International Journal of Advanced Culture Technology Vol.8 No.3 211-215 (2020)
DOI https://doi.org/10.17703/IJACT.2020.8.3.211

IJACT 20-9-26

Microbial Inhibition Test of Sustained-Release Chlorine Dioxide Gas Freshness Retaining Agent

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Abstract

Currently, most of the chlorine dioxide gas is processed at the beginning of storage or distribution. It has the disadvantage of not being able to continuously process gas since there is no system that can continuously process it during the distribution process. Therefore, in order to minimize changes in freshness and quality during the distribution process of agrifood, there is a need for a sustained-release chlorine dioxide gas treatment technology that can be continuously released.

Therefore, in this study, the film to be used was examined so that the chlorine dioxide gas can be continuously released for a certain period of time, the concentration of the reactant and the viscosity at the time of the reaction were determined, and a chlorine dioxide gas gel pack was manufactured using this optimal condition. In addition, the gel pack was used to measure the amount of chlorine dioxide gas released and the sterilization effect of food poisoning bacteria.

Keywords: *Chorine Dioxide, Chorine Dioxide Gas, Sustained-Release, Freshness Retaining Agent, Sterilization*

1. INTRODUCTION

In order to allow the chlorine dioxide gas to be gradually released, the oxygen permeability and the amount of chlorine dioxide gas permeation were measured using various film materials as shown in Table 1. That is, as a carrier of chlorine dioxide gas.

As a single film, since the film strength, printing, and bonding processability were weak, various films were bonded to produce a composite film. In addition, since chlorine dioxide gas is a strong oxidizing agent, it is difficult to avoid deterioration due to the oxidizing power of chlorine dioxide, so a nano-modifier prepared with inorganic silica is coated and used. In addition, the same composite film coated with the nano-modifier was drilled in the same manner using a pulse laser, and oxygen permeability and chlorine dioxide gas permeability were measured under the same conditions as the concentrations and pH of chlorous acid and acid.

The oxygen permeability of the prepared film was measured by setting the outside of the packaging container to a relative humidity of 90% at a temperature of 38 degrees with a PermeO2 single meter (PermTech Co.).

The generation of chlorine dioxide gas was produced by reacting chlorite and citric acid as in the above reaction equation.

The viscosity, concentration, pH, etc. were prepared under the same conditions, and the reactants produced

Manuscript Received:August 31, 2020/Revised: September 08, 2020/ Accepted: September 15, 2020
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chlorine dioxide gas were put in a film, prepared in the form of a pack with a packing machine, and then put into a flask with 300 mL of distilled water and sealed. Thereafter, the light was blocked at 25° C. and after 24 hours, the concentration of chlorine dioxide dissolved in distilled water was measured. The concentration of chlorine dioxide was measured by reacting the collected solution with a 0.01 M sodium thiosulfate solution, followed by titration and absorbance at 510 nm, and the preparation of the chlorine dioxide standard solution was prepared by concentration by the KWWA method, and a calibration curve was prepared and calculated.

Table 1. Film condition test for sustained release chlorine dioxide gas release

Division	Material of Film	g/m^2	Boring of Pulsed laser
1	PET/CPP	55	N
2	PE/CPP	55	N
3	PET/PA	80	N
4	*PA/PE/LLDPE*	*85*	N
5	*PA/PE/CPP*	*80*	N
6	PET/PE	55	N
7	PET/PE	55(nano coating)	N
8	PET/PE	55(nano coating)	Y

2. MATERIAL AND METHOD

2.1Manufacture of chlorine dioxide gas treatment gel pack using optimal conditions

Chlorine dioxide gas was produced by maintaining the pH at 3.4 during the reaction of chlorite and citric acid.

