed

- Minimize double bond generation (thermal stability and discoloration)
  Minimize interaction with additives.
  Reduce peroxide residuals in the melt (stability and organoleptic properties)