



Biodegradable Plastics Association

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COMMENT ON BRASSIOULIS PAPER

When this paper was mentioned by Prof Henderson during the Zoom meeting on 2nd August 2023, we thought there must be something wrong with either the material tested, or the experiment itself. Having read the Brassioulis paper the problem seems to have been with both.

Nevertheless, the reason for using biodegradable mulch film is well stated on page 2584/5 of the paper as follows:

“The main reason for the trend of increasing use of biodegradable agricultural plastics is the growing problem of management and disposal of large amounts of agricultural plastic waste. The mismanagement of the agricultural plastic waste represents a serious environmental problem.”

“Polyethylene (PE)-based mulching films do not break down in soil and should never be rototilled and incorporated into the soil following the end of their useful lifetime. However, the process of recovering and recycling them, following the end of the cultivation period, is difficult, or impossible, as a large percentage of the weight of the recovered mulching film waste is foreign materials (e.g. 80 % soil, sand, etc.). Also, the cost of removing from the soil and cleaning this material is prohibitively high.”

“This is the main reason why the farmers usually incorporate them into the soil by rototilling, or sometimes, they burn them in the fields, practices which, apart from being illegal, also imply a serious risk for the environment and the public health due to the accumulated PE in the soil or the toxic emissions. Thus, specifically for the case of agricultural plastic wastes that cannot be easily collected and recycled (e.g. mulching films), a very attractive alternative is the use of biodegradable materials.”

In addition, as the mulch film will have been exposed to sunlight for many months in the fields it will have become brittle and unsuitable for recycling, and fragments will scatter in the wind while the film is being removed. Even if the film were still suitable for recycling, it is expensive to transport it along country lanes in large vehicles causing congestion, and to wash and reprocess the plastic - so recycling of mulch film makes little sense in economic or environmental terms.

Long before this paper was published many distinguished scientists had researched and written in peer-reviewed publications on the biodegradation of polyethylene mulching films, and the technology was well understood. Brassioulis et al say “The behaviour of polyolefins containing pro-oxidants during photo-oxidation is explained in Arkatkar et al. (2009) by means of the cleavage occurring predominantly at the weak links of the polymers which have lower bond energies (e.g. C–H and C–O) and the subsequent formation of free radicals.

The free radicals can react further with atmospheric oxygen and trigger the oxidation of the polymer that continues in a stepwise fashion producing carbonyls, aldehydes, peracids and acids (Arkatkar et al. 2009).”

At page 47 of “Degradable Polymers, Principles and Applications” (ISBN 1-4020-0790-6) Professor Gerald Scott says “The degradation products formed by oxo-biodegradation are of benefit to the agricultural environment as biomass and ultimately in the form of humus. Carbon is retained in the soil during oxo-biodegradation in a form accessible to growing plants, rather than by being eliminated to the environment as carbon dioxide, as is the case with hydro-biodegradable polymers (e.g. pure cellulose and starch)..... Time control of biodegradation of the synthetic carbon-chain polymers is achieved by antioxidants that behave similarly to naturally occurring antioxidants present in lignin and tannin.”

See also “Polymers and the Environment” (ISBN 9780854045785) pages 109-118 and 461-466.

We know from our own experience, including the field trials in Wales, <https://www.biodeg.org/wp-content/uploads/2020/09/Pembroke-Mulch-Film-Trial-Report-30.09.13V1.pdf> that biodegradable mulch film has to be designed with regard to the timescale for growing the crop, and the weather-conditions likely to be experienced on the farm. Oxo-biodegradable mulch film can be programmed accordingly (by adjusting the composition of the masterbatch) but this cannot be done with bio-based plastic such as PLA.

If a farmer simply buys an “off the shelf” plastic mulch film, it is quite likely that it will not properly degrade and biodegrade in the timescale required for the particular crop in that part of the world, and this is what seems to have happened with the mulch film studied by Brassioulis et al.

