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Report:

Effect of mechanical recycling on the properties of films containing oxo-biodegradable additive

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1. Introduction

Oxo-biodegradable additives are typically added to materials which do not readily degrade in the bio-environment, like LDPE films. Such films are used for short service life applications like shrink and wrap film for packaging or shopper bags and are produced by typical plastics processing machinery, like blown film lines, and exhibit a close range of molecular characteristics (mostly expressed as some rheology data) to provide sufficient processing stability. For the oxo-biodegradable mechanisms in the materials to happen, oxygen and temperature are needed, as well as UV light will increase the degradation.

In terms of mechanical recycling, there are routes or material streams which can be considered, e.g in-house scrap, post-industrial and post-consumer waste. While in the case of the first two, processors usually know much about the materials and their respective constituents, but in the case of the post-consumer materials this is often not the case. For all these streams, there are two possibilities for further usage. On the one hand, some materials, like HDPE milk bottles, yoghurt cups or PET soda bottles can be sorted out due to their shape and the fact, that such materials have properties which lie within very narrow specifications, regardless the producer, to being used in the same applications again.

On the other hand, there are residual streams like films, which are also sorted out, but due to their not closely specified origin and properties, are used for low-cost applications like trash bags or shopper bags again. Also one has to mention, that many of these incoming streams, e.g. the shopper bags, are printed, which forbids their use for transparent films. The last point to mention here is that the materials cannot be interchanged at random for their second life applications, e.g. it is not sustainable to produce films from HDPE which was used for milk bottle application in the first life (and vice versa), because the properties of the one material are not matching the requirements of the other processing route. Even if there are products, where the same base polymer is used for two applications, like films and pipes from HDPE, these materials still differ in their properties, so an interchange is very unlikely due to technical reasons like issues in processing.

In our opinion it is even unlikely that recycled film grades for short lifed films are used for long lasting films applied in the building industry. These long-life films should in any event be made with virgin polymer or be stabilized to deal with loss of properties caused by the melt processing and the recycling process, whether or not any pro-degradant additive is present. Such stabilization would effectively neutralize the effect of any pro-degradant additive. Also, materials from shopping bags tend to contain high levels of fillers like calcium carbonate, which are not suitable for producing long-life films.

A further consideration into account is the thickness of the material, which limits the oxygen penetration into the plastic, and therefore reduces the effect of the pro-degradant on the bulk material [1]. Therefore the thicker the material the less susceptible it will be to oxo-degradation. Another factor limiting the availability of oxygen, and therefore reducing the degradation rate substantially, would be the case of films which are used as a lining under concrete or other building materials. Such films will generally degrade slow, at a similar rate to non-degradable plastics, due to the very limited oxygen availability and the exclusion of UV radiation.

This study here aims to investigate the effects of a selected oxo-biodegradable additive on the behaviour of LDPE films in recycling, to clarify the effects of the presence of pro-degradant in polymers after an additional recycling step after the first processing, also in different concentrations, e.g. to mimic cross-contamination of LDPE films with and without pro-degradant. To yield comparable results, related to the additive concentration, unprinted, clean films were used. The technology applied is state of the art for all the process steps.

2. Materials and Methods

The LDPE grade used in this study was FA6224 from Borealis with a melt flow rate of 2.1 g/10 min at 190°C and 2.16 kg. As the additive, d2w (grade 93390) was used, which is an oxo-biodegradable additive based on a polyethylene carrier resin. LDPE was chosen here as it is the most unstable of the commonly used polymers in regard to photo-oxidative degradation as reported elsewhere [2], and is therefore the worst-case scenario.

Two base films (180 µm thick) were produced at a Reifenhäuser blown film line with a screw diameter of 70 mm, equipped with a barrier screw. One was the unmodified LDPE (referred to as LDPE-film further on), the other the LDPE containing 1 % of d2w 93390 (referred to as oxo-film in the following). From each batch 800 kg blown film were produced at 175 – 180 °C set barrel temperatures and a throughput of approximately 70 kg/h.

These films were used in the mechanical recycling step, where an Erema 1108TE recycling machine with a hot die pelletizer was used to regrind the films to pellets again at about 200 °C barrel temperature and a throughput of 420 – 450 kg/h. From these pellets, the following mixtures were produced: 0, 5, 10, 20, 30, 50, 75, 100 wt% recycled oxo-film in recycled LDPE.