Carboxymethyl Cellulose(CMC), a gelling agent, was added so that it could be continuously released during distribution, so that it had a viscosity of 5,000 cps. The solution to which the gelling agent is added is sealed in a micro-perforated PET/PE film (LG Chemical, Lutene LB5000/7500, LDPE, Daesan, Korea) so that the oxygen permeability becomes 10,000 cc/m2/day from 5,000 $cc/m^2/day$. And prepared (8.8 cm x 2.3 cm). At this time, the concentration of the chlorine dioxide gas released from the gel pack was prepared so that an amount of about 3, 5, 7 and 10 ppm was released for 12 days, respectively. The amount of chlorine dioxide gas released was measured in the same way as the above method

2.2 Confirmation of chlorine dioxide gas elution

In order to check whether gas is eluted from the prepared chlorine dioxide gas gel pack in the form of a sustained release, add a gel pack prepared at a concentration of 3 – 10 ppm to the PCA medium to prevent gas from leaking through a para film, and then the medium for each storage period. Hunter L, a, and b values were measured using a color difference meter (CR-300Minolta Chroma Meter, Konica Minolta Sensing Inc, Tokyo, Japan) to measure the degree of yellow chlorine dioxide gas absorbed by each sample, and then measured 5 times for each sample. The average value is shown. The L*, a* and b* values of the standard plate used at this time were 95.02, 0.04, and 0.26, respectively

2.3 Microbial sterilization test

The bacteria used in this study were Escherichia coli ATCC 25922 and Staphylococcus aureus ATCC 6538, which were distributed from ATCC and used. Each strain was activated in tryptic soy broth (TSB, Difco, USA), and the culture medium was dispensed in tryptic soy agar (Difco) and then smeared. A 5 ppm chlorine dioxide gas gel pack was adhered to the lid of a petri dish, followed by 48 at 37°C. By incubating for a period of time, the change in the number of bacteria was measured.

Listeria monocytogenes KCTC 3569 was used as a strain to measure the microbial killing effect of the chlorine dioxide gas gel pack by concentration. Listeria monocytogenes culture solution activated on tryptic soy agar (Difco) was dispensed and then smeared, and 5 – 15 ppm chlorine dioxide gas gel pack Was in close contact with the lid of each petri dish and incubated at 37° C. for 48 hours to measure the change in the number of bacteria.

3. RESULTS

3.1 Film selection for sustained release chlorine dioxide gas release

In order to allow the chlorine dioxide gas to be released in a sustained-release form, the oxygen permeability and the second day chlorine dioxide gas permeability of the films to be used were first measured, and the results are shown in Table 3.

In the case of PET/CPP, PET/PA, and PET/PE (nano coating 55, without pulse laser perforation), which had low oxygen permeability, a small amount of chlorine dioxide gas was emitted, and PE/CPP, PA/PE/LLDPE ,

In the case of PA/PE/CPP and PET/PE (no pulse laser perforation), oxygen permeability was more than 1,200 cc/m2/day, but the amount of chlorine dioxide gas emitted was low. In the PET/PE film with nano coating and pulse laser perforation, the content of 1.87 mg/day was judged to be the most suitable for permeation. Therefore, the oxygen permeability of the sustained-release chlorine dioxide gas packaging film was 5,000 cc/m^2/day. A PET/PE film (LG Chemical, Lutene LB5000/7500, LDPE, Daesan, Korea) micro-perforated to be 10,000 cc/m^2/day was used.

Table 2. Oxygen and ClO_2 permeability by film material

Division	Film Material	g/m^2	Boring of Pulsed laser	**O_2 permeability (cc/m^2/day)**	**ClO_2 permeability (mg/day)**
1	PET/CPP	55	N	259	0.00
2	PE/CPP	55	N	2,450	0.23
3	PET/PA	80	N	450	0.03
4	*PA/PE/LLDPE*	*85*	N	3,130	0.31
5	*PA/PE/CPP*	*80*	N	1,658	0.15
6	PET/PE	55	N	1,259	0.09
7	PET/PE	55(nano coating)	N	569	0.05
8	PET/PE	55(nano coating)	Y	5,540	1.87

