

Accelerating the degradation of polyethylene composite mulches

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Films containing poly(methyl methacrylate)-modified titanium dioxide nanoparticles exhibit enhanced photocatalytic oxidation and biodegradation.

Polyolefins are widely used in agricultural applications (e.g., for greenhouse, mulching, or tunnel films). Indeed, 80% of plastic mulches are reportedly made from polyolefins (e.g., polyethylene).^{1,2} Although this material can promote good harvests—by providing protection from insect pests and by creating suitable growth environments (e.g., in terms of soil temperature and moisture conservation)—the disposal of most polyolefin plastic mulches is problematic. The low cost and difficulty of recycling polyolefins means that the mulches are usually released directly to the surrounding environment at the end of their service life, but this can lead to serious waste and pollution problems (because polyolefins are non-degradable).^{3,4} It is therefore highly desirable to develop an efficient, environmentally friendly, and degradable polyolefin material for sustainable use in soil environments.

Oxo-biodegradation (e.g., abiotic and biotic degradation) of polyethylene has previously been demonstrated as a promising route to solve this plastic pollution problem.^{3,5–8} In this method, pro-oxidant additives (e.g., titanium dioxide, TiO₂, nanoparticles) are introduced into the polyethylene matrix to accelerate the rate of abiotic degradation.^{9,10} The pro-oxidants react—under UV irradiation—with water and oxygen to form hydroxyl radicals that can then initiate the degradation of polyethylene. As a result, the smaller hydrophilic molecular fragments can be further biodegraded in the presence of micro-organisms (e.g., bacteria, fungi, and algae). This whole process, however, is usually very slow and is limited by the formation of nanoparticle agglomerates.

As part of our ongoing efforts to design and produce novel degradable polyethylenes, we have investigated the use of poly(methyl methacrylate), PMMA, as a graft on the surface of TiO₂ nanoparticles to hasten the polyethylene photo-oxidation process.¹¹ This hydrophilic coating promotes water adsorption and therefore more water is available for photo-oxidation. In addition, we have unexpectedly found

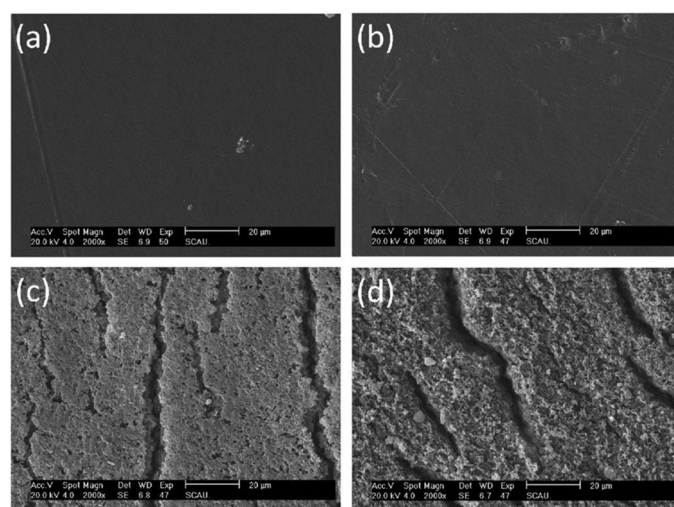


Figure 1. Scanning electron microscope (SEM) images of the low-density polyethylene (LDPE) film (a) before and (b) after UV irradiation for 415 hours. Images of irradiated LDPE composite films that contain (c) titanium dioxide (TiO₂) nanoparticles and (d) poly(methylmethacrylate)-modified TiO₂ nanoparticles are also shown (TiO₂/LDPE and TiO₂-g-PMMA/LDPE, respectively).¹¹

that this hydrophilic modification of TiO₂ nanoparticles improves their dispersibility and compatibility within the polyethylene matrix (thus resulting in further enhanced photocatalytic oxidation).

For our experiments, we used samples of pure low-density polyethylene (LDPE), as well as LDPE composites containing either TiO₂ nanoparticles (TiO₂/LDPE) or PMMA-modified TiO₂ nanoparticles (TiO₂-g-PMMA/LDPE). We performed photocatalytic oxidation of the films under ambient air in a UV lamp box. For each sample, we created three replicated discs and weighed them every 24 hours during a 415-hour irradiation cycle. We measured a 39.6% weight loss for the TiO₂-g-PMMA/LDPE film, and a 96.5% reduction in average

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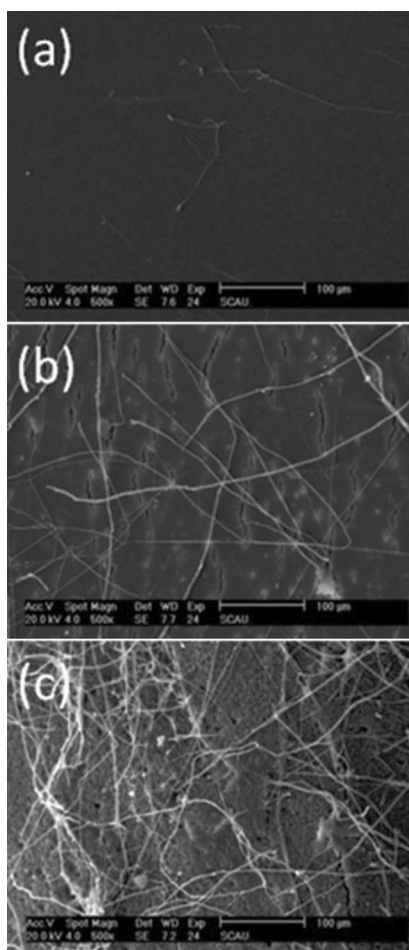


Figure 2. SEM images of the pure LDPE, TiO_2/LDPE , and $\text{TiO}_2\text{-g-PMMA/LDPE}$ composite films after fungal metabolic action.¹¹

molecular weight, after 415 hours. These results are much better than for the pure LDPE sample (weight and average molecular weight reductions of 0.5 and 46.3%, respectively).

