Properties of Different Chitosan/Low-Density Polyethylene Antibacterial Plastics

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ABSTRACT: A series of low-density polyethylene (LDPE) antibacterial functional plastics were prepared by mechanical blending with commercial chitosan (CS), self-made water-soluble chitosan (W-CS), and microchitosan as antibacterial agents. The effects of the antibacterial agent content on the elongation at break of the obtained plastics were tested, and the bacteriostatic effects against *Escherichia coli, Bacillus subtilis*, and *Proteus* species were investigated. The results indicate that the elongation at break of LDPE with antibacterial agent decreased and had a slower decline when the mass ratio of CS to LDPE was greater than 0.5 : 100. The LDPE-based plastics showed different antibacterial activities against the three experimental strains, and plastics with W-CS exhibited the best antibacterial activity against *B. subtilis*. However, the antibacterial content had little effect on the antibacterial ratio. Moreover, 6-week soil burial tests indicated that the addition of CS caused a decrease in the resistance of LDPE to microbiological deterioration in a natural environment. © 2009 Wiley Periodicals, Inc. J Appl Polym Sci 113: 2018–2021, 2009

Key words: blending; composites; mechanical properties

INTRODUCTION

Plastic products bring much convenience to people's lives and have a steadily growing market. However, many components of polymeric materials, especially plasticizers, provide a source of carbon that can sustain growth and enable the proliferation of microorganisms on the surface. The problems caused by microbial attack, such as usability decrease, becoming a source of disease spread to threaten people's health,[1] has caused considerable interest in the development of antibacterial plastics.[2] Nowadays, most antibacterial plastic are prepared by the addition of certain antibacterial agents to common plastics.

In view of the development of environmentally friendly materials, antibacterial agents should have a lower toxicity to humans and the environment and greater heat stability. Therefore, among common organic[3,4] or inorganic[5,6] antibacterial agents, natural ones derived from plants and animals may be ideal antibacterial additives. Because of its nontoxicity, biocompatibility, and antibacterial activity, chitosan (CS) has become a much sought-after material for a variety of applications. To extend the applications of CS, many efforts have been made to research its antibacterial activity,[7] modification,[8–11] graft polymerization,[12,13] and blending with other polymers,[14,15] yet little research on the preparation of antibacterial plastics with CS and its derivatives has been reported.

This study was designed to investigate the application of CS as a plastic antibacterial agent. For this purpose, a series of CS/low-density polyethylene (LDPE) composites were prepared by mechanical blending. Then, the effect of the CS species and content on the elongation at break and antibacterial activity of the composites were studied.

EXPERIMENTAL

Materials and bacteria

CS (deacetylation degree >90%) was purchased from Yuhuan Ocean Biochemical Co. (Taizhou, China). Water-soluble hydroxypropyl chitosan (W-CS; viscosity-average molecular weight = 7.42×10^5) and micrometer chitosan (M-CS; D_{50} (median particle diameter) = 1.25 μm) were prepared in our laboratory. LDPE was commercial grade, and other chemicals were analytical grade.

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TABLE I
Influence of Antibacterial Species and Content of Elongation at Break of LDPE

	Antibacterial agent	Antibacterial agent : LDPE mass ratio				
		0 : 100	0.1 : 100	0.5 : 100	1.0 : 100	2.0 : 100
Elongation at break (%)	CS	287.77	138.58	87.15	78.39	69.66
	W-CS		131.43	79.87	74.98	68.53
	M-CS		136.28	77.42	73.23	69.24
Rate of change of the elongation at break (%)	CS		51.84	37.11	10.05	11.14
	W-CS		54.33	39.23	6.12	8.60
	M-CS		52.64	43.19	5.41	5.44

Gram-positive bacteria *Proteus* species, *Bacillus subtilis*, and Gram-negative bacteria *Escherichia coli* were provided by the School of Life Science, Taizhou University, and were incubated on nutrient agar ([peptone] = 1%, [beef extract] = 0.5%, [NaCl] = 0.5%, and [agar] = 2%; pH = 7.2).

