Preparation of Antibacterial Polyimide Film by Vapor Deposition Polymerization

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1. Introduction

Recently, antibacterial plastic is used for many commodities. Generally, antibacterial plastic is produced by means of mixture processing of an antibacterial agent. However, the antibacterial agent is required to be heat-resistant over 250–300°C. Moreover, antibacterial plastics are required to have no weight variation or discoloration, but the antimicrobe effectiveness of antibacterial agent is lowered by high temperature. The antibacterial plastic is produced by mixing plastic pellets which contain antibacterial agent of about 5~30 % into the base material. Base materials used are polyethylene, polystyrene, chloroethylene, polypropylene and so on. The antibacterial agent is diluted and then molded. The antibacterial agent dosage in the end product is about 0.3~2 % [1, 2].

Generally, the method for applying to the plastic film is to use an adhesive, etc. to provide an antibacterial agent to the metal and ceramic component. It is difficult to uniformly apply an antibacterial agent to all the metal surfaces of a complicated shape. We have developed vapor deposition polymerization [3] to solve these problems in conventional technologies. Vapor deposition polymerization in a high temperature environment is known as a technique which uniformly forms polymer films on the surface of parts with complicated shapes. We tried to synthesize antibacterial polyimide films by vapor deposition polymerization of 3,5- diamino benzoic acid (DBA) and anhydrous pyromellitic acid (PMDA) with the structure of benzoic acid as the antibacterial agent (Figure 1).

2. Experimental

The vapor pressure of the monomers measurement and thermogravimetric analysis were carried out in vacuo (10⁻³Pa) or in a nitrogen atmosphere at a heating-rate of 1°C/min using a thermobalance (VAP-9000:ULVAC-Riko Inc). The polyimide film was produced in vapor deposition polymerization equipment {VDP2001 (ULVAC, Inc)}. The spectrum was measured on a micro infrared spectrophotometer {MFT-2000 (JASCO Corporation)} using the reflection method for the film produced on the stainless steel substrate.

Fig.1 Chemical equation of antibacterial polyimide.

3. Results and Discussion

The result of thermogravimetric analysis (TG) and differential thermal analysis (DTA) of DBA are shown in Figure 2. An endothermic reaction was shown to be generated near 230°C from this DTA curve. It is considered that this is indeed an endothermic reaction as polycondensation of DBA. The polycondensation reaction of DBA is shown in Figure 3. The weight loss near 230°C indicates the elimination of base water in the polycondensation.

Fig.2 TG,DTA~temperature curve of DBA
heating rate : 1°C/min
(In the nitrogen atmosphere)

The weight loss from near 400°C seems to be due to decomposition of DBA. It is considered that the

Fig. 3 Condensation reaction of DBA.

Fig.4 DBA and PMDA saturated vapor pressure ~ temperature chart

polycondensation of DBA over 230°C causes rapid reduction in the evaporation rate. The evaporation temperature of DBA was therefore set at the 200°C as this did not approach the condensation reaction temperature. The evaporation temperature of PMDA was set at 170°C in order to obtain a pressure equal to the saturated vapor pressure [4] of DBA at 200°C (Fig. 4). For the deposition condition, DBA 200°C, PMDA 170°C and substrate temperature of 200°C, the deposition rate was about 1 μ m/hr. Figure 5 is a FT-IR spectrum of the synthesized film. There are peaks which originate for imide absorption at 1780, 1720, 1380 cm^{-1} . The peak at 3650 cm^{-1} indicates vibration hydroxyl base in carboxylic acid. This suggest the existence of benzoic acid in polyimide main chain structure.