From scanning electron microscope (SEM) images of our films (see Figure 1), we observe several morphological features that suggest the extent of oxidation of the $\text{TiO}_2\text{-g-PMMA/LDPE}$ sample was much higher than that of the pure LDPE and TiO_2/LDPE films (after 415 hours of UV irradiation). In particular, we find that the surface of the pure LDPE film is very smooth and unchanged by the irradiation. In contrast, the structure of the composite films was substantially destroyed by the irradiation process. We also see a number of cavities and cracks on the surface of the composite films, which are created by the escape of volatile products from the LDPE matrix. The cavities are larger on the $\text{TiO}_2\text{-g-PMMA/LDPE}$ surface than on the TiO_2/LDPE film.

In a subsequent part of our study, we aseptically transferred our irradiated films onto agar plates and inoculated them with selected fungal strains (previously isolated from soil and purified). We then incubated the samples at 28°C , and used SEM images (see Figure 2) to analyze colony growth after 30 days. The SEM images reveal profuse fungal growth on both of the composite films, but no colonization of the mycelia-forming fungus on the pure LDPE film. Furthermore, the more vibrant growth of mycelia on the surface of the $\text{TiO}_2\text{-g-PMMA/LDPE}$ composite film indicates more robust fungal metabolic activity than on the TiO_2/LDPE sample.

In summary, we have studied the use of PMMA-surface-modified TiO_2 nanoparticles as additives to promote the degradation of polyethylene. We find that composite films made from LDPE and these modified nanoparticles exhibit much greater weight loss after UV irradiation than pure LDPE samples. In addition, we observe vibrant fungal growth on our irradiated composite samples, which can lead to further biodegradation of the films. In our future work, we plan to evaluate the impact of photo-oxidized and biodegraded LDPE fragments on the environment and on human health. We would also like to test the use of the resultant plastic mulches in the field, as well as investigate the scale-up of our approach.

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References

1. M. S. Dopico-García, J. M. López-Vilariño, and M. V. González-Rodríguez, *Antioxidant content of and migration from commercial polyethylene, polypropylene, and polyvinyl chloride packages*, **J. Agricult. Food Chem.** **55**, pp. 3225–3231, 2007.
2. P. K. Roy, M. Hakkarainen, I. K. Varna, and A.-C. Albertsson, *Degradable polyethylene: fantasy or reality*, **Environ. Sci. Technol.** **45**, pp. 4217–4227, 2011.
3. M. Koutny, M. Sancelme, C. Dabin, N. Pichon, A.-M. Delort, and J. Lemaire, *Acquired biodegradability of polyethylenes containing pro-oxidant additives*, **Polym. Degrad. Stabil.** **91**, pp. 1495–1503, 2006.
4. W. Y. Liang, Y. Luo, S. Song, X. Dong, and X. Yu, *High photocatalytic degradation activity of polyethylene containing polyacrylamide grafted TiO_2* , **Polym. Degrad. Stabil.** **98**, pp. 1754–1761, 2013.
5. M. M. Reddy, M. Deighton, S. Bhattacharya, and R. Parthasarathy, *Biodegradation of montmorillonite filled oxo-biodegradable polyethylene*, **J. Appl. Polym. Sci.** **113**, pp. 2826–2832, 2009.
6. M. M. Reddy, R. K. Gupta, R. K. Gupta, S. N. Bhattacharya, and R. Parthasarathy, *Abiotic oxidation studies of oxo-biodegradable polyethylene*, **J. Polym. Environ.** **16**, pp. 27–34, 2008.

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7. J. Šerá, P. Stloukal, P. Jančov'a, V. Verney, S. Pekařová, and M. Koutný, *Accelerated biodegradation of agriculture film based on aromatic–aliphatic copolyester in soil under mesophilic conditions*, **J. Agricult. Food Chem.** **64**, pp. 5653–5661, 2016.
8. K. Lubkowski, A. Smorowska, B. Grzmil, and A. Kozłowska, *Controlled-release fertilizer prepared using a biodegradable aliphatic copolyester of poly(butylene succinate) and dimerized fatty acid*, **J. Agricult. Food Chem.** **63**, pp. 2597–2605, 2015.
9. C. Abrusci, J. L. Pablos, I. Marín, E. Espí, T. Corrales, and F. Catalina, *Photodegradation and biodegradation by bacteria of mulching films based on ethylene-vinyl acetate copolymer: effect of pro-oxidant additives*, **J. Appl. Polym. Sci.** **126**, pp. 1664–1675, 2012.
10. D. M. Wiles and G. Scott, *Polyolefins with controlled environmental degradability*, **Polym. Degrad. Stabil.** **91**, pp. 1581–1592, 2006.
11. W. Yang, S. Song, C. Zhang, W. Liang, X. Dong, Y. Luo, and X. Cai, *Enhanced photocatalytic oxidation and biodegradation of polyethylene films with PMMA grafted TiO₂ as pro-oxidant additives for plastic mulch application*, **Polym. Compos.**, 2017. doi:10.1002/pc.24358