On the Influence of Nutrient Agents on Accelerated Physical Aging of LDPE Based Mulch Foil

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Abstract: - Accelerated physical aging of polymeric materials play unsubstitutable role in simulation of life cycle prediction of polymeric products. In the presented study influence of selected nutrient agents used for fertilization in agriculture on plastic foil was experimentally determined in order to evaluate its contribution to physical aging acceleration. Tested samples were treated using nutrient bath and UV radiation. The influences of chemical and physical treatments were evaluated using thermal analysis and mechanical testing.

Key-Words: - Polyethylene, Plastic Mulch, UV Radiation Treatment, Nutrient Agent, Mechanical Testing, Thermal Analysis

1 Introduction

Utilization of polymeric materials in agriculture is becoming increasingly popular in modern agriculture. The term “Plasticulture” is defined by the American Society of Plasticulture as “the use of plastics in agriculture for both plant and animal production including” [1]. Even there is a huge potential of plastic utilization in this field as silage and compost bags, greenhouses, and drip irrigation the production of covering aids made of non-woven fabrics, shading nets made of fibbers or mulch foils is probably the most extended and comprise the major amount of fabricated polymeric materials. The material being used for mulch foil is mostly low density polyethylene (LDPE) but some LLDPE and HDPE (linear low density and high density, respective) is also used. The very thin films are very popular with the growers, since the growth benefits of the thin mulch are the same and cost 30 percent less.

Introduction of plastic mulches, covering in 1999 more than thirty million acres of agricultural land worldwide, provides several advantages as earlier crops due to raised soil temperature, reduction of evaporation and nutrient leaching, fewer weed problems, improved disease and insect resistance, root pruning eliminated, and cleaner vegetable product. Clearly plastic mulch foil can increase yield and improve product quality by modifying soil temperature and controlling soil moisture, moreover it was shown that reflective mulches offer the advantage of not overheating the soil [2-4]. In several investigations [5] it was proved that it could increase yields in several crops, such as tomatoes, peppers, eggplant, watermelons, or strawberries, even doubling production in some cases.

However, there are still some disadvantages with plasticulture, including the costs of removal and disposal of the used plastics and environmental concerns, since most of the used mulch ends up in landfills overburdened with waste plastic. To overcome these problems, the use of degradable mulch films right at the field seems to be a promising solution bringing the costs of removal and disposal reduction, preventing mulches interference with future tillage, and cutting-down the amount of landfilled waste.

Nevertheless, utilization of biodegradable mulches is still in the experimental stage. The most promising film formulations based on renewable sources contain about 40 % of starch and 30 percent each of poly(ethylene-co-acrylic acid) and polyethylene, furthermore wastes of potato starch and cheese whey are being put through a fermentation process the end product, lactic acid, appear to be a viable candidate for conversion to environmentally safe degradable plastics. When good biodegradable mulches come onto market a great breakthrough will have been made in reducing the cost of plastic removal from the field and eliminating the problem of plastic disposal.

ISBN: 978-1-61804-022-0

Also photodegradable plastic mulches are currently receiving much attention. The plastic mulches have many attributes of standard polyethylene mulch: they are easy to lay and provide the usual benefits associated with mulch. The major difference is that photodegradable mulches decompose after the film has received a predetermined amount of UV light. The sun will start to break the material down over time. When the degradable mulch has received sufficient light it become brittle and develops cracks, tears, and holes. Even small sections of mulch may be torn off and blown away by the wind; the film finally disintegrates into small flakes and disappears into the soil. The chemical composition of the film determines the amount of light required to initiate breakdown. Time length of degradation varies and depends also on climate, cloud cover, intensity of the sun and chemical usage. The normal age of the mulch film should be designed for 2-4 months, starting from the laying of the film until the harvesting of the produce. However, there are many factors affecting the photodegradation and biodegradation rate of films, and they should be considered to design, produce, and control the right degradation rates [6].

Regarding the fact of various effect complexities on lifecycle of photodegradable plastic mulches, very influence of selected commercially available fertilizer on degradation kinetics is investigated in the present work on the case of starch filled mulch foil based on LDPE.

2 Experimental

Influence of chemical/physical aging on thermal properties of tested mulch foils were characterized using differential scanning calorimeter (DSC), while changes in mechanical behaviour was recorded by the help of universal tensile test machine.

