BIODEGRADABILITY OF IRRADIATED POLY(BUTYLENE SUCCINATE-CO-ADIPATE) IN THE PRESENCE OF ADITIF

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ABSTRACT

BIODEGRADABILITY OF IRRADIATED POLY(BUTYLENE SUCCINATE-*co*-ADIPATE) IN THE PRESENCE OF ADITIF. Poly(butylene succinate-co-adipate) (PBSA) was mixed with Silicon dioxide, Carbon black, and Trimethallyl Isocyanurate (TMAIC), respectively. The rate of biodegradability was investigated using Microbial Oxidative Degradation Analyzer (MODA), enzymatic and soil burial test. It was pointed out that the rate of biodegradability of irradiated PBS1 containing 2% silicon dioxide and 2% carbon black, respectively, much faster than that of irradiated pure PBS1. This phenomenon is due to the enlargement of the sample's surface caused by the presence of inorganic material in the sample, thus easier for enzymes to introduce inside polymer. On the other side irradiated PBSA contains TMAIC has lower biodegradation rate than irradiated original PBSA at the same irradiation dose, in this case the biodegradation rate depend on gel fraction of the sample.

Key words : Poly(butylene succinate-co-adipate), carbon black, silicon dioxide. trimethallyl isocyanurate, microbial oxidative degradation analyzer, enzymatic test

ABSTRAK

BIODEGRADABILITAS IRADIASI POLI(BUTILEN SUKSINAT-*CO*-ADIPAT) DENGAN ADANYA PENAMBAHAN ADITIF. Poli(butilen suksinat-co-adipat) (PBSA) dicampur masing-masing dengan silikon dioksida, karbon dan Trimethallyl Isocyanurate (TMAIC). Kecepatan biodegradasi di observasi menggunakan mikrobial oksidatif degradasi (MODA) tes, enzymatik test dan penguburan dalam tanah. Diperoleh hasil bahwa kecepatan biodegradasi dari iradiasi PBSA yang mengandung masing-masing 2% silikon dioksida dan 2% karbon lebih cepat dibandingkan dengan PBSA murni. Hal ini karena terjadi perluasan pada permukaan sampel dengan adanya silikon dioksida dan karbon tersebut, sehingga lebih mudah bagi enzym untuk penetrasi kedalam sampel. Disisi lain iradiasi PBSA-TMAIC mempunyai kemampuan biodegradasi lebih rendah bila dibandingkan dengan PBSA tanpa TMAIC pada dosis iradiasi yang sama. Hal ini karena iradiasi PBSA murni mengandung fraksi gel lebih rendah dari pada PBSA-TMAIC. Pada keadaan ini kecepatan biodegradasi sampel tergantung pada fraksi gel sampel tersebut.

Kata kunci : Poly(butylene succinate-*co*-adipate), *carbon black*, silikon dioksida. *trimethallyl isocyanurate, microbial oxidative degradation analyzer, enzymatic test*

INTRODUCTION

Recent increasing laymen's concern on the environmental protection has roused public opinions to impose duties on the producers and the distributors to dispose the waste matters properly. The development of environmentally benign materials for commodities and packaging have become increasingly important to meet the international regulations such ISO 14000.

Current commercial biodegradable polymers are limited only to aliphatic polyesters, polyethers, poly(vinil alcohol) and polysaccharides. The most important requirement for biodegradation of polymer systems is the presence of hydrolizable and/or oxidizable linkages along the main chain; for example ester, ether, amide, urea, urethane and glycosidic linkages are susceptible to undergo biodegradation by microorganisms and hydrolytic enzymes [1-4]. Enzymes are known to be involved in the metabolism of synthetic polymers through hydrolysis and oxidation processes for polymer degradation.

It has been reported that the biodegradability of aromatic and aliphatic copolyesters is strongly affected by the composition, sequence distribution, crystallinity, crystalline structure and melting temperatures [5]. The biodegradation of aliphatic polyesters is influenced not only by the chemical structure of repeating units and hydrophilicity–hydrophobicity balance, but also by

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highly ordered structures thus affecting crystallinity, orientation and other morphological properties [6]. Among the degradable aliphatic polyesters, a polymer having a lower melting point is generally more susceptible to biodegradation than one having a higher melting temperature [7]. Those polymer with lower melting temperatures have more flexible chains which can fit into the active sites of the enzymes.

