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Study on Characteristics of Paper Laminated with Biodegradable Plastics, 1. Burial Test in Soil

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Paperboards laminated with biodegradable plastics were buried in soil for six months to evaluate the biodegradability. The degradation rate of biodegradable plastics was slower than that of our expectations. These results are partly similar to those previously obtained. It is considered that a longer period than one year is required for the observation of significant change such as a disappearance of materials when a temperature and humidity are not controlled. The concerted effect of composite consisting of paper and biodegradable plastic was not found on the biodegradation in the present work. Their degradation might independently take place. The rate of biodegradation decreased in the following order; simple paperboard>paper coated with biodegradable plastic> paperboard laminated with biodegradable plastic> simple biodegradable plastic>plastic made from fossil fuel. It was suggested that the biodegradation might be promoted by the design of complexity.

INTRODUCTION

In recent years, considerable attention has been focused on the global problems on environment and the social consciousness on environmental protection and resources circulation has been extremely raised. For example, the political bargaining is worldwide under way for the ratification of Kyoto Protocol at COP3 (COP: The Conference of Parties to the United Nations Framework Convention on Climate Change) held in 1997 in Kyoto. Fortunately, specific consequences for the Kyoto Protocol were adopted at COP7 held in Morocco from October to November 2001, though USA which discharges the greatest amount of CO_2 dropped away. It is anticipated, however, that steady efforts with a lot of pains must be paid to achieve the aim.

The global warming originates from the consumption of a large amount of fossil fuel. Also plastics made from fossil fuel raised the environmental problems. Plastics have been developed as materials, which are light, strong, tough, moldable and chemicals–resistant, and contributed our convenient daily life. Refused plastics, on the contrary, have enlarged the environmental problems because of very high stability. The fossil fuel must be saved as much as possible because of the exhaustive resource.

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In Japan, 14 million tons of plastics are produced every year and 10 million tons of refused plastics are discharged. On the refused plastics, 5 million tons are utilized for generating electric power, although the residuary 5 million tons are burned up and/or reclaimed. The most portion of unutilized plastics are estimated to be originating from the packaging container.

Authors are research workers who belong to the packaging industry and believe that it is our mission to contribute to pursue the beneficial plans for reducing, reusing and recycling the products. Upon these circumstances, the use of biodegradable plastics, which can be degraded to H_2O and CO_2 under natural condition, is ardently noted.

Biodegradable plastics are defined as the plastics which are degraded to low molecular compounds by microorganisms such as bacteria, mold, and algae (Ikada *et al.*, 2000; Mohanty *et al.*, 2000)

There are already many reports on physical characteristics of biodegradable plastics themselves (Jacobsen *et al.*, 1999; Amass *et al.*, 1998; Anderson *et al.*, 1997). But there are little papers on combined products between biodegradable plastics and other materials. Then our attention was focused on the complex of biodegradable plastics and papers which are made from unexhausted renewable wood resources by well-organized afforestation and aimed to develop a substitute with the function of styrofoam used as food containers. We have set about a study on characteristics of paperboards laminated with biodegradable plastics because these products are expected to be reused as compost even if they are randomly discharged in the open air.

Biodegradable plastics belong to the field of green chemistry, and the trends of research and development in green chemistry are available from internet (http://www.chemsoc.org/network/gcn/; http://www.epa.gov/greenchemistry/; http://www.lanl.gov/greenchemistry/; http://www.cefic.be/sustech/).

MATERIALS AND METHODS

Materials

Biodegradable plastics are classified into three categories, biosynthetic products, chemically synthesized products and natural polymers. There are also three kinds of their raw materials, plants, petroleum and their mixture. Among them, poly (lactic acid) (PLA) produced by the polymerization of lactic acid which is prepared by the fermentation of corn, sugar cane, long stored rice or palm are employed as a biodegradable plastic which fits our purpose (Nolasco-Hipolito *et al.*, 2001).

Some samples of paperboards and functional papers laminated with PLA were prepared. They are given in Table. PLA films and paperboards themselves were also tested as reference samples.