2.1 Plastic Mulch Foil Treatment

Starch filled plastic mulch foil of thickness of 70 μm based on low density polyethylene was used for the investigation of the influence of commercially available nutrient agents on the kinetic of physical aging evoked by photodegradation.

Mulch samples were cut into the rectangle form with dimensions of 150x45 mm. Prepared samples were treated in three various ways. Some of the samples were put into the baths containing nutrient agents, others were exposed to the UV light activity, and the rest of them were treated by the combination of the both effects.

Xenotest Alpha+ (Atlas Material Testing Technology GmbH, Germany) providing reproducible and repeatable test results of lightfastness using an air-cooled xenon arc light source was employed as a mean of accelerated weathering in order to evaluate change of photodegradability rate due to chemical effects of chosen fertilizers. For the weathering simulation purposes humidity conditions of 80 RH and chamber, and black standard temperature of 48, and 60 °C, respectively were chosen.

Baths of four various nutrient agents produced by Bio Nova (Netherlands) were employed in order to separately evaluate influence of individual components usually utilized in combination. For the study BN NUTRI NOVA A+B substrate nutrient (marked as *NN* below in the text), BN-ZYM Enzyme (*B*) natural bio-catalyst system based on specific enzymes, TML-The Missing Link (*T*) ultimate flowerbooster stimulating the plant's natural defence system, and fertirtilizer BIO NOVA PH (*BN*) were selected. While the concentration of nutrient agents ten times exceed the recommended dosage, bathing times of samples at room temperature were set to be approximately the same as times of UV treatment (for details see Table1).

2.2 Thermal Properties

Melting (Tm) and crystallization (Tc) temperatures of the un/treated plastic mulch foil were determined using DSC 1 apparatus (Mettler-Toledo Inc., Switzerland) equipped with autosampler and intracooler. The testing temperature range from 25°C to 140 °C was used with a ramping rate of 20°C/min in the first scan in order to increase sensitivity of measurements, while the rate of 5 °C was chosen for the second temperature ramp.

2.3 Mechanical Properties

Tensile tests with speed of 100 mm/min carried out using TESTOMETRIC M350-5CT universal testing machine (Testometric Company Ltd., UK) on the samples of the rectangular shape with the size of 8x45 mm approximately and initial grip length of 30 mm were applied with the purpose to determine influence of accelerated aging on Young modulus, tensile strength and elongation at break.

3 Results and Discussion

Summarization of treating UV/bathing conditions of the tested plastic mulch foil samples are given in Table 1.

Table 1 – Legend for sample description defining conditions of UV and bath treatment together with UV dosage applied on the samples.

Number of cycles x	UV (x)		/ *bath*(x)
	Treatment time (h)	UV Dosage (kJ.m^{-2})	Treatment time (h)
0	0	0	0
1	80	7452	85
2	175	16386	194
3	266	24897	306
4	338	31641	401

It should be noted that while type of fertilizer is used in the description of bath cycles further in the text, labelling *b*0 could be found for the case of un-bathed samples. For example UV0/*NN*4 stands for the sample untreated by photodegradation process using Xenotest and bathed in BN NUTRI NOVA fertilizer for 401 hours, while UV3/*b*0 describes the sample subjected to UV dosage of 24897 kJ.m^{2} but not inserted into any nutrient bath.

As it clear from the Figure 1, where results of the first scans of thermal analysis for selected samples of mulch foil is shown, there are rather significant variations in DSC curves of tested samples. Even there are only slight deviations in main melting and crystallization peaks, covering the temperature ranges of 105-115 and 95-105°C, respectively, namely connected with the changes of area under these peaks; there is meaningful divergence in thermal behaviour described during heating ramp between temperatures of 40 and 80°C.

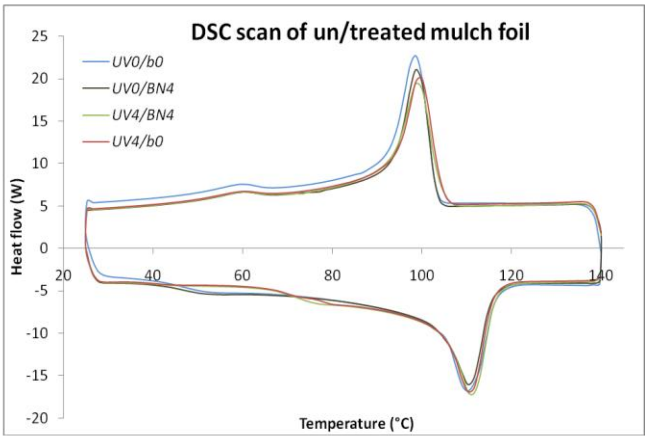

Figure 1 – DSC scans of UV0/*b*0, UV0/*BN*4, UV4/*BN*4 and UV4/*b*0 samples of mulch foil.