The biodegradability of Poly(butylene succinate-co-adipate), PBSA has been widely investigated, as well as the influence of its structure on biodegradability. Investigation on the biodegradability of copolymers of poly(butylene succinate) and some aromatic polyesters was also performed. It has been found that poly(butylene adipate), has a lower melting temperature and is more readily biodegradable than PBSA [8].

At present, PBSA is expected as a feasible biodegradable polymer for the applications in the packaging, agricultural and medical fields, etc., unfortunately very low resistance to thermal degradation seems to be the most serious problem related to processing of PBSA. Since the melting temperature of PBSA and its copolymer is around 90-120°C, the processing temperature should be at least 130°C. Thermal degradation at this temperature proceeds rapidly so the acceptable residence time in the processing equipment is only few minutes. By adding additive subtance and using irradiation technique, the thermal resistant of PBSA increased. On the other side the adding of additive and radiation technique benefits supposedly will affect the biodegradability of PBSA samples. This study observed the effects of additive adding and irradiation technique on the biodegradability of PBSA samples.

EXPERIMENTAL METHOD

Materials

Some properties of PBSA sample used in this study are shown in Table 1. This polymer was produced at Showa High Polymer Co. Ltd., Japan.

To prepare the composite material, Trimethallyl Isocyanurate (TMAIC); Carbon black (Perkebunan Malaysia) and Silicon dioxide (Wako Pure Chemical Industries. Ltd) were used as additive respectively.

Preparation of Samples and Irradiation

The content of additive in final compositions were expressed as percent ratio of additive to total mass of samples, PBSA and additive were mixed in a labo plastomill model 50C150 (Toyo Seiki). The speed of mixing was 20 rpm, at 150°C. Each sample was press to form 0.5 mm thickness sheet in an Ikeda hot press at 150°C. Then cooled to room temperature by cold press using water as a coolant for 3 min. Irradiation of samples was carried out in the atmosphere of air or vacuum using an accelerator with energy of 1 MeV and current of 1 mA, at various doses from 30 to 200 kGy at a dose rate of 10 kGy/pass.

Biodegradation Under Controlled Conditions in Composted Soil

The microbial degradability of polymer in composted soil was evaluated by measurements of produced CO_2 gas. Specially designed apparatus Microbial Oxidative Degradation Analyzer (MODA), comprised of 4 independent lines of columns was used (Figure 1). Polymer sample was mixed with rinsed sea sand - 450 g, and compost - 130 g, then placed in a heated reactor. Temperature inside the column was set to 35°C and the flow of the carbon dioxide-free but moisturized air was 30 ml min^{-1}. After flowing through the sample reactor, the air, caring formed due to polymer decay CO_2, was passing through a series of columns filled in turn with silica gel, calcium chloride, soda lime and calcium chloride. Ammonia, which could be formed from the

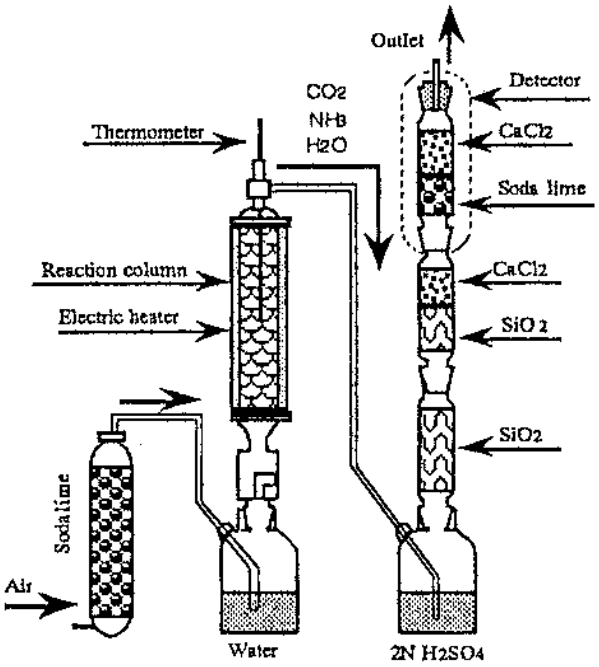

Figure 1. Microbial Oxidative Degradation Analyzer (MODA)