Experimental fields

Following two places which might be different in nature of soil were selected.

A: Kami-ohshima, Tsukuba city, Ibaragi (the factory site)

B: Arao, Tohkai city, Aichi (the orange orchard)

Table. Samples subjected to the burial test in soil.

Category	Commercial sample	Film thickness (μm)	Basis weight of base sheet (g/m²)
Laminated papers	Polypropylene–laminated paper UNI–S*1	15	350
	TERRAMAC TL–15*2 / Card B*3	15	350
	Ecoloju*4 / Card B*3	25	350
	Palgreen LC*5 / Card B*3	20	350
Film individuals	Oriented polypropylene AF–642*6	30	–
	TERRAMAC TL–15*2	15	–
	Ecoloju*4	25	–
	Palgreen LC*5	20	–
Paperboards	Card B*3	–	350
	ECOBARRY KN*1	–	350
PLA–coated paper	LANDY*7–coated paper / Card B*3	–	350

*1 Koyo Paper MFG Co. Ltd., *2 Unitika Co. Ltd., *3 Ide Paper MFG Co. Ltd., *4 Mitsubishi Plastics Co. Ltd., *5 Tohcello Co. Ltd., *6 Futamura Chemical Industries Co. Ltd., *7 Miyoshi Oil & Fat Co. Ltd. All products from *2, *4 and *5 suppliers are classified into a poly (lactic acid) film.

Experimental period

Six months (from June to November, 2001)

Testing method (Procedure)

1) Each sample cut in 150 mm × 150 mm was inserted in the plastic net (250 mm × 250 mm) (Photo. 1).

2) The eleven kinds of samples were arranged as one set, and they were buried into the soil at the depth of 100 mm on the upper edge (Photo. 2).

3) The set of samples was dug out after a week and each month thereafter, and their degraded situations were carefully observed.

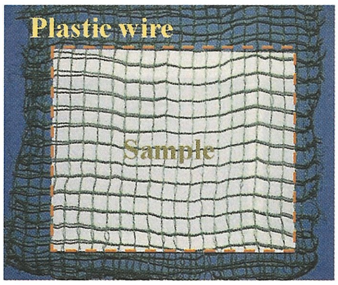

Photo. 1. Sample piece.

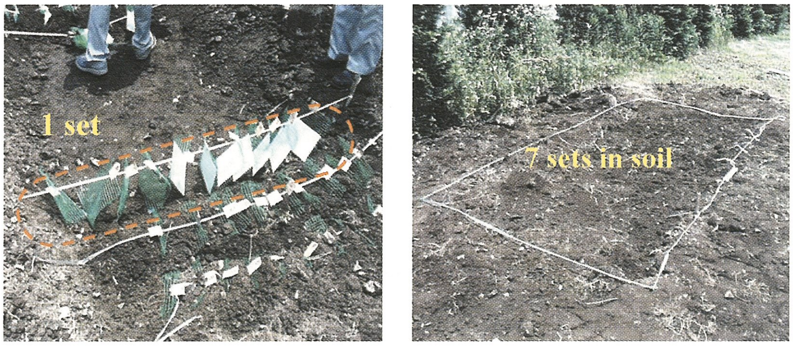

Photo. 2. Experimental case of burial test in soil at Tsukuba.

RESULTS

Biodegradation behavior of laminated papers

Appearances of typical samples dug out from the soil after one, three and six months are shown in Figures 1 and 2. The parts of paperboards in all laminated samples were degraded in a similar manner. They were degraded in an early stage and disappeared almost after six months. The degradation took place evenly on the whole parts without any deviation. On the other hand, there are large differences in the degradation of films. The decomposition of films in biodegradable plastic/paperboard composite started to take place after one month and increased gradually (Fig. 1) while that of film in polypropylene/paperboard composite never took place (Fig. 2). But the original form was almost preserved in analogy with film itself even after six months and thus the rate of degradation was not faster than that we expected at first. The effect of experimental places on