Formation of the LDPE-based plastic samples

Before compounding, the dried CS, W-CS, or M-CS as the antibacterial agent was premixed with the LDPE pellets by the same operation at various mass ratios: 0 : 100, 0.1 : 100, 0.5 : 100, 1 : 100, and 2 : 100. The mixed components were then heated in an oven at 80°C overnight to remove residual water. Then, the mixtures were compounded in a counterrotating roll-mill- type SK-160B instrument (Shanghai Sinan Rubber Machinery Co., Ltd.) for 8 min, in which the temperatures of the two rolls were 100 and 105°C. Then, LDPE-based plastic samples, with a thickness of 2.0 ± 0.2 mm, were obtained from the resulting mixtures by compression molding at 155°C for 5 min under a pressure of 14.0 MPa with a hot press (a plate vulcanizing press machine type XLB63-D, Huzhou Xingli Rubber Machinery, Ltd.), followed by a cool press with the same pressure for 10 min.

For elongation-at-break testing, samples were cut into strips 20 mm in width and 140 mm in length and then machined into an ASTM type I dumbbell configuration. For antibacterial assays, specimens were cut to 40 × 40 × 2 mm^3.

Elongation at break

After the samples were dried at 60°C for 5 h, elongation-at-break tests of the CS/LDPE, W-CS/LDPE, and M-CS/LDPE blend dumbbell samples were performed with a universal tensile machine type AGS-J (Shimadzu) at a crosshead speed of 100 mm/min and at room temperature. All evaluations reported are the average values of three measurements.

Antibacterial assays

The antibacterial activities of the specimens were evaluated by two methods as follows:

For the membrane-covering test, according to China national standard QB/T 2591-2003, each specimen was washed twice with sterilized water, sterilized in 75% ethanol for 30 min, and then dried in the clean cabinet. A fresh overnight culture of *E. coli*, *P*. species, or *B. subtilis* was diluted to equal concentration and spread evenly onto the specimens. After a thin PE film was covered, all specimens were incubated at 37°C for 24 h. Then, the bacteria on the specimens was collected and spread onto an LB plate to culture for 24 h. The antibacterial rate was calculated as follows:

$$R = \frac{B - C}{B} \times 100\% \quad (1)$$

where R is the antibacterial rate and B and C are the bacterial amounts on the control specimen (pure LDPE sample) and the specimen with antibacterial agent, respectively. All final antibacterial rate values are the means of three duplicates.

For the soil-burying test, dumbbell specimens were buried at a distance of 50 mm at a depth of 100 mm under garden soil. Six weeks later, the changes in weight and breaking elongation of the specimens were investigated to compare to those of the unburied samples.

RESULTS AND DISCUSSION

Influence of the antibacterial agents on the elongation at break of LDPE

Mechanical properties are essential for plastics, so the influence of antibacterial agent species and content on the elongation at break of the LDPE-based composites were investigated in this study. The results are shown in Table I.

Table I indicates that the elongation of break of the CS/LDPE, W-CS/LDPE, and M-CS/LDPE blend composites decreased significantly in comparison with LDPE. Moreover, the change rate of elongation

TABLE II
Influence of Antibacterial Species and Content of Antibacterial Activities of LDPE Based Blends

Microorganism	Antibacterial agent	*R* (%) with the antibacterial agent : LDPE mass ratio			
		0.1 : 100	0.5 : 100	1.0 : 100	2.0 : 100
E. coli	CS	59.3	73.3	76.7	78.7
	W-CS	62.6	72.7	77.3	78.7
	M-CS	22.0	26.0	32.0	31.3
B. subtilis	CS	70.7	73.7	78.7	77.0
	W-CS	79.0	87.0	86.0	88.7
	M-CS	69.3	76.3	74.7	76.3
P. species	CS	0	0	0	0
	W-CS	28.6	45.6	56.8	61.4
	M-CS	2.8	2.0	3.8	3.4

at break decreased with increasing antibacterial agent content, whereas the downtrend became slow when the antibacterial:LDPE ratio was greater than 0.5 : 100. These facts were not in accord with the report by Xie and Liu,[16] in which the addition of CS-*g*-styrene had no adverse effect on the elongation at break of the antibacterial-function LDPE plastics. Here, the reason for the decrease might have been the bad compatibility between LDPE and W-CS and M-CS prepared in our laboratory according to refs. 10 and 11, respectively.