Table 1. Some properties of Poly(butylene succinate-co-adipate) sample used in this work

Sample type	Mw	Mw/Mn	Melting point (°C)	Density (g/cm^3)	△H (J/g)
PBSA (Poly(butylene succinate-co-adipate))	2.96×10^5	2.0	92	1.23	45

decomposing sample, was trapped in sulphuric acid solution, and water vapor was absorbed into first two columns (silica gel and calcium chloride). The CO_2 was collected quantitatively by soda lime and producing during the reaction water was caught in the last $CaCl_2$ column. Thus mass of produced carbon dioxide was calculated as a difference in the weight of two last columns (containing soda lime and calcium chloride) at the beginning and the end of the test. Pure compost mixed with sea sand was used as a blank. The mass of initial polymer was 10 g, it had a form of dry powder.

Enzymatic Degradation Test

Enzymatic degradation of samples was carried out by determining the rate of their solubilization in a solution according ASTM D 1924-63 and ASTM D 2676. The samples were immersed in phosphate buffer solution (pH 7.4) with composition of reaction mixtures as follows:

0.2 M phosphate buffer (pH 7.0)	4 ml
Enzyme, Lipase AK (10 mg/ml)	1.0 ml
0.1% surfactant ($MgCl_2$)	1.0 ml

The thin PBSA films with a dimension of 10 x 10 x 0.1 mm and initial weight about 9 mg were oven dried at 40 °C for 24 h in vacuum condition. The films were put into test tubes, 5.0 ml of reaction mixtures was added and incubated at 55 °C with shaking for various times. Then the films were taken out from the test tubes and washed with distilled water, methanol and dried in oven to constant weight at 40 °C. The progress of enzymatic degradation was expressed as percentage of weight loss.

Soil Burial Test

The soil burial test was performed in plastic troughs 57 cm long, 17 cm wide and 14 cm high. The soil consisted of composted top soil, black garden soil and pond sludge in equivalent ratios maintained at a pH 7 and about 40% moisture content. The dumbbell cut samples with thickness of 0.5 mm was buried about 3 cm from the soil surface, for various burial times from 1 month to 6 months. After each interval, the samples were removed from the soil and wiped by tissue paper, clean with distilled water and dried at 40°C in an oven to constant weight.

RESULTS AND DISCUSSION

Microbial Oxidative Degradation Test

Evaluation apparatus relating to total degradation of organic matters in the soil and in compost into CO_2 does not exist so far. In this test the biodegradable plastics are composed by activated sewage sludge microorganisms to measure the amount of CO_2 formed by decomposition. Figure 2. shows the percentage of degraded samples. It can be seen that degradation of unirradiated PBSA is highest compare to irradiated PBSA or PBSA mixed with 2% silicon dioxide. This is due to the irradiated PBSA contain a three-dimensional network formed during irradiation. The croslinked network retards the decomposition by sewage sludge microorganisms. However irradiated PBSA in the presence of 2% silicon dioxide shows higher degradation compare to irradiated PBSA without 2% silicon dioxide due to lower area of crystallinity. During blend of PBSA with silicon dioxide the crystalinity became irregular, led to form amorphous regions. It was reported that the rate of oxygen uptake in solid polyethylene during oxidation is inversely proportional to the percent crystallinity in the polymer, suggesting that the amorphous regions in the semicrystalline polyethylene were susceptible to oxygen attack.4 Another way the microorganisms and hydrolytic enzymes penetrate hydrolizable linkages along the main chain of PBSA, at the time biodegradation started.

