Advanced Materials Research Vol. 747 (2013) pp 481-484
© (2013) Trans Tech Publications, Switzerland
doi:10.4028/www.scientific.net/AMR.747.481

Anti-algal Performances for Biocide-Enhanced Low-Density Polyethylene Film

Atthapong Gitchaiwat[1,a], Somthida Likhitlert[1,b], Apisit Kositchaiyong[1,c], Kwannate Sombatsompop[2,d], Benjaphorn Prapagdee[3,e], Khokhwan Israngkura N.A.[4,f] and Narongrit Sombatsompop[1,g]

[1]Polymer PROcessing and Flow (P-PROF) research group, Materials Technology,

School of Energy, Environment and Materials, King Mongkut's University of Technology Thonburi (KMUTT), Bangkok, 10140, Thailand

[2]College of Industrial Technology,Department of Civil and Environmental Engineering Technology,King Mongkut's University of Technology North Bangkok (KMUTNB),Bangsue, Bangkok, 10800, Thailand

[3]Laboratory of Environmental Biotechnology, Faculty of Environment and Resource Studies

Mahidol University (MU), Salaya, Nakhonpathom, 73170, Thailand

[4]Koventure Co., Ltd. 563 Moo 4 Bangpoo Industrial Estate Soi 10,

Sukhumvit Rd., Praeksa, 10280 Thailand

[a]pong_pong266@hotmail.com, [b]mook_246@hotmial.com, [c]apisit.kos@kmutt.ac.th, [d]kwn@kmutnb.ac.th, [e]enbrp@mahidol.ac.th, [f]khokwan@purity.co.th, [g]narongrit.som@kmutt.ac.th

Key words: Low Density Polyethylene, Terbutryn, Anti-algal performance, *Chlorella vulgaris*, *Phormidium angustissimum*

Abstract. In this work, low-Density Polyethylene (LDPE) films incorporated with 2-methylthio-4-ethylamino-6-tert.butylamino-triazin-1,3,5, or Terbutryn (TT) was used as anti-algal agent, at different concentrations were evaluated for anti-algal performances. Clear zone test and chlorophyll *a* measurement method were used for anti-algal evaluations against *Chlorella vulgaris* (TISTR 8580) and *Phormidium angustissimum* (TISTR 8979) as testing algae. Mechanical properties and surface color changes of LDPE were also observed for the effect of algaecide addition. It was found that addition of TT in the LDPE specimen did not significantly alter the tensile strength, tensile elongation and toughness properties of materials. For anti-algal test, it should be noted that the greater clear zone area (clear zone test) or smaller chlorophyll *a* content (chlorophyll *a* measurement method) the better anti-algal activities. It was found that the clear zone of the TT filled LDPE sample was observed with *C. vulgaris* but was not seen with *P. angustissimum*. When the TT concentration in LDPE was greater than 600 ppm, the *C. vulgaris* did not grow.

Introduction

Plastic products have been widely used in many applications including; medical devices, packaging products, automotive parts, electronic components and agricultural equipment. For agriculture and packaging portions, low density polyethylene (LDPE) is one of the most common plastic materials to be used in different forms such as sheet and films [1]. Main purposes for this product form are to retain moisture, to protect pest and weed, and to increase yields. Though the LDPE materials have been known to have the resistances from environmental deteriorations, in a proper condition they could be risked for microbial colonization. Colonization by the microorganisms like fungi, algae and bacteria have been frequently reported and caused for health and economic problems for human [1-3].

Algae are a primary organism that can grow in fresh water or at the surface of most materials under high moisture content and sunlight exposure. The aim of this study was to improve anti-algal properties of LDPE film by incorporating an anti-algal agent or an algaecide into the film. Commercial biocide, 2-methylthio-4-ethylamino-6-tert.butylamino-triazin-1,3,5, or Terbutryn (TT), was used as an algaecide in this study. Anti-algal performance, mechanical properties and physical appearances of LDPE were observed for the effects of algaecide loading. Clear zone test and chlorophyll *a* measurement technique were used for anti-algal evaluations. The anti-algal evaluations were compared between *Chlorella vulgaris* and *Phormidium angustissimum* used as testing algae.

