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## **Mechanics - Recycling – Seawater and Microplastics**

#### Mechanics

d2w Oxo-biodegradable plastics are made from conventional polymers with a low (typically 1%) addition of a prodegradant masterbatch. The d2w masterbatch itself is predominantly carrier resin (>80% - sometimes also made up with a mineral filler). The remaining <20% is made up of the prodegradant catalyst package and the stabiliser package:

The prodegradant catalyst package promotes the rate and extent of oxidation of the polymer which leads to molecular weight reduction and accelerated biodegradability - this is the identical mechanism by which conventional plastics degrade and fail/fragment in the environment, but which does not happen quickly enough or to a sufficient extent to permit significant biodegradability. The stabilisation package protects the polymer from the action of the catalyst, for the duration of the product shelf-life or until it is littered in the environment. Whichever is sooner.

The shelf-life of the d2w oxo-biodegradable product relates directly to the concentration of stabilisers in the finished product. The d2w prodegradant additive masterbatch formulation contains a stabilisation package which will supplement any stabilisers already present in the polymer resin(s) in order to give the shelf-life required by the customer. 12-18 up to 36 months is typical.

Note that the agreed shelf-life period corresponds to the dwell time before the onset of degradation (i.e. degradation only begins at the end of the shelf-life, it is not a process which proceeds through the life starting from extrusion), while in indoor storage conditions and protected from extended sunlight exposure. Over the course of the storage period, the stabilisers will be gradually consumed by the action of the d2w prodegradant catalyst. At some time after the shelf-life period, when these stabilisers are depleted, the onset of degradation will occur and the products would eventually degrade even without sunlight exposure.

However, if at any time (e.g. even in the first few months of a 3-year shelf-life) during this period the products are used and subsequently disposed of in the environment as litter, the stabilisers are very quickly destroyed by exposure to sunlight, leaving the polymer accessible to the degradation action of the prodegradant catalyst. This is how oxo-biodegradable products are able to maintain a long shelf and service-life but will degrade rapidly and without delay if at any point they are accidentally or deliberately discarded in the environment.

### Recycling

It is by this same mechanism that oxo-biodegradable plastics can be recycled without detriment to the recyclate/downstream recycled products and without degradation. In normal circumstances (post-industrial, back-of-store, post-consumer curbside) the recyclate is collected and reprocessed within its shelf-life period and before sufficient outdoor exposure to disrupt the stabilisation package - in which

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case the material will perform in the same manner as an equivalent conventional material.

Depending on the proportion of oxo and non-oxo recyclate, and virgin material during recycling the recycled product will either retain it oxo-biodegradable character (normal suited to the kinds of products made from high levels or recycled materials) or the prodegradant catalyst will be diluted below the level where it is effective. Stabiliser content will be replenished by the addition of any virgin (and to some extent non-oxo recyclate) material, by the inclusion of a prodegradant additive or (if deemed necessary) additional antioxidant stabiliser - this will restore/extend the shelf-life of the recycled product.

For situations where confidence in long-term stability is critical, such as in the production of building films, irrigation pipes or plastic lumber (normally unlikely to be made using mixed, post-consumer recyclate without protection), there are stabilisers which will completely and permanently retard the effect of the prodegradant catalyst.

Successful film recycling of oxo-biodegradable products has been demonstrated most recently in <u>TCKT (March 2016)</u>. Interestingly here we found that because of the additional contribution of stabiliser from the prodegradant masterbatch formulation, films made using higher proportions of oxo recyclate demonstrated greater stability.

We also demonstrated in <u>TCKT (July 2016)</u> that thick-walled products (i.e. such plastic lumber intended for street furniture) experienced sufficient degradation to cause product failure during simulated sunlight exposure, and that the measures taken to protect from degradation during sunlight exposure were equally effective in the product made from 100% oxo recyclate.

Polyethylene derived from biological feedstock (such as Braskem green PE) is chemically identical to fossil-PE and therefore is compatible with prodegradant catalyst technology as described above.

#### **Seawater – Microplastics**

As mentioned the prodegradant catalyst package promotes the rate and extent of oxidation of the polymer which leads to molecular weight reduction and accelerated biodegradability - this is the identical mechanism by which conventional plastics degrade and fail/fragment in the environment but which does not normally happen quickly enough or to a sufficient extent in order to permit significant biodegradability (B.Gewert, Environ. Sci.: Processes Impacts, 2015, 17, 1513) and therefore after failure and fragmentation remain persistent as microplastics. The stabilisation package protects the polymer from the action of the catalyst, for the duration of the product shelf-life or until it is littered in the environment. Whichever is sooner.

We have demonstrated abiotic degradation of oxo-biodegradable plastics leading to the formation of low molecular weight oxidised oligomers, specifically in the marine environment in natural ageing studies based in the south of France. In reports <u>Bandol Summer (2015)</u> and <u>Bandol Winter (2016)</u>, the accelerated oxidation of the plastic product made with the d2w prodegradant additive masterbatch is demonstrated against the behaviour of a conventional equivalent product. In each case we see the onset of degradation occur at roughly the same time for the oxo-bio and conventional products,

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however the degradation of the oxo-bio proceeds much more quickly. At the point where advanced degradation is observed in the oxo-bio product, the conventional material remains largely intact. After abiotic degradation, samples from that natural seawater exposure were passed to Queen Mary, Universtiy of London who demonstrated biodegradation of the reduced molecular weight products of abiotic degradation (publication expected later this year).

The characterisation of the products of abiotic degradation as low molecular weight, water-soluble oxidised oligomers which are biodegradable has been examined at ICCF, France (<u>B.Eyheraguibel</u>, <u>Chemosphere</u>, <u>2017</u>, <u>366</u>). Further consideration of the impacts of the litter environment (including marine) on the rate of degradation is done in follow up work (<u>B. Eyheraguibel</u>, <u>Chemosphere</u>, <u>2018</u>, <u>182</u>)

The majority of the evidence focuses on film products - however, this can also be mirrored for PP Straws, which is simply in a different form. Similarly, the above work focuses on oxo-polyethylene whereas straws are typically extruded polypropylene. The degradation of PP is mechanistically analogous to PE (Gerwert 2015) and therefore the principles remain identical.

We have demonstrated accelerated rate and extent of degradation of PP straws, leading to oxidation and molecular weight reduction, many times in accelerated ageing studies. As in the natural ageing work (Bandol 2015 & 2016), the demonstration of oxidation is directly related to molecular weight reduction and therefore increased biodegradability (Eyheraguibel 2017).

In summary, we can demonstrate that the application of a suitable prodegradant additive to polyolefin polymers (including polypropylene straws) has effectively accelerated the rate of oxidation and molecular weight reduction causing an increase in the rate and extent of biodegradability. By increasing the rate at which plastic litter in the environment becomes available for biodegradation, the persistence of plastic in the environment as microplastic particles are significantly reduced.