Table 2 – Results of thermal analysis of UV untreated samples.

Sample	Charact. values	Number of cycle		
		0	1	4
UV0/ *NN*(x)	Ts1/Ts2/Ts3 (°C/°C/°C)	47.0	47.2	47.1
	Tm/Hm (°C/W)	110.3/769.9	112.0/747	112.5/738
	Tc/Hc (°C/W)	98.2/699	97.8/576.8	98.3/632
UV0/ *BN*(x)	Ts1/Ts2/Ts3 (°C/°C/°C)	47.0	46.4	44.8
	Tm/Hm (°C/W)	110.3/769.9	110.7/658	109.7/661
	Tc/Hc (°C/W)	98.2/699	98.4/636	98.6/615
UV0/ *T*(x)	Ts1/Ts2/Ts3 (°C/°C/°C)	47.0	45.8	47.8
	Tm/Hm (°C/W)	110.3/769.9	110.2/693	110.3/658.7
	Tc/Hc (°C/W)	98.2/699	98.7/652.8	99.0/615
UV0/ *B*(x)	Ts1/Ts2/Ts3 (°C/°C/°C)	47.0	47.0	46.1
	Tm/Hm (°C/W)	110.3/769.9	110.9/714	110.6/693
	Tc/Hc (°C/W)	98.2/699	98.3/664	98.8/650

While graphical description of the mentioned discrepancies in thermal behaviour could be seen in Figure 1, it could be in more details analysed from the results numbered in Tables 2 and 3. For each evaluated samples presented in these tables the three different rows are given.

1) In the first row possibility to express three various temperatures Ts1, Ts2, and Ts3, specifying the temperature where melting of relevant amount of crystallinity structure occurred, is offered. Nevertheless, it should be noted that these temperatures are not presented in all cases. Even these temperatures represents the region where melting of least-organized structure is arisen, their values were evaluated in the similar way as glass transition, in other words from the drop in steady DSC curve which was again followed by a constant heat flow level.

2) Main melting temperature (°C) together with total heat of melting (W) covering the region where also Ts1-Ts3 are presented is given in the second row.

3) Finally, main crystallization temperature of PE matrix is numbered in the third row together with complete heat of crystallization comprehensive of temperature region roughly 105-40°C.

Table 3 – Results of thermal analysis of photodegradated samples un/treated in nutrient bath.

Sample	Number of cycle			
	0	1	2	4
UV(x)/ *b*0	47.0	64.8	42.5/70	41.8/69.5 /77.7
	110.3/769.9	111.25/662	109.8/697	110.6/709
	98.2/699	97.6/647	98.8/634	99.5/647
UV(x)/ *NN*(x)	47.0	64.9	42.0/70.5	39.3/69.8
	110.3/769.9	111.0/703	111.9/621	110.9/786.4
	98.2/699	98.5/632	99.2/583	99.1/702
UV(x)/ *BN*(x)	47.0	63.2	44.6/73.0	39.6/70.9
	110.3/769.9	110.4/648	110.8/679	111.0/758
	98.2/699	98.4/614	98.6/630	59.9/660
UV (x)/ *T* (x)	47.0	64.2	44.6/73	67.8
	110.3/769.9	110.3/675	111.0/736	110.1/714
	98.2/699	98.8/644	98.4/644	99.4/629.9
UV(x)/ *B*(x)	47.0	63.9	41.6/69.7	41.0/71.0
	110.3/769.9	110.2/665	110.4/739	110.8/735
	98.2/699	98.8/596	98.6/682	99.1/646