Fig. 5 FT-IR spectrum of polyimide film

Figure 6 shows photograph of a porous ceramic

(50 mm × 50 mm × 40mm) which was covered with the antibacterial polyimide. As seen in the A-B cross sectional view, all pores in the ceramic are covered with polyimide film. The antimicrobe performance of polyimide film was evaluated using film contact printing method (JIS Z 2801) as following. Each fungus liquid was dropped to the sample (approxiaamately 50 mm × 50 mm), and polyethylene film (40 mm × 40 mm) was put onto the sample to spread the fungus liquid on a constant area. The viable count was measured after keeping these samples at 35°C for 24 hours. Antibacterial activity value is a different between logarithm value of the viable counts estimated for non-processed test piece and for processed one by the film contact printing method. The resistance to each bacteria of the antibacterial polyimide (PMDA/DBA) and poly-4,4'-oxidiphenylene pyromellitimide (PMDA/ODA) is summarized in Table. 1. The antibacterial polyimide showed antibacterial effects on *Staphylococcus aureus*, *Escherichia coli*, *Bacillus subtilis*, *Pneumonia bacillus*, *Pseudomonas aeruginosa* and MRSA.

Fig.6 Porous ceramics covered with antibacterial polyimide.

4. Summary

Vapor deposition polymerization of anhydrous pyromellitic acid and 3,5- diamino benzoic acid, was used to produce an antibacterial polyimide film for antibacterial action. The film

Table 1 Antibacterial test result

Sample	Viable count	Antibacterial activity
Poly(PMDA/ODA)	5.6×10^7	-0.8
Poly(PMDA/DBA)	1.1×10^6	0.9
Non-processed test piece(Right after the inoculation.)	2.4×10^5	-
Non-processed test piece (after 24hr)	8.5×10^6	-

Sample	Viable count	Antibacterial activity
Poly(PMDA/ODA)	1.3×10^6	0.1
Poly(PMDA/DBA)	under 10	over 5.2
Non-processed test piece(Right after the inoculation.)	1.9×10^5	-
Non-processed test piece (after 24hr)	1.8×10^6	-

Sample	Viable count	Antibacterial activity
Poly(PMDA/ODA)	1.9×10^6	-1.8
Poly(PMDA/DBA)	under 10	over 5.4
Non-processed test piece(Right after the inoculation.)	3.5×10^5	-
Non-processed test piece (after 24hr)	2.5×10^6	-

Sample	Viable count	Antibacterial activity
Poly(PMDA/ODA)	1.6×10^7	0.1
Poly(PMDA/DBA)	2.0×10^5	2.0
Non-processed test piece(Right after the inoculation.)	3.9×10^5	-
Non-processed test piece (after 24hr)	2.0×10^7	-

Sample	Viable count	Antibacterial activity
Poly(PMDA/ODA)	1.9×10^6	-0.3
Poly(PMDA/DBA)	1.9×10^5	0.6
Non-processed test piece(Right after the inoculation.)	1.9×10^5	-
Non-processed test piece (after 24hr)	8.0×10^5	-

Sample	Viable count	Antibacterial activity
Poly(PMDA/ODA)	2.9×10^5	0.0
Poly(PMDA/DBA)	1.1×10^4	1.4
Non-processed test piece(Right after the inoculation.)	2.7×10^5	-
Non-processed test piece (after 24hr)	2.9×10^5	-

MRSA

Sample	Viable count	Antibacterial activity
Poly(PMDA/ODA)	6.6×10^4	0.7
Poly(PMDA/DBA)	4.5×10^1	3.8
Non-processed test piece(Right after the inoculation.)	1.9×10^5	—
Non-processed test piece (after 24hr)	3.5×10^5	—

Serratia

Sample	Viable count	Antibacterial activity
Poly(PMDA/ODA)	2.9×10^6	0.1
Poly(PMDA/DBA)	3.4×10^6	0.0
Non-processed test piece(Right after the inoculation.)	3.0×10^5	—
Non-processed test piece (after 24hr)	3.7×10^6	—

contained benzoic acid in the polyimide main chain structure.

Tests (JIS Z 2801) on the antimicrobe

performance of the polyimide film revealed 2.0 antibacterial activity values for *Staphylococcus aureus* and over 5.4 for *Escherichia coli*.

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