Degradability of Multi-Degradable HDPE and LDPE Food Packaging Films

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Abstract Degradable plastic additives (MCC-101, MCC-102) were prepared, and pure low-density polyethylene (LDPE), high-density polyethylene (HDPE) food packaging films, and multi-degradable films containing HDPE and LDPE resins and MCC series master batches (M/B) were manufactured by inflation film processing. The amount of M/Bs added in multi-degradable films was 40%, and the thickness was about 50 μm. The films were exposed to UV radiation, fungi, and heat in order to observe their photolysis, biodegradability, and thermal degradability, respectively. While pure PE films maintained more than 90% of their original elongation after 40 days of UV radiation, an almost perfect loss in the elongation of PE films containing 40% M/B was observed. Significant decreases in the elongation of PE films by heat treatment (68±2°C) were also observed for samples containing the multi-degradable M/B. By observing changes in film surface after the inoculation of fungi with scanning electron microscopy (SEM), the accelerated biodegradability of plastic films by adding multi-degradable M/B was confirmed. Overall results showed that the addition of multi-degradable M/B has a strong potential to effectively degrade plastic films in natural conditions.

Keywords: degradable plastic additives, low density polyethylene (LDPE), high density polyethylene (HDPE), food packaging film, photolysis, biodegradability, thermal degradability

Introduction

Owing to their excellent rheological property, manufacturability, and durability, plastic materials or synthetic polymers have a very wide range of usage, from industrial materials to disposable products, and contributes to the bountiful daily life and industrial advancement of today. Especially, plastic is the most important material in the manufacture of packaging film, flexible packaging material, and containers

for a variety of foodstuffs in the food industry. However, most of the commercialized plastic materials for food packaging are semi-permanent and non-degradable, which leaves all sorts of waste including vinyl, Styrofoam, plastic container. Hence, environmental hormone leakage due to incineration or reclamation, difficulty in securing reclaiming sites, detection of deadly poisonous dioxins, and air pollution generated by incomplete incineration of waste substances are becoming grave social issues. In particular, plastic materials have been criticized as a 'principal offense of the environmental contamination (1,2)'. To solve these problems, developing and commercializing degradable plastics that are environment-friendly, non-harmful, and easily decomposable by sunlight, soil microbes, and heat generated from reclaimed lands is urgent, so that they can be both stable and convenient during and after the use.

In some advanced countries like the U.S., Japan, Germany, and Italy, the use of degradable polymers for shopping bags, plastic containers and so forth is obligatory (3), and studies on the practicability of degradable plastics and the development of new materials are actively in progress. Degradable plastics can be generally classified into three types: biodegradable, bio-disintegrated, and photodegradable, according to the manufacturing material and the reaction mechanism (4-6). Biodegradable plastic is manufactured by synthesizing new polymers using natural polymers, such as biopolymers, like poly-hydroxyl butyric acid (PHB) and hyaluronic acid (HA), produced by microorganisms, cellulose, and chitin products derived from plants or animals. This plastic has great qualities in tensile strength, moisture resistance, and industrial process, but is rarely used as food packaging material due to slow decomposition and high cost (5). Bio-disintegrated plastic is manufactured by mixing naturally decomposed polymers like starch with commonly used plastic like polyethylene (PE), polypropylene (PP) and polystyrene (PS). Degradation is promoted by adding diverse additives, as chemical degradation accelerators, into the polymer (6). Bio-disintegration plastic is comparatively cheap in price, but their quality is low. Accordingly, this kind of plastic can be partially used only for waste bags or shopping bags and is not suitable for food packaging containers that require durability and strength. On the other hand, photodegradable plastic is basically decomposed through the initiation of a

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polymer ring breakage, which deteriorates physical properties of the polymer and ultimately lowers molecular weight, by ultraviolet (UV) rays. For photodegradable plastic, transition metals, such as iron and nickel, oxidation accelerators and photosensitive materials are added to photodegrade main fractions of polymers or to induce carbonyl radicals, as photosensitive radicals, into the main fraction during polymerization. The UV ray for the photodegradation of approximately 290 nm range is reported to be sufficient to break a covalent carbon-hydrogen bond forming the plastic (7). Photodegradable plastic is cheap, but can be applied only to thin films with the present technology. Moreover, since the use of excessive photosensitive additives is essential to manufacturing degradable plastic that depends only on the photodegradation, it could be a problem to connote the risks of heavy metal contamination of soil by reclaiming after the use (7).