These pellets were subsequently reprocessed at a Hosokawa-Alpine blown film line at a throughput of about 20 kg/h and a maximum barrel temperature of 200 °C. Melt flow rate of these films was measured according to ISO-1133 at 190°C and 2.16 kg at film flakes to determine the influence of the mixture.

These films were cut into strip samples (15x150 mm²) and were exposed for different time intervals between 0 and 640 h at 70 °C in hot air cabinets. Afterwards, tensile tests in accordance to ISO 527-3 at a Zwick-Roell Z0.5 with a test speed of 100 mm/min were conducted. Tensile strength and according strain (σ_{Max} and ε_{Max}), breaking stress and according strain (σ_{Break} and ε_{Break}) as well as stress at 200 % strain (σ_{200}) were tested for 5 replicates per series and average values with standard deviations are shown in this study. All the film properties were measured in machine direction.

3. Results and Discussion

As can be seen in Figure 1, the melt flow rate is relatively uninfluenced by the oxo-film content in the mixture. In the range from 0 to 75 wt%, the MFR values are in a range from 2.02 to 2.09 g/10min, which is within the measurement uncertainty, especially when taking into account that the measurement was carried out on shredded film pieces, which are more complicated to pre-compact than granules. In the case of the 100 wt% oxo-film, we see some deviation from the average value towards a higher MFR of 2.2 g/10min. This indicates some degradation due to the concentration of the d2w 93390, but the difference is below 5 %, and was therefore considered unproblematic.

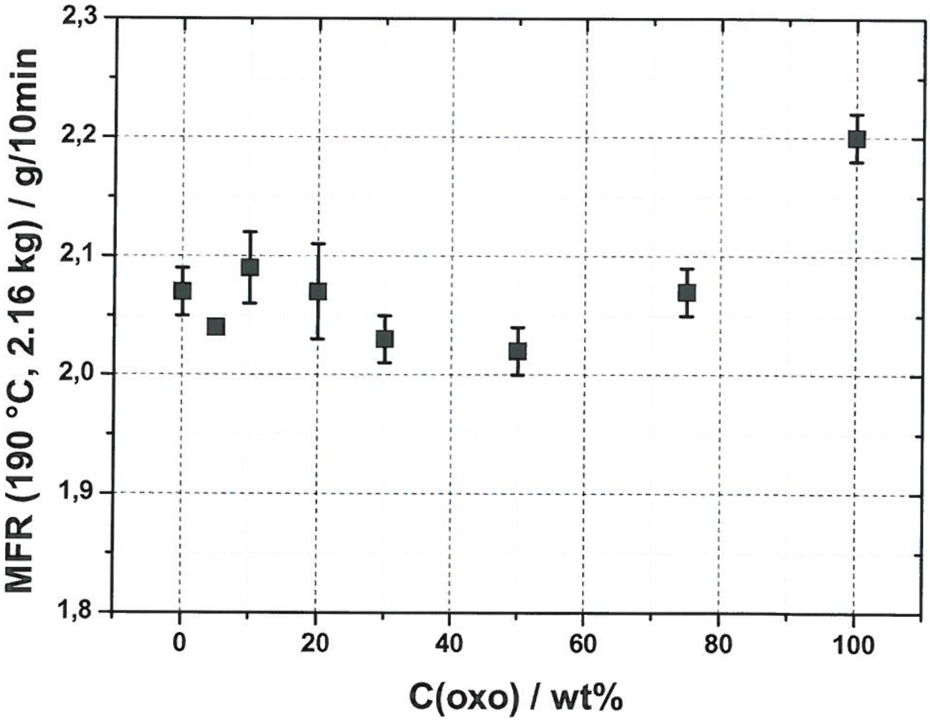


Figure 1: Melt flow rate vs. oxo-film content for LDPE films with varying content of oxo-film in LDPE-film

In the case of the tensile strength (Figure 2), we can see that the different films exhibit tensile strengths which are not significantly different from each other, regardless of oxo-film content in the formulation, up to 320 hours of storage. At the 0 h storage time, i.e. for the unaged films, we can see that the films with 100 %, 75 % and 10 % all give the same average value, and looking at the other data points, all of these are within their respective standard deviations.

This trend continues also for the aged samples, up to 320 h. At 640 h, all the films containing oxo-material exhibit a decrease in materials properties. One interesting point is here, that the films containing 100% oxo-pellet show less degradation than the films with lower oxo-content. This could be an effect of the stabilizer package which is part of the d2w material together with the pro-degradant.