3.2 Manufacture of chlorine dioxide gas gel pack under optimal conditions

For the generation of chlorine dioxide gas, the pH was adjusted to 3.4 during the reaction between chlorite and citric acid, and a reaction solution of about 3,000 cps was prepared by adding CMC, a viscosity modifier, so that chlorine dioxide gas could be continuously released during distribution. The prepared reaction solution was prepared by sealing in a PET/PE film having an oxygen permeability of 5,000 cc/m^2/day to 10,000 cc/m^2/day (8.8 cm × 2.3 cm). At this time, the concentration of the chlorine dioxide gas released from the gel pack was prepared so that about 3, 5, 7, 10 and 15 ppm of the concentration was released for 12 days, respectively, and the results are shown in Table 3.

Table 3. The amount of chlorine dioxide gas gel pack released during storage by concentration

Concentration of ClO_2 gas (ppm)	Storage period (day)								Total release content (mg/8 day)
	1	2	3	4	5	6	7	8	
3	0.28	0.20	0.23	0.18	0.18	0.15	0.13	0.13	1.48
5	0.53	0.46	0.40	0.35	0.33	0.38	0.43	0.36	3.24
7	0.76	0.91	0.66	0.76	0.56	0.51	0.46	0.43	5.05

3.3 Microbial sterilization test

Figure 1 Chlorine dioxide gas gel pack Antibacterial effect of Staphyllococcus aureus, E.coli O157H:7 and Listeria monocytogeneses

a. Staphyllococcus aureus

b. E.coli O157H:7

c. Listeria monocytogeneses

In all three strains, it was found that bacteria did not grow when treated with chlorine dioxide gas gel pack. It was found that the higher is, the greater the microbial sterilization effect. In particular, in the case of the 5 ppm treatment group, it was found that chlorine dioxide gas was eluted from the packaging material, killing the bacteria around the gel pack, and at 15 ppm with a high concentration, the amount of released chlorine dioxide gas diffused to the entire petri dish and killed near the edges. .

The results of measuring the microbial sterilization effect when the chlorine dioxide gas gel pack was treated is shown in table 4.

Table 4. Sterilization test of Escherichia coli and Staphylococcus aureus by chlorine dioxide gas gel pack

Division		Early Concentration (CFU/mL)	After 48 hr Concentration (CFU/mL)	Reduction rate (%)
Escherichia coli	Blank	1.7×10^4	1.7×10^4	-
	ClO_2 gel pack	1.7×10^4	<10	99.94
Staphylococcus aureus	Blank	1.4×10^4	1.4×10^4	-
	ClO_2 gel pack	1.4×10^4	<10	99.93

4. CONCLUSION

For the convenience of life and the convenience of distribution, the packaging format of various agricultural and fishery products is changing to small-sized containers, and agricultural products and fruits distributed in small-sized containers are rapidly progressing into small-scale packaging when exporting agricultural products, especially fruits and related crops. In addition, there is an active interest and demand for the use of vegetable freshness maintenance agents.

At the time of export, freshness treatment such as gas filling is performed, but it was difficult to guarantee the freshness of the crops stored in the package by only refrigerated transportation treatment when the transportation period was prolonged.

Chlorine dioxide preparations are used as food additives as the best sterilization and disinfectant without reaction by-products, but their use was limited due to rapid boiling at room temperature. By applying the technology to control chlorine dioxide, it maintains freshness by releasing trace amounts of chlorine dioxide during distribution of agricultural products. It was confirmed that if this Gelpack is applied, it is a method that can be applied to agricultural products distributed in small package containers as a freshness maintenance agent to prevent crops from being deteriorated by bacteria or microorganisms at least during transportation or display during distribution. Through the above experiment, we can confirm that bacteria control is effectively performed by the gel pack in which a trace amount of chlorine dioxide gas is ejected slowly.

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