Multi-degradable plastic, which contains the features and functions of the three types of degradable plastics mentioned above, has been researched and developed and is being sold in some advanced countries including Canada, the U.S., and Japan. However, the plastic is almost never applied in Korea due to its high cost (8). Generally, the degradation of the multi-degradable plastic films can be explained by the following three steps. In the first step, the plastic structures showing decomposition of biodegradable materials contained in the plastic becomes porous, causing the deterioration of strength, elongation percentage, and the expanding effect of a surface area. In the next step, automatic oxidation progresses by the oxidation accelerator, generating chemical degradation and inducing molecular weight decrease and ultrafine particlization. In the final step, microorganisms or enzymes induce actual degradation. However, under the actual natural conditions, most of these degradation steps progress simultaneously or complementarily, rather than in sequential order.

In the present study, we estimated product safety, thermal degradation, photodegradation, and biodegradation of the multi-degradable low-density polyethylene (LDPE) and high-density polyethylene (HDPE) films most commonly used as food packaging materials.

Materials and Methods

Master batch (M/B) manufacturing Table 1 shows how master batches (M/B), with multi-degradation functions, are manufactured. Firstly, LDPE (Samsung Chemicals, grade 530G, Korea) or HDPE (Samsung Chemicals, grade F120A, Korea) resins, starch, polycaprolactone (PCL), photodegradation agents, and benzophenone are put in a kneader with two rotors and reacted for 30 min and maintained at 20 and 25 rpm. After this mixture is mixed with calcium carbonate, chemical degradation accelerator, radical initiator, auto-oxidizer, and various kinds of additives, the second mixture is reacted for 20 min, and then penetrated through a single extruder at 170°C. The mixture is cut to manufacture M/Bs (MCC-101 for LDPE and MCC-102 for HDPE) in pellet shapes of 2-3 mm diameter. When the M/Bs are produced according to the above method, high shear force is applied to melting polymers, breaking the chains of the polymers and producing many polymer radicals. Later, these radicals play a part in generating photosensitive sites to absorb UV rays by reacting with surrounding oxygen (9).

Film manufacturing The MCC-101 and the MCC-102 were respectively mixed with LDPE and HDPE for degradability, and films were manufactured using T-Die film processor (LABTECH Engineering Co., Cast Film & Sheet Chill Roll Machine, Bangkok, Thailand). They were put and mixed in a blender, transported into a hopper, penetrated through a single screw extruder of 220°C and

Table 1. Compositions of master batch

Functions	Materials	Recipes (%)
Biodegradable polymers	Polycaprolactone (PCL), Starch from corn and tapioca	30-40
Inorganic filler	CaCO₃	25-35
Stabilizer	Antioxidant (Benzene propanoic acid etc.)	0.1-1.0
Chemical degradation accelerator	1-st Transition metal, 2-nd Transition metal, Photodegradation agents	0.1-1.0
Oxidation accelerator	Aromatic ketone group (benzophenone etc.), Organic acids, sugars	0.1-1.0
Oxidizable component	Unsaturated fatty acids	0.5-3.0
Lubricant	Waxes	1.0-5.0
Adhesive agent	Low density polyethylene (LDPE) for MCC-101	5-10
	High density polyethylene (HDPE) for MCC-102	

Table 2. Medium for the culture of fungi

Fungi	ATCC No.[1]	Medium
Aspergillius niger	9642	Potato Dextrose Agar
Penicillium pinophilum	11797	Harrold's M40Y
Trichoderma virens	9645	Potato Dextrose Yeast Agar
Aureobasidium pullulans var. *pullulans*	15233	Sabourauds Agar
Penicillium funiculosum	11797	Potato Dextrose Agar

[1]Available from Korean Collection for Type Cultures.

through a cylinder for cooling, to process the films to an average thickness of 50 μm. The mixing rate of M/B was regulated to be 40% based on weight.