Due to the scattering of the data in the region between 0 and 320 h, the trends are not properly visible in the tensile strength of the samples. This is also due to the shape of the stress strain curve, which does not show yielding and therefore the tensile strength is very close to the breaking stress. This is showing some influence on the scattering of the data, therefore we used another data point for the comparison, i.e. the stress at 200 % strain, to get a better defined state of the films in the test and therefore being able to interpret the data more in detail.

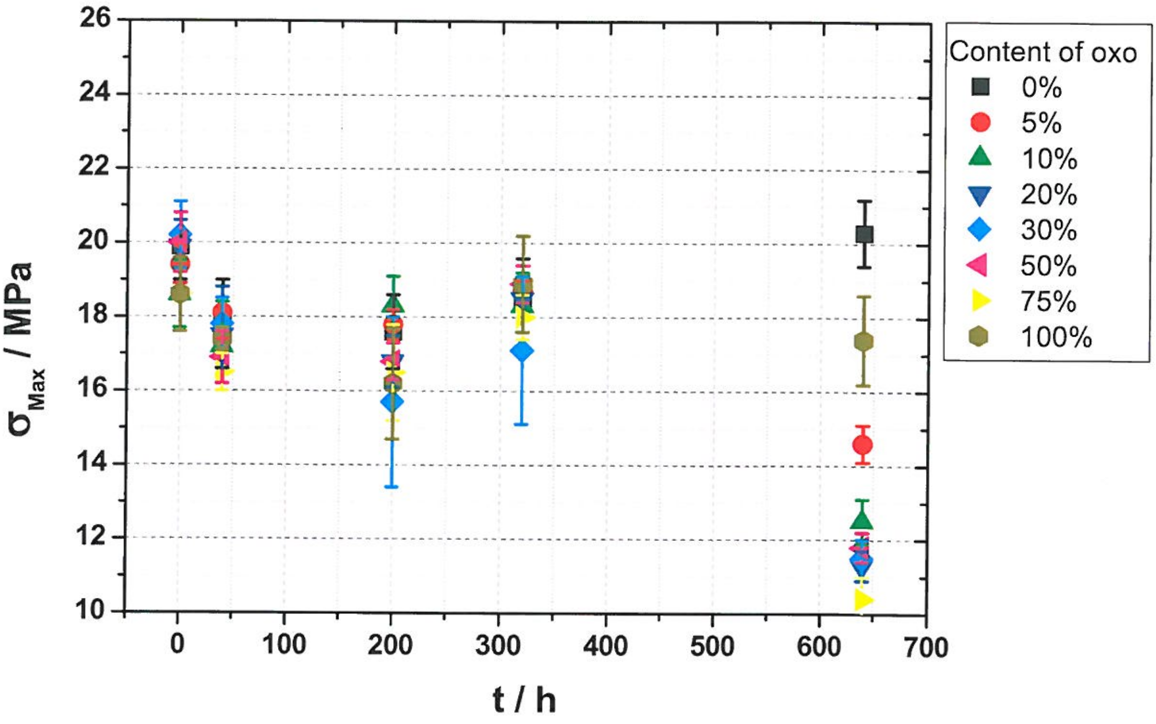


Figure 2: Tensile strength σ_{Max} vs. accelerated ageing time at 70°C for LDPE films with varying content of oxo-film in LDPE-film

As shown in Figure 3, the stress at 200 % strain (σ_{200}) exhibits less scattering between the data points, although also here there is no significant difference found between the films with varying content at the different storage times. In addition, the data points do not show any significant change up to 320 h, thus indicating a good stability of all the films tested. The reason that the data points for the films with a content of oxo-pellets lower than 100 % are missing at 640 h is due to the fact, that these film samples break at lower elongations, as can be seen from strain at break (ε_{Break}, Figure 4). Here, one can see no significant difference between the different formulations up to 320 h, as well as some scattering between the data points and the storage time points. The latter can also be accounted to the sample preparation, which was conducted with fresh blades and at a proper cutting mat, nevertheless a cut surface always shows some microcracks, which can serve as initiation sites for film rupture, therefore resulting in higher scattering of the strain data. For a storage time of 640 h, again the films with a content of oxo-pellets lower than 100 % show a similar behaviour in degradation as found already for the tensile strength.