From the results listed in Tables 2 and 3 it could be seen that bathing in *NN* medium led to increase of melting temperature and maintenance of melting heat, whereas similar trend was determined also for the photodegradated samples bathed in *NN* and *BN*. In the case of other treatments decline of melting heat was accompanied with conservation of melting temperature value. Concerning crystallization behaviour there is no significant variations in obtained results. Definitely, more interesting results could be found in Ts1-Ts3 temperature behaviour. As it is clear from the tables only Ts1 of 47°C was determined for original mulch foil material. This value is more or less kept constant for samples treated in the baths, even some small Ts1 drops to the value of 44.8 and 46.1 for *BN* and *B* nutrient agents, respectively, were found. In the case of UV treatment partition of Ts1 into two or even three different values was observed. Interestingly, with increasing cycling of UV treatment the value of Ts1 is firstly increased to the value of approximately 64°C (within first UV cycle), consequently this temperature was farther increased to the value of 70°C c. and simultaneously Ts2 of value 41.6-44.6 was risen after 2 UV cycles. Moreover, temperature Ts3 of 77.7°C was found for un-bathed samples after fourth UV cycle. Reason of increasing of crystalline structure organization obviously interconnected with increase of Ts values could be however connected with the UV activity or with increased temperature in UV chamber and as such it need to clarified in further work.

As it is clear from the Figures 2-4, where selected results of the mechanical testing of un/treated mulch foil samples are displayed, there is obvious variations in mechanical response of the tested samples, especially at limiting factor of sample breaks. Moreover, it could be shown that while for Young Modulus found discrepancies are disappearing with increase number of treating cycles, for the case of tensile strength and elongation they are even more pronounced.

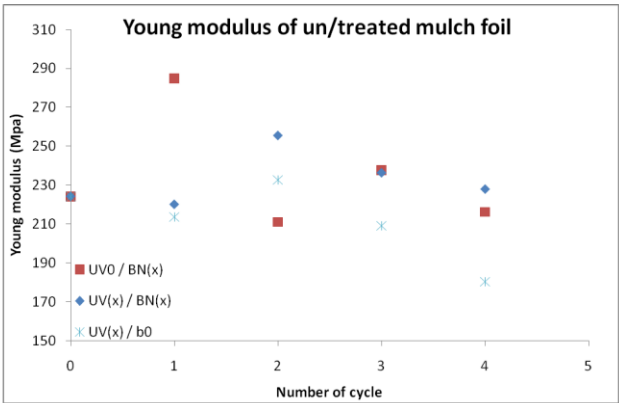

Figure 2 – Young modulus of UV0/*BN*, UV/*BN* and UV/*b*0 mulch foil samples.

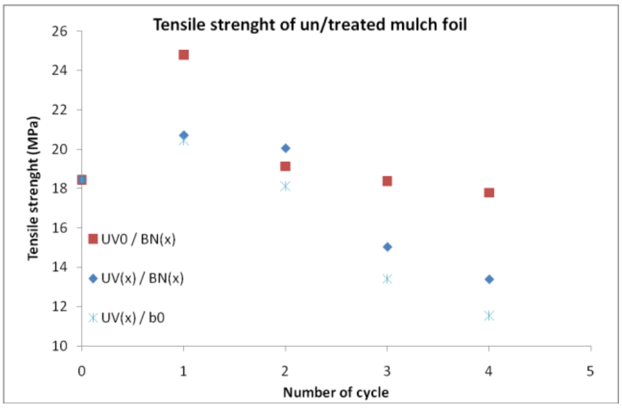

Figure 3 – Tensile strength at sample break of UV0/*BN*, UV/*BN* and UV/*b*0 mulch foil samples.

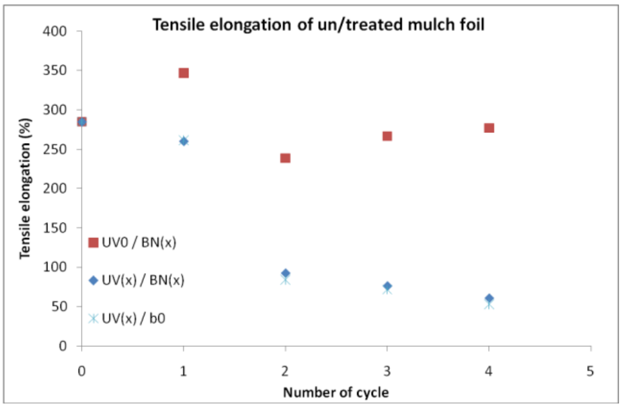

Figure 4 – Tensile elongation at sample break of UV0/*BN*, UV/*BN* and UV/*b*0 mulch foil samples.