Product safety test as food packaging material To determine compliance, as a food packaging material, to the regulations of the Korea Health Industry Development Institute, the product safety of MCC-101 and MCC-102 was investigated by measuring heavy metal content (mg/L), potassium permanganate consumption (mg/L), lead content (mg/kg), evaporating residue (mg/L), cadmium content (mg/kg), and others on the basis of the standard test method (10) for plastics among standard baselines for tools, container and packaging of the Korean Food and Drug Administration (KFDA).

Evaluation of photodegradation Photodegradation was tested by the ASTM D 3826-98 method (11). Film samples cut into 13×80 mm pieces were placed in a self-manufactured box (160 cm×50 cm×50 cm) attached with a 40 W mercury lamp (SANKYO DENKI F40T10BLB) and exposed to the air at room temperature. The samples were placed 10 cm below the mercury lamp in order to perform the UV irradiation. Elongation, a mechanically extendable degree for the point where the film is cut at 100 mm/min tensile speed, is represented as a percentage (%), in contrast with initial length. After collecting the samples every 10 days, the degree of elongation was measured six times and averaged using the Instron Universal Testing Machine (Model 5565, Instron Corp. Canton, MA, USA), and the shape changes of the pre- and post-specimens were observed through a digital camera.

Evaluation of thermal degradation To evaluate thermal degradation, the specimens were cut into 13×80 mm pieces and stored in an incubator with a constant temperature and humidity of 68±2°C and 85%, respectively. The specimen was collected at 10 day intervals and the changes in elongation were measured six times for the average value. The shape changes of the pre- and post-specimens were also observed through the digital camera.

Thermal degradation test of film through fungi The degradation of the film was estimated by the ASTM G 21-96 method (12). Five types of fungus strains distributed from the Korean Collection for Type Cultures were sub-cultured twice on each culture medium. Then, one loop of the formed spores was collected with a platinum inoculating wire, and the suspension was filtered to separate the lump of spores and mycelial fragments. Each separated mycelial fragment was put in a sterilized flask so that the fungal spore suspension contained 1,000,000 ± 200,000 spores per 1 mL, and each spore suspension mixed with the same amount of the five fungi was used as the final mixed spore suspension. The 13×80 mm film specimens were placed on a nutrient-salts agar medium prepared by a ratio shown in Table 3 and was sprayed with the mixed spore suspension to fully wet the specimen and the medium. In order to verify the surface changes of the specimen developed during the biodegradation process, surface morphology was observed through scanning electron microscopy (SEM, XL 30 ESEM-FEG, Phillips, Holland).

Results and Discussion

Product stability as food packaging material As shown in Table 4, the safety of the PE polymer additives, MCC-101 and MCC-102, passed all items testing for usage as a food packaging material.

Evaluation of photodegradation Elongation and tensile strength are the most important mechanical and physical properties in estimating photodegradation, but, elongation is known to be more sensitive to degradation (13, 14). Figure 1 shows changes in the elongation of each sample during the periods of UV irradiation. The values were measured at a brittle point and compared to determine degradation. As shown in Fig. 1, initial increases in elongation were observed, followed by fast decreases in film integrity after 10 days as a result of the fragmentation of the polymer chain. These behaviors are similar with the results reported by Chiellini et al (4). They suggested that the initial increase of the strength at break is attributed to a sort of

Table 3. Composition of nutrient-salts agar

Materials	Recipes (g)
$KH_2 \cdot PO_4$	0.7
$MgSO_4 \cdot 7H_2O$	0.7
NH_4NO_2	1.0
NaCl	0.005
$FeSO_4 \cdot 7H_2O$	0.002
$ZnSO_4 \cdot 7H_2O$	0.002
$MnSO_4 \cdot H_2O$	0.001
K_2HPO_4	0.7
Agar	15.0

Table 4. Results for safety tests for MCC-101 and MCC-102 as a material for food packaging