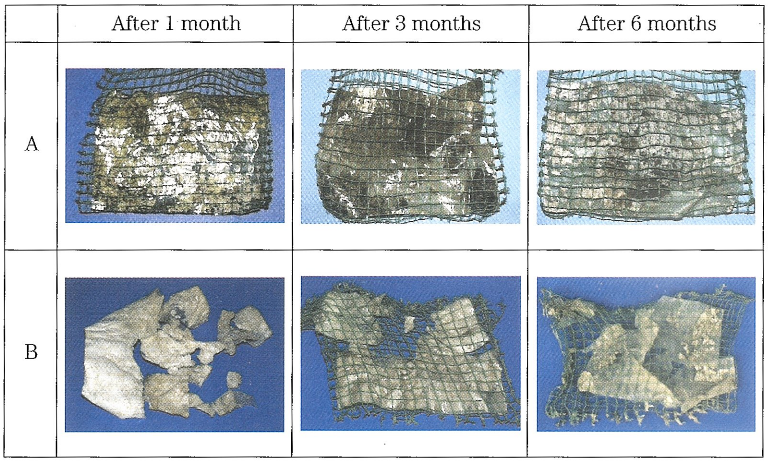

Fig. 1. Biodegradation behaviors of PLA–laminated papers at the Ibaragi (A) and Aichi (B) burial locations. The PLA film corresponds to TERRAMAC TL–15 listed in Table.

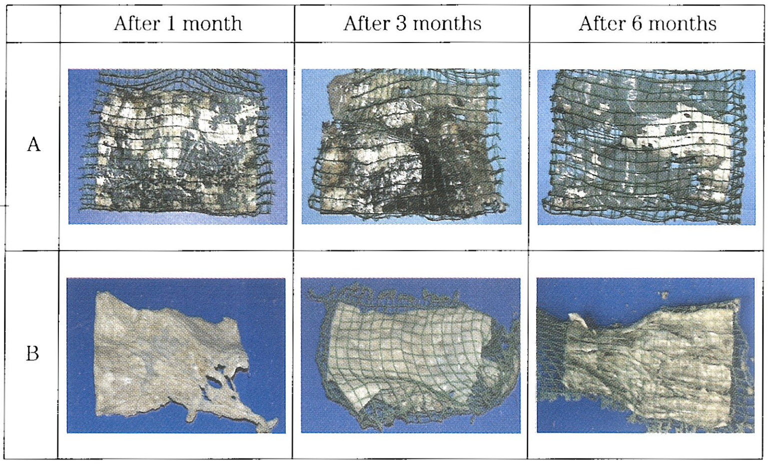

Fig. 2. Biodegradation behaviors of polypropylene-laminated papers at the Ibaragi (A) and Aichi (B) burial locations.

the biodegradation was also quite small.

Individual decomposition of biodegradable and synthetic polymer films

Figures 3 and 4 show the external appearances of oriented polypropylene (OPP) and PLA films by the visual observation, respectively. The synthetic OPP films manufactured from fossil resources were not decomposed in soil at the different location even after six months (Fig. 3). On the other hand, the in-soil degradation of the commercial PLA films were clearly observed at the both test-places for one month, and their breakdown pro-

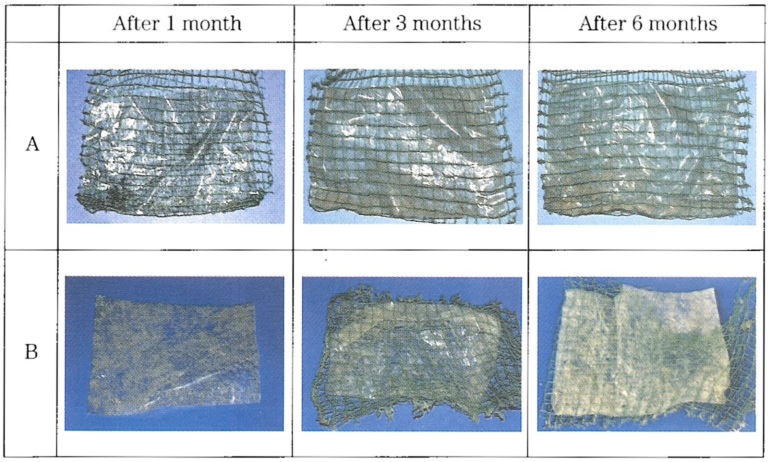

Fig. 3. Biodegradation behaviors of oriented polypropylene films at the Ibaragi (A) and Aichi (B) burial locations.