Experimental

Materials and chemicals: Low density polyethylene (LDPE, grade LD1905F), supplied in from pellet by Siam Cement Company (Bangkok, Thailand), was use as a polymer matrix. 2-methylthio-4-etylamino-6-tert.butylamino-triazine-1,3,5 (Terbutryn, TT) supplied by Troy Asia Co. LTD. (Bangkok, Thailand) was used as an anti-algal agent.

Specimen preparation: The procedure for test specimen preparation was commenced by direct mixing LDPE pellets with Terbutryn at various concentrations ranging from 0 to 1,000 ppm, using a twin-screw extruder ((Haake Polylab-Rheomex CTW 100P, Germany). The mixture were then transformed into film specimens having 1.0 mm thick using a hydraulic press under processing conditions of processing temperature, holding pressure and time of 160^{o}C, 100 kg/cm^2 and 10 min, respectively. The molded pieces were cut into the standard test pieces as given by the testing methods used in this study.

Tensile test: Mechanical properties of LDPE with TT at different concentrations were carried out through tensile test using universal testing machine (Autograph AG-I, Shimadzu Co., Ltd., Japan). The test specimens were prepared in a dumbbell test piece as followed by standard test method of ASTM D638-10 (Type IV). The results were reported in terms of ultimate tensile strength, % elongation and toughness value which were averaged from at least five independent determinations.

Discoloration test: Surface discolorations of specimens after introducing TT for different loadings were investigated through LAB color space system in terms of lightness (L*), chromatic coordinate value (a* and b*). The a* and b* values represent magenta/green and yellow/blue chromatic coordinate, respectively. The measurements were carried out by UV-Vis spectrophotometer (model 3100; Shimadzu, Kyoto, Japan) and calculated based on D65 light source in a spectrum range of 380 to 780 nm.

Anti-algal performance evaluations:

Testing algae: Two types of algae, including *Chlorella vulgaris*, green algae (TISTR 8580), and *Phormidium angustissimum*, blue green algae TISTR 8979, obtained from the Thailand Institute of Scientific and Technological Research (Pathum Thani,Thailand), were used as testing algae.

Clear zone test: This test is a qualitative method to perform anti-algal properties of materials by investigating clear zone area around test specimens. Greater clear zone area indicates higher anti-algal performance. Circular disk having 5 mm in diameter was used as testing specimen. The details for this method were obtained elsewhere [4]. The results were illustrated using digital camera images.

Chlorophyll a measurement method: This test is a quantitative analysis for evaluating anti-algal efficacies of materials. The test mode is conducted by dynamic shake flask method by which the method was slightly modified from standard testing method ASTM3731-04. Test specimen in a square test piece of 5×5 cm was put into the flask having algal cell suspension at a certain cell content. The procedures of the test were given in the previous study [4]. Anti-algal performance of materials was considered by a reduction of chlorophyll *a* value (C_a) accounting from the chlorophyll substance after extraction from algal cell suspension at a given contact time. Anti-algal properties of algaecidal effect of materials were taken into accounted from a reduction of C_a value as compared with that in the control flask (without specimen).

Results and discussion

Table 1 shows mechanical properties of LDPE doped with TT at different loadings. The results also suggested that the addition of TT did not significantly affect the tensile properties of the film specimens. For physical appearance as given in Table 2, lightness value (L*) as well as chromatic coordinate (a*, b*) remained unchanged with increasing TT content. The findings clearly suggest that the 2-methylthio-4-etylamino-6-tert.butylamino-triazine-1,3,5 or Terbutryn (TT) did not influence the chemical and mechanical changes of LDPE film significantly.

Table 1 Mechanical properties of LDPE doped with TT for different concentrations

TT Content (ppm)	Ultimate tensile strength (MPa)	Elongation at break (%)	Toughness (J)
0	22.7 ± 0.9	1117 ± 36	2.8 ± 0.1
50	20.9 ± 1.0	993 ± 53	2.4 ± 0.1
100	20.6 ± 2.7	983 ± 158	2.8 ± 0.5
150	22.2 ± 3.3	1032 ± 103	2.6 ± 0.4
200	20.6 ± 3.6	987 ± 74	2.4± 0.2
400	22.1 ± 3.0	1146 ± 23	3.2 ± 0.4
600	21.0 ± 2.8	940 ± 47	2.3 ± 0.2
800	21.0 ± 1.2	1021 ± 83	2.6 ± 0.6
1000	22.4 ± 1.6	1,55 ± 81	2.6 ± 0.4