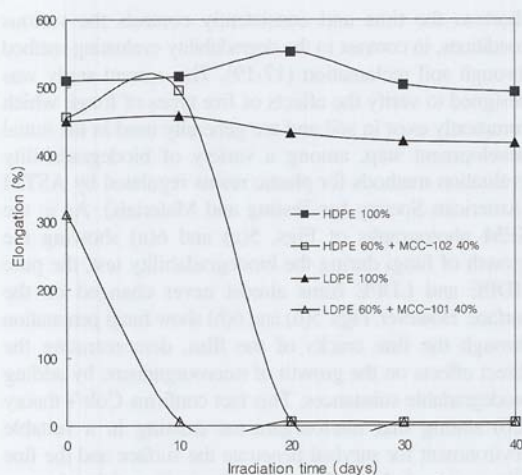| Items	Contents		Regulation
	MCC-101	MCC-102	
Amount of heavy metal	Trace	Trace	below 1.0 mg/L as Pb
Amount of lead (Pb)	Trace	Trace	below 100 mg/kg
Consumption of $KMnO_4$	0.9 mg/L	0.6 mg/L	below 10 mg/L
Evaporating residue	3.0 mg/L	4.0 mg/L	below 30 mg/L
Amount of cadmium (Cd)	Trace	Trace	below 100 mg/L

Fig. 1. Changes in elongation of films during UV irradiation.

plasticization effect exerted by a low molecular weight fraction produced in the first stage of the oxidative degradation of the polymer matrix. Another possible explanation for the initial increase in elongation is the occurrence of crosslinking through unstable peroxide bridges existing in polymers. Figure 1 also shows that both pure LDPE and HDPE films maintained more than 90% of the initial elongation after exposure to UV for 40 days. In contrast, an almost perfect loss in elongations was observed for both the HDPE film with 40% MCC-102 and LDPE film with 40% MCC-101 only after 20 days and 10 days of UV irradiation, respectively. Based on the fact that the ASTM D3826-98 regulation (10) defines the end point of photodegradation as the point when elongation reaches less than 5%, the reduced elongation signifies that photodegradation was already completed within 10-20 days. Thus, we found that M/B addition induced a rapid process of photodegradation under UV rays, because the rays influenced transition metals, benzophenone, and other photosensitive groups generated on the film by the aromatic ketones as well as a variety of photodegradable accelerants contained in M/B, as shown in Table 1. The reason the pure PE films showed some reduction in physical properties seemed to be because of the production of ketone radicals from oxidation by heat generated during film manufacturing. Since the ketone radicals act as a photo-sensitive group, they make photodegradation possible. This is already widely known from the polymer weather ability test (15). In the photographs of Fig. 2, which compares the film shapes before and after the photodegradation experiments, the pure PE films rarely changed even after 40 days, whereas the shape of the multi-degradable film manufactured by adding 40% of MCC-101 and MCC-102 were already fragmented after 40 days. From these results, the multi-degradable films were assumed to have disintegrated into very tiny pieces, losing its shape with time by wind, rain, animals, plants, or any other natural source.
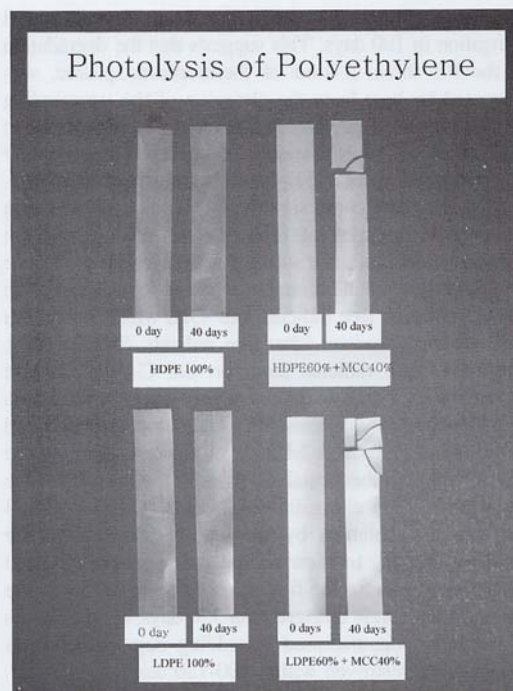