THE MATERIAL

On page 2585 the authors correctly say “Environmental degradability of plastics is a multifaceted complex process strongly influenced by the nature of the plastics, as well as biotic and abiotic conditions to which they are exposed.

At p.2587 they describe the composition of the test films, from which it becomes apparent why the films lasted so long. They contain carbon-black, which is a powerful stabiliser, and this has been added at 16%, which is a very high concentration. Also, they contain 3,000 ppm of Tinuvin 783, which contains a combination of stabilisers, and they have added even more of it (4,000ppm) in LLDPE-P2. In addition to these stabilisers they have included Envirocare® AG1000 which also contains stabilisers.

Stabilizers are intended to protect plastics from the effect of weathering, so as to give them a useful service-life, but in the case of oxo-biodegradable film it is crucial to get the balance right between the prodegradant catalyst and the stabilisers. The films used for these tests had been seriously over-stabilised, and it is not surprising that figs 1, 2 and 3 show that the material had hardly degraded at all.

If it is intended to use carbon-black as a pigment in mulching film, the polymer and/or the masterbatch would have to be adjusted accordingly, to avoid over-stabilisation.

THE EXPERIMENT

We have the following comments:

In the Introduction, the authors say: “.....Biodegradable polymers, disposed in bioactive environments, degrade by the enzymatic action of microorganisms, such as bacteria, fungi and algae, and their polymer chains may also be broken down by non-enzymatic processes such as chemical hydrolysis.....”.

However, in the case of polyethylene films, the molecular-weight of polyethylene is too high for biodegradation. It must first be reduced by oxidation, and that is the purpose of the prodegradant masterbatch.

They say that “In order to allow a controlled and repeatable method of assessing the degradability, a number of standards have been developed that define the testing of degradability under closely monitored conditions mimicking the conditions of application. They refer to ISO 14855 “Determination of the ultimate aerobic biodegradability of plastic materials under controlled composting conditions” but the relevant standards, which they do not mention, are BS8472 and ASTM D6954 for “Plastics that Degrade in the Environment by a Combination of Oxidation and Biodegradation.” One of the authors of D6954 is Dr. Graham Swift, who explained the Standard in evidence to the UK government at www.biodeg.org/wp-content/uploads/2021/02/Swift-evidence-to-BEIS.pdf

In the Introduction to the Brassioulis paper the authors also say: “.....Furthermore, all parameters involved in the natural complex phenomenon of biodegradation, including the diversity and efficiency of microbial communities, cannot be entirely reproduced and controlled in vitro...”. Yes, but the biodegradation process can be properly measured and assessed only in lab conditions, not in outdoor conditions, and this is the reason why the standards organizations have developed standard test methods such as ASTM D6954 and BS8472.

It is recognized by the standards organizations that the biodegradation of polymers, assessed in lab conditions, represents a worst-case scenario, when compared to natural, outdoor, environmental conditions. In natural conditions, there is a synergy between the microbial activity and the degradation process and there is more than one species of microorganism.

The authors say “.....The accumulative effects of PE fragments and the impact on the environment of the repeated use of these PE films remain a serious open issue.....”. This is certainly the case with ordinary PE, and farmers should not be allowed to use it, but in the case of oxo-biodegradable plastics ASTM D6954 is specifically dealing with this issue in NOTE 1—The intended use of this guide is for comparison and ranking of data to aid in the design and development and the reduction of environmental impacts of polymers that require no more than 24 months to oxidize and biodegrade in the intended use and disposal options, and create no harmful or persistent residues under the appropriate disposal conditions (for example, two seasons of crop-growing conditions in soil).....”. So, if a mulch film is properly designed, and successfully tested according to D6954 the material will biodegrade in a maximum of 24 months and will not only avoid plastic accumulation and pollution but will provide a source of carbon for the plants.