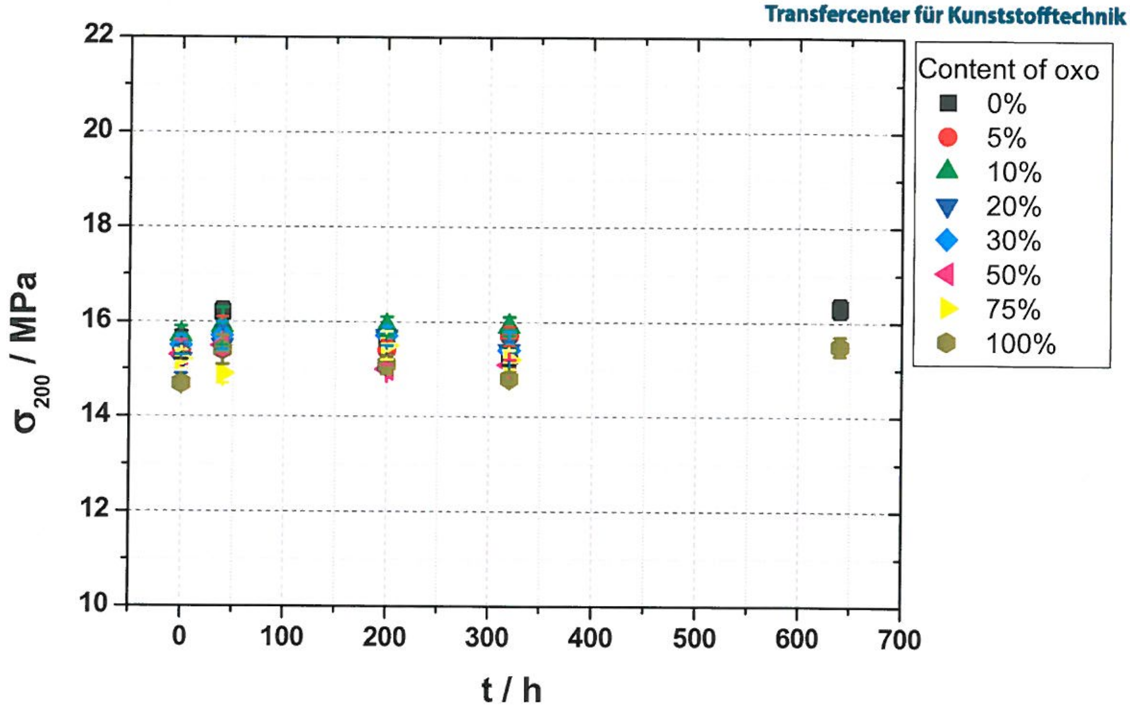


Figure 3: Strength at 200% strain σ_{200} vs. accelerated ageing time at 70°C for LDPE films with varying content of oxo-film in LDPE-film

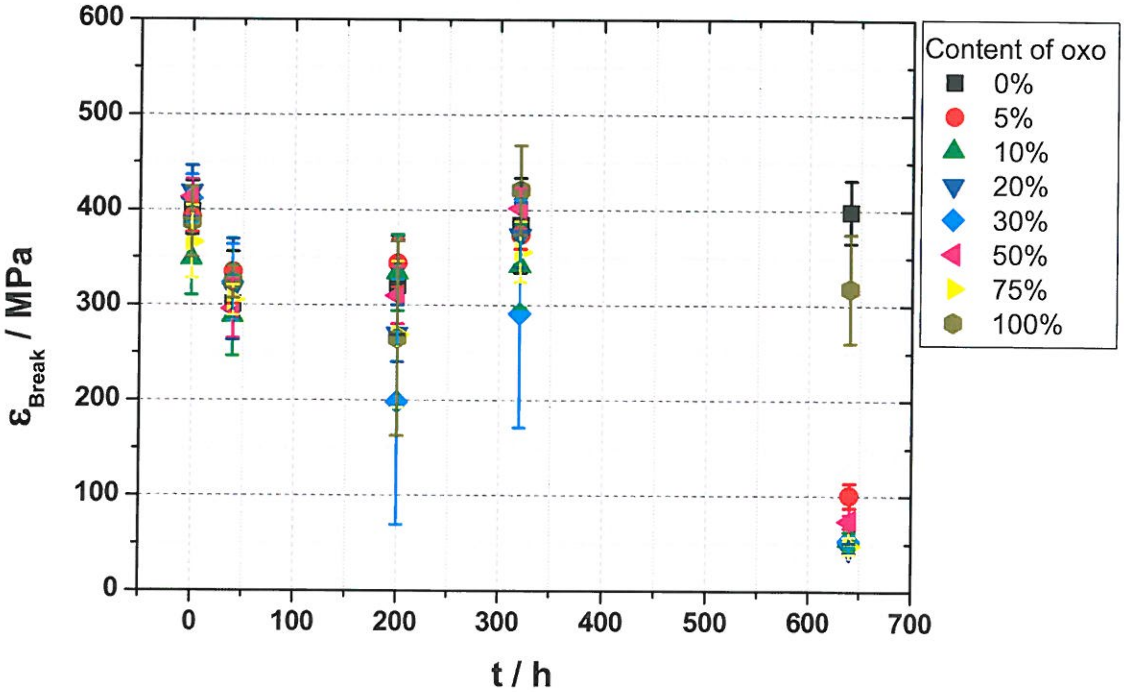
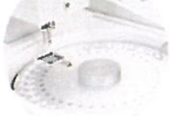