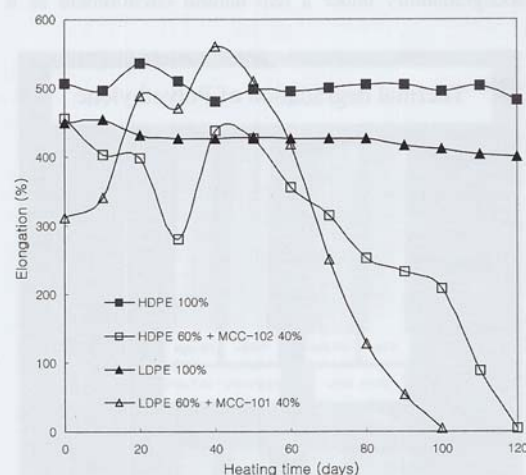**Fig. 2. Morphology of polyethylene films before and after UV irradiation.**

Fig. 3. Changes in elongation of films during heat treatment (68±2°C).

Evaluation of thermal degradation Thermal degradation tests of the film showed a somewhat slower change in elongation, but had aspects that were similar to photodegradation. As shown in Fig. 3, the elongation of the pure HDPE and LDPE films after 120 days remained at more than 90% their initial levels. Meanwhile the HDPE film manufactured by adding 40% MCC-102 almost entirely lost its initial elongation in 120 days, while the

40% MCC-101-added LDPE film totally lost its initial elongation in 100 days. This suggests that the degradation of the PE films, a kind of thermoplastic plastic, was promoted by heat from the elevation of the surrounding temperature. Generally, the degradation of thermoplastic resins starts through a variety of chemical reactions by heat generated under appropriate environmental conditions. In particular, the most significantly known degradation sequence is a series of reactions that decompose the plastic into low molecular substances like alcohol and ketone (16). That is, a small amount of iron ions contained in the plastic produces free radicals like ·OH, which react with polymers and produce other free radicals. Subsequently, these new free radicals react on the C-C bonds and decompose the bonds of the polymers. Copper or vanadium compounds, which are transition metal compounds included in the multi-degradable M/B, are known to promote the reactions due to their catalytic roles in the reactions. The initial increase in elongation by heat treatment in Fig. 3 can also be explained by the reason discussed in the previous section. In view of the pre- and post-thermal degradation tests for the film shapes shown in Fig. 4, the pure PE films rarely changed after 120 days, but the shapes of the films manufactured by adding degradable M/Bs were almost destroyed within 100-120 days.