The Brassioulis paper does not show that the molecular weight of the degraded polymer was ascertained before the material was buried and does not therefore show that Mw had reduced below 5000 Daltons. The paper says the film was tested for Tensile Elongation, but ASTM D3826, (listed in ASTM D6954 as a PASS/FAIL condition for Tier 1) requires a minimum 95% loss of mechanical properties (Elongation at Break) for 75% of the specimens tested.

The paper says: “.....The majority of these films come from the lower layer of the beds (lower film 2), and some others come from the remains of the upper layer (upper film 1)....” It is notable therefore that the lower layer of film was not exposed to direct sunlight, as it had another layer of film above, and if this is added to the fact that the films were grossly over-stabilised it is not surprising that it did not abiotically degrade as it should. Significant *biodegradation* does not occur until the molecular weight has reduced to 5,000 Daltons or thereabouts.

The way the film was gathered, folded, agglomerated, and then buried does not represent a mulch film application on a farm. The plastic film, in order to abiotically degrade and then biodegrade requires a dispersion of the material in and on the soil - which would occur on a farm. The film would not be buried as an agglomerated/multi-folded plastic mass.

On page 2590 “the losses of Tensile Strength and Elongation are relatively low, compared to the timescale for burial.” This is due to over-stabilisation, and also to the fact that the film was buried multi-folded and very probably with limited oxygen due to the folding.

Not only is carbon black a powerful stabiliser, but the authors note that “it is difficult to obtain a usable FTIR transmission spectral scan from materials with large quantities of carbon (i.e. carbon black in this case) because carbon strongly absorbs infrared light in a broad range of frequencies.”

On page 2592, “the melting temperature T_m and the crystallisation temperature T_c show only minor changes during their exposure under cultivation conditions. The same is indicated after soil burial for a very long period (8.5 years).” The reason for this is, as mentioned above, over stabilisation and the manner of burial.

“.....Similarly, Dannenberg et al. (1958) studied the peroxide free radical crosslinking reaction in polyethylene/carbon black systems and found that the crosslinking of polyethylene resulted in a decrease in density from which a subsequent decrease in percent crystallinity can be established. Furthermore, Feuilleley et al. (2005) claimed that due to the crosslinking of PE, the large PE fragments that are found in this state cannot be bioassimilated by soil bacteria, and large cumulative effects in soil cannot be ruled out.....” Yes, this is why film should be tested in the laboratory according to ASTM D6954 before being sold to farmers, as any member of the BPA would do. Para. 4.5.1 of this Standard says “It is important to establish the extent of gel and its nature or permanence in the polymer residue and report these findings.” See also paras. 6.3.1-6.3.3.

“.....The CI change during the cultivation period is in agreement with the corresponding crystallinity results from the DSC analysis (Fig. 9), and it means that the upper film degraded more than the lower one.” Yes, because abiotic degradation is accelerated by uv light, from which the lower film was to a significant extent shielded.

“.....According to Kalus (2007), as mulching film is often exposed to water under real cultivation conditions, the humidity can permeate easily the amorphous regions of the film and deactivate free radicals. Consequently, the formation of low molecular by-products such as carboxylic acids cannot proceed....” Yes, it is possible that rain can interfere with the carbonyl-based chemicals formation, but this process is dynamic and once the rain has stopped, the UV and ambient heat will restart the abiotic degradation process. If the masterbatch is correctly designed and dispersed in the polymer, rain will not therefore prevent abiotic degradation.

“...These earlier published research results explain the fact that the carbonyl index is zeroed after the long period of soil burial of the films in the field (Figs. 10 and 11).....” However, Jakubowicz et al (Polymer Degradation and Stability 96 (2011) 919-928) found that after two years of mineralization, 91% conversion to carbon dioxide was obtained in the soil test.

“After the long soil burial period of 8.5 years, and despite the further degradation of the mechanical properties of the films, no disintegration signs were observed. The buried films were recovered almost intact.” Yes, due to gross over-stabilisation and burial in an artificial manner which would not occur in use of the film on a farm.

10th September 2024