Influence of the antibacterial agent on the antibacterial activity

To analyze the influence of the antibacterial agent species and content on the antibacterial activities of the LDPE blend composites described in the section Formation of the LDPE-Based Plastic Samples, the membrane-covering tests related in the Antibacterial Assays section were carried out. After incubation at 37°C for 24 h, the antibacterial rate was calculated for the bacterial colony count on 1.44 cm^2 of solid medium. The results are shown in Table II.

The data from Table II indicate that the antibacterial rates of the LDPE-based composites against the three experimental bacteria, except for the values of CS/LDPE against *P.* species, increased slightly with increasing antibacterial agent dose. This implied that the content of CS and its derivatives were not the main factor affecting the antibacterial activities of the prepared composites.[17]

Table II also shows that the W-CS/LDPE composites presented higher antibacterial rates, especially against *B. subtilis*, compared to the other two composites. When the mass ratio of W-CS to LDPE was 2.0 : 100, the antibacterial rate against *B. subtilis* was 88.7%, which was the highest value in all of the test results. Although the CS/LDPE and M-CS/LDPE composites had antibacterial activities against *E. coli* and *B. subtilis*, there was no or weak activity against *P.* species. Therefore, the main factor affecting the antibacterial activity was not the content of CS or its derivatives but the structural difference caused by different modification approaches. The high antibacterial activity of W-CS/LDPE was due to its good adherence ability to the microorganism cell surface, which prevented the transport of nutrition needed by the microorganism for growth.[7] In addition, the limitation of bacterial behavior, which led to a decrease of bacterial multiplication fecundity, which was caused by $-NH_3^+$ in the W-CS molecule combining with the negative ions in the bacterial cell wall, might have been another reason for these results.[18,19]

Furthermore, the molecular structure change from CS to M-CS should have been a reason that CS/LDPE was superior to M-CS/LDPE in terms of antibacterial activities. Related research is underway in our group.

Soil burial tests of the LDPE-based composites

Studies have suggested that CS has antibacterial activity, although it can be decomposed by certain microorganisms in the environment.[20,21] The biodegradation of antibacterial agents in composites will lead to a decrease in the mechanical properties. To determine the antibacterial activities of the obtained

TABLE III
Weight Change and Elongation at Break of CS/LDPE Composites Before and After 6 Weeks Soil Burial

CS : LDPE mass ratio	Weight (g)		Elongation at break (%)	
	Before burial	After burial	Before burial	After burial
0 : 100	2.8539	2.8513	287.77	284.34
1 : 100	2.9736	2.9708	78.39	63.40
5 : 100	2.9899	2.9877	69.16	61.06

LDPE-based composites in the soil, the samples were buried in garden soil for 6 weeks. Comparisons of the weight changes and elongations at break of the composites before and after burying are shown in Table III. Clearly, the elongation at break of all of the specimens decreased after burial, regardless of the presence of CS. However, the elongation-at-break changes of CS/LDPE with CS:LDPE mass ratios of 1 : 100 and 5 : 100 were 19.12 and 11.71%, respectively, which were much higher than the change of LDPE of 1.12%. That is, the CS in the composites was really eroded by the microorganisms in the soil. However, there was only an unobvious change in weight because of the slight biodegradation of CS.

CONCLUSIONS

Antibacterial LDPE-based plastics with CS, W-CS, and M-CS as antibacterial agents were prepared by mechanical blending. Antibacterial experiments indicated that the main factor affecting the antibacterial activities of these composites was not the antibacterial agent content but its molecular structure. By comparison, W-CS was a better agent for the preparation of antibacterial plastics.

The bad compatibility between LDPE and CS and its derivatives used in this study was the reason of for the elongation-at-break decrease of the composites. However, the change became slow when the CS:LDPE mass ratio was greater 0.5 : 100.

From these points, the high CS content could not increase the antibacterial activity effectively but also decreased the elongation at break, so we suggest the choice of CS with a high antibacterial activity and good compatibility with base plastics as an agent to prepare perfect antibacterial plastics.

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