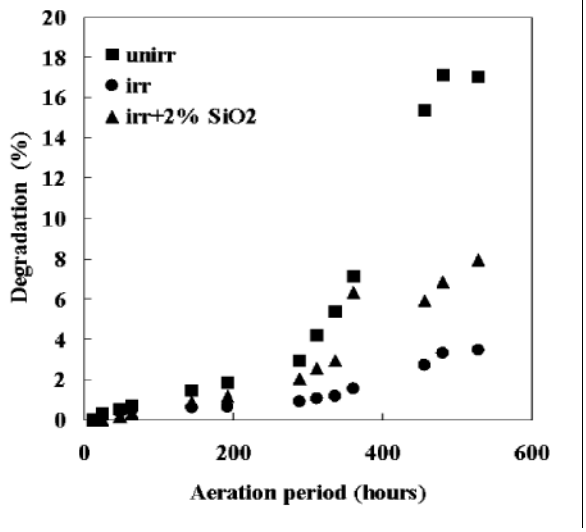

Figure 2. Microbial Oxidative Degradation Analysis (MODA) of PBSA in the presence of SiO_2

Figure 3. Shows Microbial Oxidative Degradation Analysis (MODA) of PBSA in the presence of 1%TMAIC. It can be seen that degradation of unirradiated PBSA is highest than that irradiated PBSA or PBSA contains 1% TMAIC. It is clear that increasing of gel fraction retards the enzyms to penetrate inside the three dimensional network. The increasing of gel fraction means increasing of three dimensional network.

Enzymatic Test

Enzymatic test is a convenient method to evaluate the rate of biodegradability of polymers for short time. It was reported that esterase and lipase enzymes cause degradation of the poly(butylene succinate) [7]. In this

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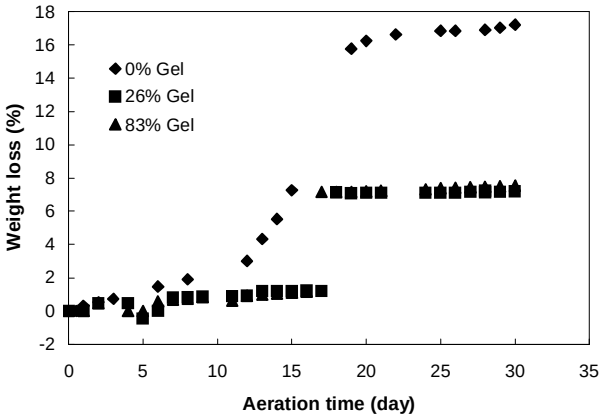

Figure 3. Microbial Oxidative Degradation Analysis (MODA) test of unirradiated original PBSA (0%), irradiated original PBSA (26%), irradiated PBSA contains 1% TMAIC (83%).

study we used lipase AK for analyzing the biodegradation of PBSA.

In Figure 4. shown that PBSA samples without gel fraction degraded completely at 48 hours immersion in enzyme bath. PBSA, which contains 26% of gel degraded completely at 72 hours immersion. While PBSA samples which contain 43% and 83% of gel degraded 44.08% and 12.9 % respectively at 96 hours immersion in enzyme bath. It can be deducted that PBSA with high gel fraction degraded slower than that of PBSA with low gel fraction, which indicates that the increase of weight loss is caused of more sol fraction part.

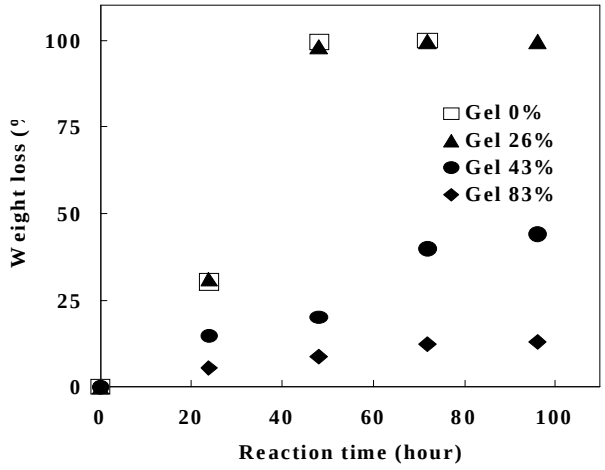

Figure 4. Enzymatic test of unirradiated original PBSA (0%), irradiated original PBSA (26%), irradiated PBSA contains 1% TMAIC (43% and 83%).