Table 2 Color change of LDPE doped with TT for different concentrations

TT Content (ppm)	L*	a*	b*
0	94.7 ± 0.4	0.0 ± 0.1	0.8 ± 0.1
50	95.7 ± 0.0	0.1 ± 0.1	0.7 ± 0.1
100	95.8 ± 0.0	0.2 ± 0.1	0.7 ± 0.0
150	95.7 ± 0.0	0.1 ± 0.0	0.7 ± 0.0
200	95.8 ± 0.0	0.1 ± 0.0	0.7 ± 0.1
400	95.7 ± 0.2	0.1 ± 0.0	0.6 ± 0.1
600	95.4 ± 0.2	0.1 ± 0.0	0.7 ± 0.1
800	95.9 ± 0.0	0.1 ± 0.1	0.7 ± 0.1
1000	96.1 ± 0.0	0.1 ± 0.1	0.5 ± 0.0

Fig. 1 demonstrates the clear zone results for TT doped LDPE samples at various dosages of TT. The greater the clear zone area the more the anti-algal performance of the LDPE film. It was interesting to note that the TT had an obvious effect, showing the inhibition area of algal growth, when testing against *C. vulgaris*, but seemed to be insensitive when testing against *P. angustissimum.* A possible explanation for this was associated with the protection mechanism of blue green algae (*P. angustissimum*) by slime layer formation when being attacked by toxic chemicals [5].

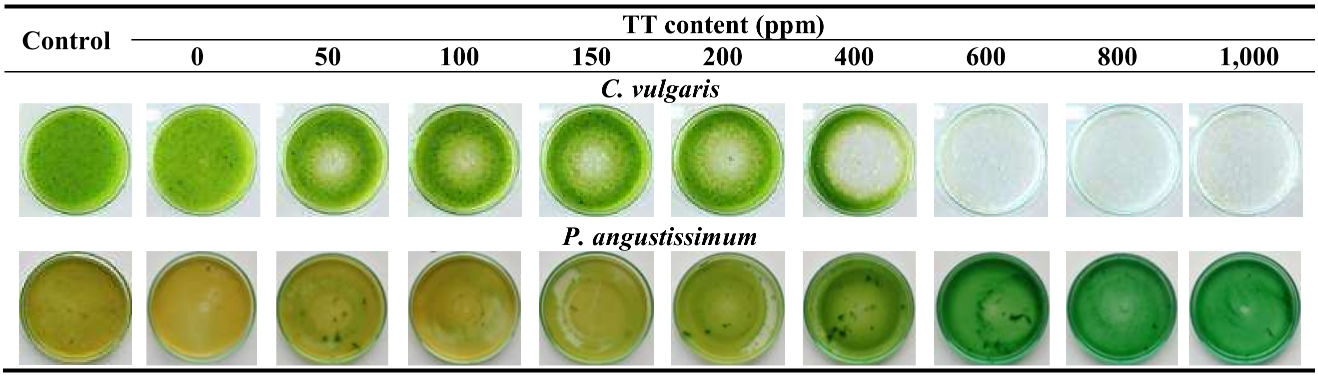

Figure 1 Digital camera images for clear zone test under 28 days of incubation period: the upper and the lower represent *C. vulgaris* and *P. angustissimum*, respectively.

Fig. 2 shows the quantitative results of anti-algal performance form chlorophyll *a* measurement in terms of chlorophyll *a* value (C_a). It was found that adding TT in LDPE from 0 to 1,000 ppm and tested against *C. vulgaris* resulted in a progressive decrease in the C_a value, which indicated the algaecidal properties of the film. However, when testing against *P. angustissimum*, the C_a value of LDPE doped with TT in a range from 50 to 200 ppm appeared to be unexpectedly higher than that of the neat LDPE as well as the control experimental flask (without film specimen). Rioboo et al [6] and Chen et al [7] suggested that at low loading, TT could possibly act as nitrogen element to the algae, especially for relatively high resistances to the environmental conditions like blue-green *P. angustissimum*.