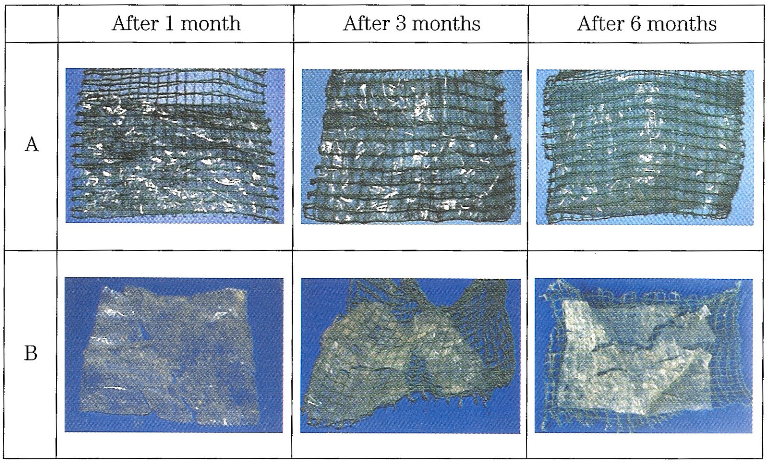

Fig. 4. Biodegradation behaviors of commercial PLA films at the Ibaragi (A) and Aichi (B) burial locations. All of biodegradable plastic films in this study showed the similar behavior in their degradation.

ceeded gradually as shown in Fig. 4. However, the original shapes of the PLA films were recognized even after six months, and the biodegradation rate of the PLA films was slower than expected and reported so far as well as that of the PLA–laminated paperboards. In this study, nearly no biodegradable difference was confirmed at the different burial locations.

Biodegradation of paperboards coated with or without emulsion–type PLA

Figure 5 shows the optical images of paperboards coated with or without emul-

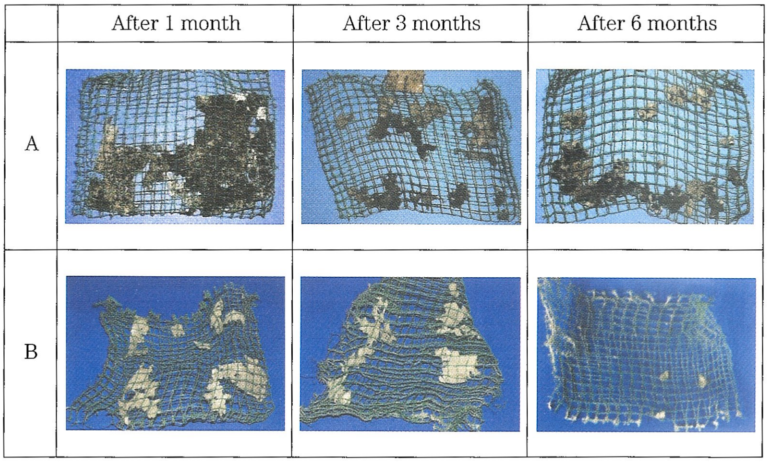

Fig. 5. Biodegradation behaviors of paperboards coated with or without emulsion–type PLA at the Ibaragi (A) and Aichi (B) burial locations. This sample corresponds to LANDY–coated paper / Card B listed in Table.

sion–type PLA after the burial test in soil for one, three and six months. Both paperboards were quite rapidly decomposed in soil; the 50%, 80% and 100% in each area were broken down for one, three and six months, respectively. Paperboards with and without PLA coating demonstrated the quick decomposition rather than the PLA–laminated paperboards. No deviation of the disappearance was observed, and the overall degradation of the paperboards coated with and without emulsion–type PLA proceeded similarly.