The PBSA without gel fraction has 100% sol fraction, the enzym easy to penetrate in sol fraction. By increasing the gel fraction means reduction in sol fraction. In this situation the gel fraction inhibit the enzyms to penetrate in side the PBSA samples.

The important factors affecting the biodegradability of polymers are the structure and physical properties such as the type and amount of crystal, degree of crystallinity, orientation, and mechanical properties. Consequently, the decrease of biodegradation rate observed in the sample with increasing gel content could be tentatively attributed to the parallel steady increase of the overall crystallinity and/or mechanical properties.

From the experimental results are deduced that biodegradability of irradiated PBS1 containing 1% TMAIC strongly affected by the yield of gel formation in the sample.

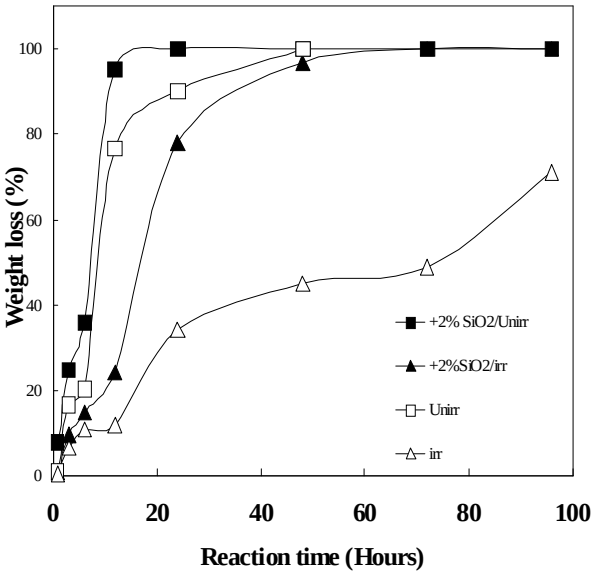

Figure 5a. Enzymatic test of PBSA contains silicon dioxide.

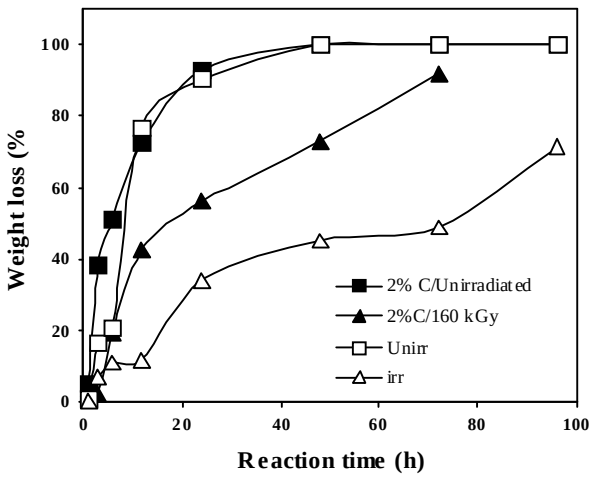

Figure 5b. Enzymatic test of PBSA contains carbon black (C).

It can be seen in Figure 5a and 5b. that PBSA samples contained 2% silicon dioxide and 2% carbon black respectively, have faster rate of degradation than that of PBSA sample without aditive (silicon dioxide, carbon black). After 24 hours immersion in enzyme bath, unirradiated PBSA contains 2% silicon dioxide degrades completely, and PBSA without additive loses about 90%

of its weight. Irradiated pure PBSA degrades only about 71% after 96 hours, where as PBSA contains 2% of silicon dioxide decays completely after 72 hours. It is due to the fact that the enzymatic degradation proceeds rapidly from the surface of the polymer to its interior part. By adding silicon dioxide or carbon black, the amorphous part of sample become larger than that original sample, thus the enzyme can penetrates the sample faster than that without additif adding. The enzymatic degradation of PBSA contain 2% of silicon dioxide or 2% carbon black occurs easily even after crosslinking induced by irradiation. This is because of alteration of physical and chemical integrity of the aliphatic polyester mixed with an inorganic material.[5] As a result, silicon dioxide and carbon black has considerable effect on biodegradation of irradiated PBSA. The PBSA contains 2% of silicon dioxide easier to be penetrated than that of PBSA contains 2% carbon black due to the smaler size of silicon dioxide compare to carbon black. So the penetration of enzym in to PBSA sample contains 2% of silicon dioxide faster compare to PBSA sample contains 2% of carbon black.