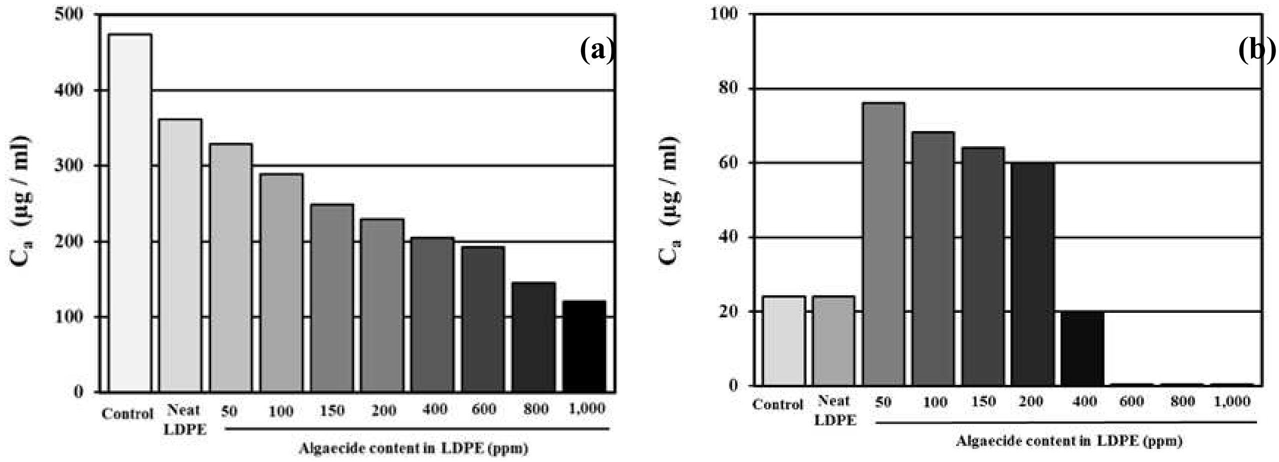

Figure 2 Chlorophyll *a* value (C_a) from chlorophyll measurement method: where (a) *C. vulgaris* and (b) *P. angustissimum*

Summary

Mechanical properties and physical appearance of LDPE were not affected by the addition of Terbutryn (TT). For anti-algal test, addition of TT in LDPE exhibited much greater clear zone area when testing against *C. vulgaris* whereas there was no clear zone when testing against *P. angustissimum.* The results by Chlorophyll A measurement suggested that the TT doped LDPE could perform algaecidal effect at all TT concentrations used (0-1,000 ppm) for the *C. vulgaris* while for the *P. angustissimum*, the algaecidal effect could be effective only when the TT concentrations were greater than 400 ppm.

Acknowledgement

The authors thank for the Thailand Research Fund under the TRF Senior Scholar Grant (RTA 5580009) and the Office of the Higher Education Commission (OHEC) under the National Research University (NRU) for financial support. King Mongkut's University of Technology North Bangkok is acknowledged for micro-biological instruments and laboratory.

References

[1] V.L. Finkenstadta, B. Tisserat, Poly(lactic acid) and osage orange wood fiber composites for agricultural mulch films, Ind. Crop. Prod. 31 (2010) 316-320.

[2] T. Galya, V. Sedlarik, I. Kuritka, J. Sedlarikova, P. Saha. (2008). Characterization of antibacterial polymeric films based on poly(vinyl alcohol) and zinc nitrate for biomedical applications, Int. J. Polym. Anal. Charac. 13 (2008) 241–253.

[3] S. Wallström, E. Strömberg, S. Karlsson, Microbiological growth testing of polymeric materials: an evaluation of new methods, Polym. Test. 24 (2005) 557-563.

[4] A. Gitchaiwat, A. Kositchaiyong, K. Sombatsompop, B. Prapagdee, K. Isarangkura, N. Sombatsompop, Assessment and characterization of anti-fungal and anti-algal performances for biocide-enhanced linear low-density polyethylene, J. Appl. Polym. Sci. 128 (2013) 371–379.

[5] N. G. Carr., B.A. Whitton, The Biology of Blue-Green Algae., University of California Press, California, 1973.

[6] C. Rioboo, O. Gonzalez, C. Herrero, A. Cid.. Physiological response of freshwater microalga (*Chlorella vulgaris*) to triazine and phenylurea herbicides. Aquat. Toxicol. 59 (2002) 225–235.

[7] S. Chen, X. Chen, Y. Peng, K. Peng, A mathematical model of the effect of nitrogen and phosphorus on the growth of blue-green algae population Appl. Math. Model. 33 (2009) 1097-1106.