ISBN: 978-1-61804-022-0

From the results presented in Figure 2 and Table 4 it could be proved that Young Modulus of tested samples was only unsbustantialy affected by performed treatments. Even due to the most significant effects determined for the samples treated by the combination of UV and nutrient bathing slight increase in modulus values was recorded, in contrast with the effects at sample break it is rather meaningless. Mechanical performance in response to initial stresses thus seems to be very little affected by UV radiation.

Table 4 – Young Modulus of un/treated samples determined from tensile test.

Sample	Young Modulus (MPa) at various cycle number			
	1	2	3	4
UV(x)/*b*0	214	233	209	180
UV(x)/*NN*(x)	217	240	219	263
UV(x)/*BN*(x)	220	256	236	228
UV(x)/*T*(x)	218	214	244	264
UV(x)/*B*(x)	215	238	243	209
UV0 /*NN*(x)	220	247	229	239
UV0 /*BN*(x)	284	211	237	216
UV0 /*T*(x)	235	221	250	204
UV0 /*B*(x)	226	218	220	212

Absolutely different results were verified for tensile properties in the limiting case of sample break. Based on the results presented in Figures 3 and 4 together with Tables 5 and 6 it could be shown that while tensile strength and elongation of UV untreated samples are only slightly affected by bathing in nutrient agents, pure UV treatment of the tested samples is the most significant effect influencing mechanical performance of investigated material. Moreover, it could be also demonstrated that bathing in nutrient agent slightly inhibits the influence of UV treatment on tensile strength and elongation of tested samples, with except of *B* medium which was found to be not muting effects of UV treatment.

Table 5 – Tensile elongation un/treated samples determined from tensile test.

Sample	Tensile strength (MPa) at various cycle number			
	1	2	3	4
UV(x)/*b*0	20.5	18.1	13.4	11.6
UV(x)/*NN*(x)	21.0	18.7	14.5	14.3
UV(x)/*BN*(x)	20.7	20.0	15.0	13.4
UV(x)/*T*(x)	20.0	17.2	15.3	14.5
UV(x)/*B*(x)	19.7	19.8	16.6	11.8
UV0 /*NN*(x)	20.2	22.7	19.5	19.0
UV0 /*BN*(x)	24.8	19.1	18.4	17.8
UV0 /*T*(x)	19.5	21.0	19.8	17.0
UV0 /*B*(x)	21.2	22.3	17.9	19.9

Table 6 – Tensile elongation un/treated samples determined from tensile test.

Sample	Tensile elongation (%) at various cycle number			
	1	2	3	4
UV(x)/*b*0	262	84	72	53
UV(x)/*NN*(x)	287	87	65	59
UV(x)/*BN*(x)	260	92	76	61
UV(x)/*T*(x)	289	100	61	56
UV(x)/*B*(x)	308	98	78	43
UV0 /*NN*(x)	298	368	248	261
UV0 /*BN*(x)	347	239	267	277
UV0 /*T*(x)	339	254	266	244
UV0 /*B*(x)	354	299	266	276

4 Conclusion

Comprehensive study on chemical influence of nutrient agent in combination with UV treatment on starch filled photodegradable mulch foil based on LDPE is presented in the work in order to evaluate potential negative effects of fertilizers on a tailored UV stability of investigated polymeric foil material. Accelerated physical/chemical aging of studied samples was performed utilizing Xenotest apparatus in combination with baths in selected commercially available fertilizers. Thermal analysis of ongoing changes and mechanical testing describing impacts of these changes on mechanical performance were employed for foil characterisation purposes. Results of thermal analysis revealed that there are significant variations in crystallinity structure arrangement comparing UV treated and untreated samples; moreover some minor changes were traced also in melting temperature values. Mechanical tests clearly proved that while UV untreated samples are only slightly affected by bathing in nutrient agents, UV treatment of samples is the most important effect on investigated material performance; this means that bathing in nutrient agent retard the influence of UV radiation on mechanical properties of tested foils except of BN-ZYM Enzyme natural bio-catalyst system which was found to not interfere effects of UV treatment.

Acknowledgment

This article was created within the framework of project Centre of Polymer Systems (reg. number: CZ.1.05/2.1.00/03.0111). The Ministry of Education, Youth and Sports of the Czech Republic, (Grant. No. MSM 7088352101) is gratefully acknowledged for the financial support.

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