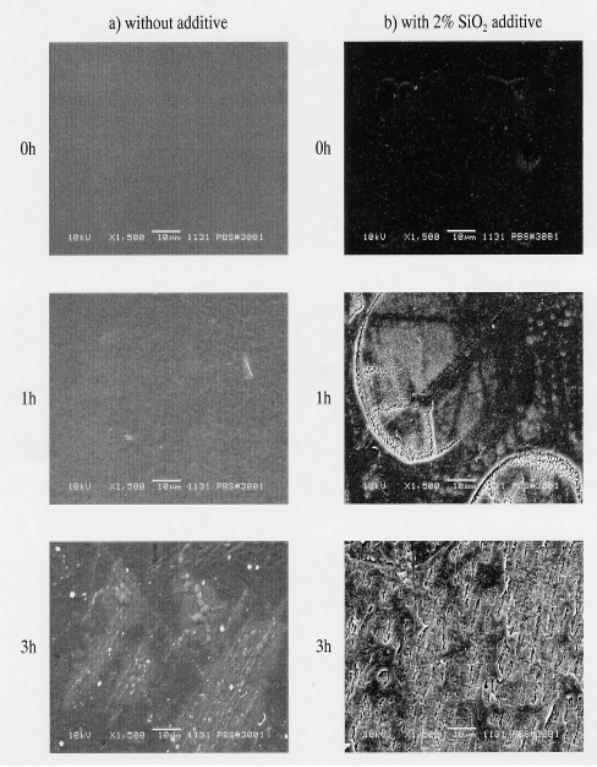

Figure 6. SEM photomicrograph of PBSA (Magnification x 1500).

Figure 6. SEM photographs of irradiated original PBSA and PBSA contains 2% silicon dioxide with different weight reduction before and after enzymatic degradation. Before degradation both samples have a smooth surface. By degradation, roughness of the film surfaces gradually increases and holes due to the surface erosion appear. Irradiated original PBSA do not shows significant difference before and after one hour of reaction time of enzymatic degradation. After 3 hours of reaction only small holes appear, which probably originate in the amorphous regions, are created. The surface of the PBSA film contains 2% silicon dioxide is quite different after enzymatic degradation. After 3 hours of reaction. PBSA sample contains 2% silicon dioxide shows numerous aggregated spherulites. The sample obtains a sponge-like character evidencing a dramatic erosion of the material.

Soil Burial Test

Soil burial test is a standard examination of biodegradability of irradiated samples by bacteria in soil. Figure 7 shown that samples have no gelfraction degraded faster the samples contain 29% gel fraction degraded slower actually. But since the range of examination time enough long so the unsignificant difference weight lost of the examinated samples seem to be similar. From Figure 7 also can be seen that all the samples weght loss have similar behaviour up to 6 months, then after 6 moths burried the sample contains 83% gel fraction tend to degrade slower than that samples without gel fraction and with 26% gel fraction. This phenomenon due to the existence of gel fraction inhibit the enzyme to penetrate into the samples, similar results were obtained by enzymatic test. From the soil burial test results of the PBSA samples contain TMAIC, deduced that the biodegradability of irradiated PBSA containing 1% TMAIC strongly was affected by the yield of gel formation in the sample.

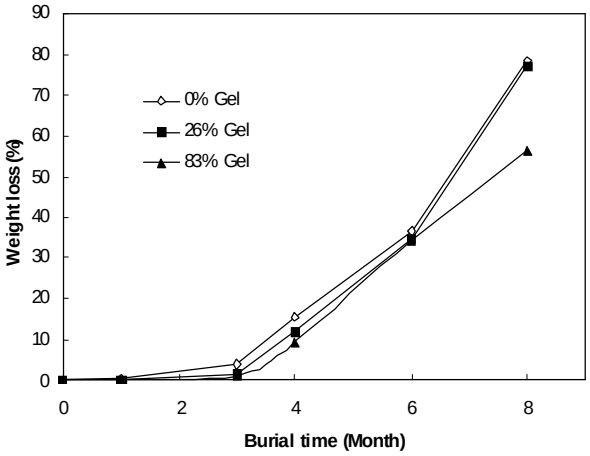

Figure 7. Weight loss of unirradiated original PBSA (0%), irradiated original PBSA (26%), irradiated PBSA contains TMAIC (83%) in soil. burial degradation test.