Evaluation of biodegradability A microorganism-culturing method is widely used as a pre-step in measuring biodegrada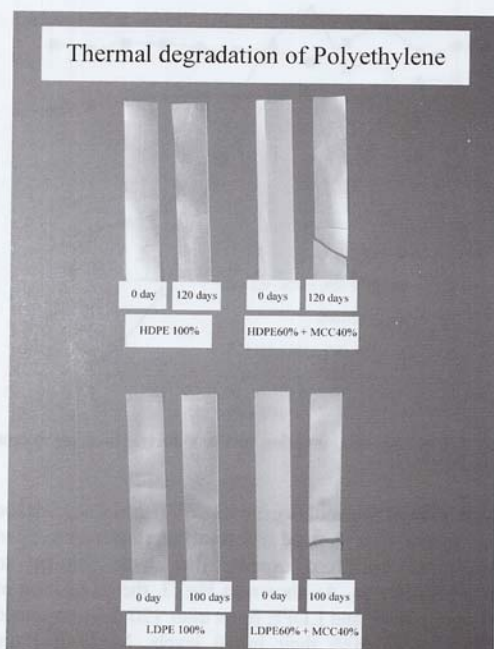bility under a real natural environment as it shortens the time and consistently controls the various conditions, in contrast to the degradability evaluating method through soil reclamation (17-19). The current study was designed to verify the effects of five types of fungi, which commonly exist in soil and are generally used in the initial development step, among a variety of biodegradability evaluation methods for plastic resins regulated by ASTM (American Society for Testing and Materials). As in the SEM photographs of Figs. 5(a) and 6(a) showing the growth of fungi during the biodegradability test, the pure HDPE and LDPE films almost never changed on the surface. However, Figs. 5(b) and 6(b) show fungi penetration through the fine cracks of the film, demonstrating the direct effects on the growth of microorganisms by adding biodegradable substances. This fact confirms Cole's theory (20) stating that microorganisms existing in a suitable environment for survival penetrate the surface and the fine micropores of plastic films. The observation of the changes in surface of the specimens clearly showed that biodegradable substances, such as starch, PCL, and saccharides contained in the M/Bs of Table 1, induce complete degradation through the initial decomposition by microorganisms, which makes more cracks on the surface and inside of the film, and the gradual reduction in the molecular weight of the polymer plastic.
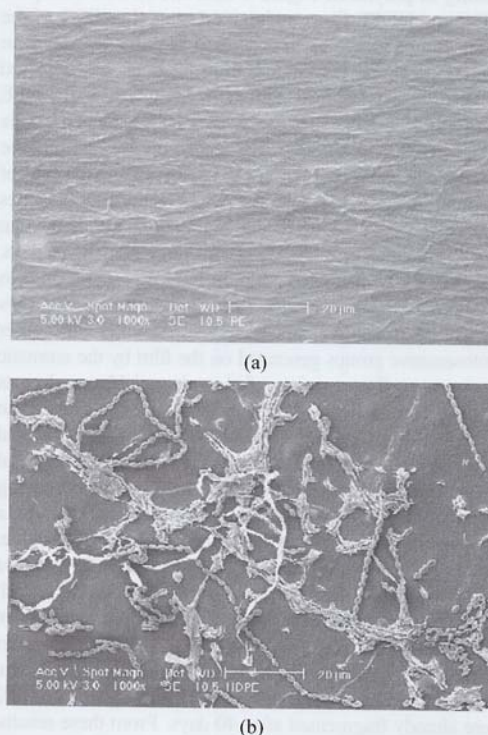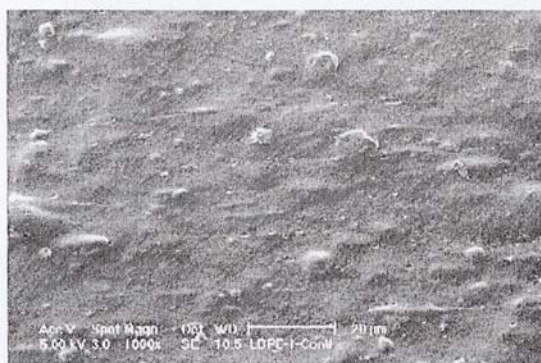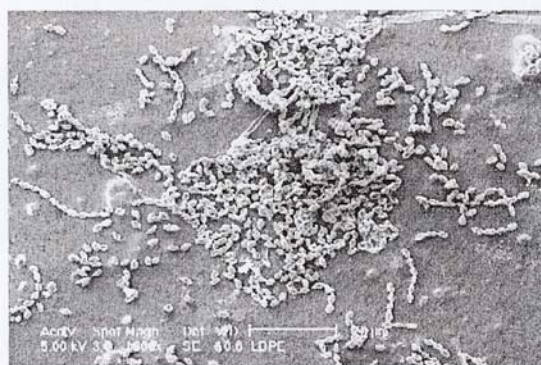

Fig. 4. Morphology of polyethylene films before and after heat treatment.

(a)

(b)

Fig. 5. Scanning electron microphotographs of the surface of (a) 100% HDPE, (b) 60% HDPE + 40% MCC-102 after 30 days of microbial attack.

(a)

(b)

Fig. 6. Scanning electron microphotographs of the surface of (a) 100% LDPE, (b) 60% LDPE + 40% MCC-101 after 30 days of microbial attack.

This article reported only the results of photodegradability, thermal degradability, and biodegradability as a fundamental study on the degradation of multi-degradable plastics available for use as diverse food packaging materials. However, the degradation of used and discarded plastics in the actual environment, such as a waste-reclaiming site, can be accelerated by various factors other than those examined in this study. Therefore, further studies on degradation should be conducted on the complex conditions of UV processing, heat treatment, and fungus growth, under conditions similar to the natural environment. Meanwhile, degradation should be estimated by expansively applying the thick food container sheets manufactured by adding M/Bs instead of the comparatively thin films used in this study. Moreover, the biodegradability test of the current study used only fungi as the experimental strains. However, further studies should focus on the effects of aerobic and anaerobic bacteria, birds, and other factors existing in the natural environment, based on the ASTM standard.