Figure 4: Breaking strain ε_{Break} vs. accelerated ageing time at 70°C for LDPE films with varying content of oxo-film in LDPE-film



4. Conclusions

Drawing some conclusion from the data here, one can see that the addition of films containing the oxo-biodegradable additive d2w 93390 do not show negative effects on the film properties up to 320 h for the investigated films, and 640 h for the film containing 100 % reprocessed oxo-pellets, respectively, nor on the shelf life investigations according to the AFNOR TC51-808 standard. From this standard one can deduce a shelf life of at least 2 years for the oxo-films containing 100 % reprocessed oxo-pellets, which were stored for 640 h at 70 °C without any additional environmental impacts like UV or moisture. Also the formulations with less oxo-film, i.e. containing between 5 and 75 %, do not show any significant influence up to 320 h, which equals a shelf life of one year.

These results support the conclusion of a report by Roediger in 2012, where they stated "...We are therefore able to confirm that plastic products made with Symphony's d2w oxo-biodegradable technology may be recycled without any significant detriment to the newly formed recycled product...." [3]. The cited report also shows that there is little to no influence up to an ageing time of 200 h at 60 °C. Any differences with the report prepared by us may arise from the different polymer grade used.

This shows, in our opinion, that it is viable to recycle such oxo-biodegradable materials into other short service lifed products like trash or shopper bags.

On the basis of the data generated in this study, and our knowledge of the degradation mechanisms of polyolefins due to recycling, and our experience of the recycling processes applied in the polymer industry and the stabilisation necessary for that, the presence of oxo-biodegradable additives in polyethylene shopping bags is most unlikely to prevent compliance of the bags with EN 13430-2004 "Packaging — Requirements for packaging recoverable by material recycling".

5. Literature

1. Cunliffe A.V. and Davis A. Photo-oxidation of thick polymer samples – Part II: The influence of oxygen diffusion on the natural and artificial weathering of polyolefins, Polymer Degradation and Stability 4 (1982) 17-37

2. Chiellini E., Corti A., D'Anone S. and Baciu R. Oxo-biodegradable carbon backbone polymers – Oxidative degradation of polyethylene under accelerated test conditions, Polymer Degradation and Stability 91 (2006) 2739-2747

3. Roediger Agencies CC, Recycling report on d2w oxo-biodegradable plastics, 6th March 2012

6. Appendix

DI Dr. **Christoph Burgstaller** holds a diploma as well as a PhD in chemical engineering from Johannes Kepler University in Linz and has more than 10 years of experience in plastics industries. Currently he holds the position of managing director and head of R&D at TCKT. He worked in many different projects on materials development, including blends and composites, fillers and reinforcements as well as polymer stabilisation and processing. One part of his work is dedicated to the recycling of thermoplastic materials, with emphasis on reactive processing and compatibilisation of inseparable plastic waste streams. He is a lecturer at the University of Applied Sciences in Wels for materials science, i.e. for composites and lightweight polymeric materials, as well as for organic chemistry. He supervised more than 20 master and bachelor students for the preparation of their thesises. He is a senior member of the Society of Plastics Engineers and has published his work in over 50 national and international conferences, as well as in several peer-reviewed papers.

DI **Volker Reisecker** holds a diploma in plastics engineering from the Mountains University of Leoben and is the deputy director and head of industry orders at TCKT. He has more than 10 years of experience in heading the test laboratory at TCKT, dealing with different aspects of plastics materials investigations, e.g. solid plastics, films, fibres and composites. Furthermore, he is experienced with different aspects of polymer processing and the incorporation of nano-materials in plastics. He is a lecturer at University of Applied Sciences in Wels for materials testing and characterisation and has supervised several master and bachelor students while their work.