Figure 8. shows the effect of carbon black on biodegradability of irradiated and unirradiated PBSA. It can be seen that the the weight loss of both irradiated and unirradiated PBSA increases gradually with increasing of the burial time. The degradability of unirradiated PBSA without or with 2% of carbon black is 16.9% and 29.7%, respectively. Whereas for irradiated

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PBSA without carbon black the degradation is 15.5%, and 39% for irradiated PBSA contains 2% of carbon black after 6 months of the burial time. One can see that irradiated PBSA contains 2% of carbon black has higher degradability than that unirradiated one. This behavior is different from the enzymatic degradation.

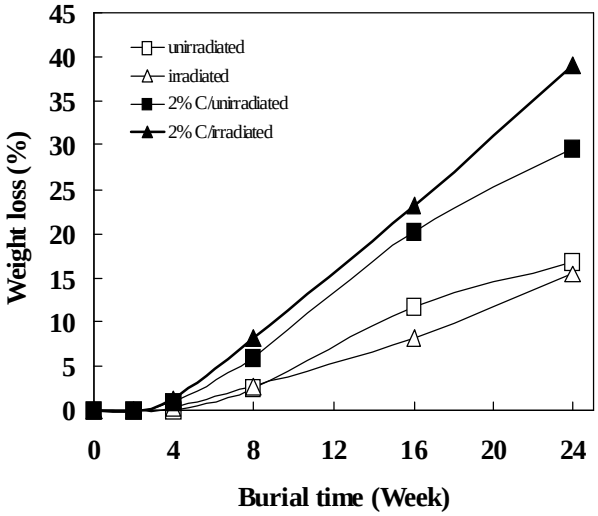

Figure 8. Weight loss in soil burial degradation test of PBSA contains Carbon Black (C). Irradiation dose of 160 kGy.

There are several important factors, however, which may affect results of the soil burial test, e.g., temperature, humidity, pH, oxygen concentration, insufficient number of active microorganism, availability of mineral nutrient, etc. To evaluate their effect is a complex task, which needs to follow a set of the parameters in co-ordinance. It was not performed in this work. The typical photograph of PBSA sample buried in soil for different periods is shown in Figure 9.

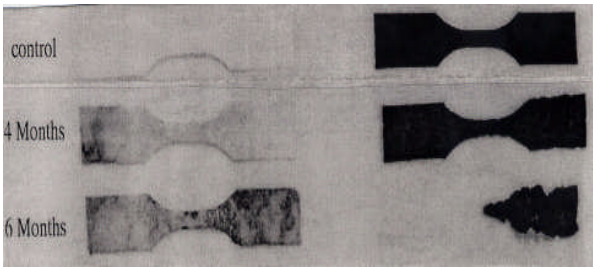

Figure 9. Photograph of PBSA after buried in soil for different periods, A: original PBSA, B: Irradiated PBSA containing 2% carbon black, irradiation dose of 160 kGy.

CONCLUSIONS

1. Biodegradability of samples increases by adding carbon black or silicon dioxide, respectively.
2. Biodegradability of crosslinked samples in the presence of TMAIC depends on the yeld of gel formation.
3. All of the sample degraded faster in enzymatic degradation test compare to MODA test or soil burial test.
4. The biodegradation rate of modified polymers is slightly diminished with increasing of gel fraction, however, the polymers are still biodegradable.

ACKNOWLEDGEMENTS

The author would like to express deep appreciation to Prof. Dr. Hiroshi Mitomo of Department of Biological and Chemical Engineering, Faculty of Engineering, Gunma University; Dr. Fumio Yoshii, Head of The Environment Functional Materials Laboratory, TRCRE-JAERI. And Dr. N. Nagasawa of TRCRE-JAERI for their continuous guidance, help and valuable discussion throughout the course of this study.

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