References

1. Garcia, C., Hernandes, T. and Costa, F. Comparison humic acids derived from city refuse with more develc humic acids. Soil Sci. Plant Nutr. 38: 339-346 (1992)
2. Brown, D.T. Plastic Waste Management, pp. 1-35. Mus N. (ed.). Marcel Dekker Inc., New York, USA (1993)
3. Narayan, R. Impact of governmental policies, regulati standards activities on an emerging biodegradable pla industry, pp. 261-272. In: Biodegradable Plastics and Polyr Doi, Y. and Fukuda, K. (eds.). Osaka, Japan (1993)
4. Chiellini, E., Corti, A. and Swift, G. Biodegradation thermally-oxidized, fragmented low-density polyethyle Polym Deg. Stabil. 81: 341-351 (2003)
5. Bloembergen, S., David, J., Geyer, D., Gustafson, A., Sn J. and Narayan, R. Biodegradation and composting studic polymeric materials, pp. 601-609. In: Biodegradable Pla and Polymers. Doi, Y. and Fukuda, K. (eds.). Osaka, J: (1993)
6. Doane, W.M. USDA research on starch-based biodegrac plastics. Starch 44: 292-295 (1992)
7. Albertsson, A.C., Barenstedt, C. and Karlsson, S. Suscepti of enhanced environmentally degradable polyethylene to the and photo-oxidation. Polym. Deg. Stabil. 37: 163-168 (1
8. Lee, S.I., Sur, S.H., Hong, K.M., Shin, Y.S., Jang, S.H. Shin, B.Y. A study on the properties of fully photodegradable composite film. J. Int. Ind. Technol. 129-134 (2001)
9. Shin, B.Y., Lee, H.B. and Cho, M.H. Photodegradatio HDPE film containing mechanically induced photosens groups. Environ. Res. 15: 31-40 (1995)
10. Korea Food and Drug Administration. Test method plastics. Chapter 6. Standards for containers and packa: pp. 28-60. In: Food Code, Seoul, Korea (2001)
11. ASTM D3826-98. Standard practice for determining degrad end point in degradable polyethylene and polypropylene u a tensile test. American Society of Testing and Mate: Philadelphia, USA (1998)
12. ASTM G21-96. Standard practice for determining resist of synthetic polymeric materials to fungi. Annual boc ASTM standards. American Society of Testing and Mate Philadelphia, USA (1996)
13. Jitendra, K.P. and Singh, R.P. UV-irradiated biodegradal of ethylene-propylene copolymers, LDPE, and I-PP in compc and culture environments. Biomacromolecules 2: 880 (2001)
14. Shin, B.Y., Jang, S.H. and Jung, B.W. A study on the pl biodegradable film containing calcium carbonate, starch crab shell. J. Int. Ind. Technol. 25: 103-119 (1997)
15. Willet, J. Mechanical properties of LDPE / granular s composites. J. Appl. Polym. Sci. 54: 1685-1695 (1994)
16. Nakasuka, S. and Andrady, A.L. Thermo-gravim determination of starch content in starch-polyethylene b films. J. Appl. Polym. Sci. 45: 1881-1887 (1992)
17. Ryu, K.E. and Kim, Y.B. Biodegradation of polymers. Po Sci. and Technol. 9: 464-472 (1998)
18. Koenig, M.F. and Huang, S.J. Biodegradable blends composites of polycapolactone and starch derivatives. Pol 36: 1877-1882 (1995)
19. Na, K., Shin, E.K., Kim Y.E., Kim, D.W. and Lee, Preparation of biodegradable film using polysaccharid Res. Int. Catalysis 20: 117-123 (1998)
20. Cole, M.A. Agricultural and Synthetic Polymers, p. 76. Gr S. (ed.). America Chemical Science, USA (1988)