No distinct difference in the product degradation at the burial locations became remarkable, however, the biodegradation in the fruits farm seemed to be greater than that in the factory site. Probably, larger numbers of soil microbes inhabit in the fields than in the industrial places, and must promote to biodegrade the composite materials.

DISCUSSION

The general decomposition rate of PLA plastics is over 80% disappearance for 45 days under the experimental conditions of ISO 14855, and the industrial products such as a PLA film perfectly vanish in soil for 1–2 years. However, in this work, the decomposition rate of the biodegradable plastics was obviously slower than that reported above. The Biodegradable Plastics Society also reported the poor degradability of PLA similarly to the results obtained in this study (http://www.bpsweb.net/).

The degradation behaviors of every piece of the PLA–laminated paperboards distinctly differed from each other in the burial test in soil. The plastic film parts remained unchanged even after 6 months, as well as the individual films and the laminates, although most of the paperboard piece disappeared. The variation of the biodegradation behavior probably depends on the kinds and the distribution of soil microbes degrading each component.

On the biodegradation mechanisms, the polymeric products such as polyesters were at first hydrolyzed non–enzymatically and then the resulting low molecular fragments were finally converted to water and carbon dioxide by the metabolic reaction of soil microorganisms (Tsuji *et al.*, 2001). Therefore, the differences in the degradation behaviors between the paperboard and the PLA film of the laminated product under the same conditions suggested that the PLA–degrading microbes were smaller in number than the cellulose–degrading ones in soil for the burial test.

Little synergistic effect by the lamination of biodegradable polymers with polysaccharide materials on their degradability was recognized, and then the biodegradation of composite materials would proceed individually. As mentioned above, the decomposition of biodegradable composites depends on the fungus characteristics, and the combination of biodegradable plastics and matrix materials has little influence on their biodegradation, excluding an exceptional example that the composite materials themselves breed and activate the microorganisms with an ability to decompose the biodegradable plastics.

The biodegradability of the products subjected to this study was as follows; paperboard, paperboard coated with biodegradable polymer, paperboard laminated with biodegradable plastics, biodegradable plastics and petroleum plastics. The significant differences between the PLA–coated and PLA–laminated paperboards strongly suggested that the biodegradation rate of the composite products could be accelerated by the hybrid design of the each composite material, and the further investigation would be necessary for the practical application. Higher crystallinity of biopolymers offers the excellent physical properties and the poor biodegradability, and thus, the manufacturing conception of new products must be carefully administered for solving the antinomy.

The Japanese Industrial Standards (JIS) Committee and the International Organization for Standardization (ISO) define three types of evaluation indices for the material biodegradability as follows;

1) Determination of ultimate aerobic biodegradability of plastic materials in an aqueous medium: Method by measuring the oxygen demand in a closed respirometer (JIS K 6950 / ISO 14851),
2) Determination of the ultimate aerobic biodegradability of plastic materials in an aqueous medium: Method by analysis of evolved carbon dioxide (JIS K 6951 / ISO 14852) and
3) Determination of the ultimate aerobic biodegradability and disintegration of plastic materials under controlled composting conditions: Method by analysis of evolved carbon dioxide (JIS K 6953 / ISO 14855).

In addition, the four JIS methods are under consideration according to Final Draft of International Standard (FDIS); 1) Determination of ultimate anaerobic biodegradability of plastic materials in an aqueous medium (FDIS 14853), 2) Determination of ultimate anaerobic biodegradability of solid plastics (FDIS 15985), 3) Determination of breakdown of plastic materials in composting systems (FDIS 16929) and 4) Determination of ultimate aerobic biodegradability of plastic materials in soil (FDIS 17556).

The burial test in soil in this study was performed at the ground out of environmental control, being different from the above standard methods. However, the practical cases are very complicated, and most of packaging materials are frequently put into disposal with other wastes. Therefore, the suitable determination for the biodegradability of composite components must be established for promoting the research and development of the functional design of biodegradable materials.

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