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METHODS FOR DETERMINING PHYSICAL PROPERTIES OF BIO-DEGRADABLE POLYMERS

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The physical properties were determined by the following methods.

(1) Bending Modulus of Elasticity [MPa]

A bending test (Japanese Industrial Standards (JIS) K 6911) was carried out using a tensilon universal tester Model RTC-1310 (ORIENTEC CO.). A test piece 12 mm wide and 6 mm thick was subjected to the-test in an atmosphere at 30° C. at a distance between clamps of 120 mm and a test speed of 3 mm/min.

(2) Weight Loss Rate After Dry Heat Treatment [%]

After subjecting to moisture conditioning at a temperature of 23° C. and relative humidity of 65% for one day or longer, a sample pressed sheet or biaxially stretched film was weighed to determine a weight before heat treatment. Next, the sample was treated in a hot-air oven at 90° C. for 30 minutes, was then subjected to moisture conditioning under the same conditions as before the treatment and was weighed. The weight loss rate was determined as a percentage of change in weight (weight loss) between before and after the treatment based on the weight before the treatment.

(3) Weight Loss Rate After Hot-Water Treatment [%]

After subjecting to moisture conditioning at a temperature of 23° C. and relative humidity of 65% for one day or longer, a sample pressed sheet or biaxially stretched film was weighed to determine a weight before heat treatment. Next, the sample was treated in distilled water at 90° C. for 30 minutes, was then subjected to moisture conditioning under the same conditions as before the treatment and was weighed. The weight loss rate was determined as a

percentage of change in weight (weight loss) between before and after the treatment based the weight before the treatment.

(4) Transparency Retention Temperature [$^{\circ}$ C.]

A test sample pressed sheet or film was attached under a tension without wrinkle to an aluminum frame having an inside size of 150 mm square, was fixed to the frame using a plurality of alligator clips for stationary and was left in a hot-air oven held at a set temperature for 30 minutes. The sample was then taken out from the oven and was visually observed. The test procedure was repeated while changing the set temperature of the hot-air oven in steps of 5° C. In this procedure, the transparency retention temperature was defined as a highest temperature at which the sample did not undergo losing transparency and showed no change in transparency.

(5) Heat of Crystal Fusion (ΔH_{po}) [J/g]

A sample plasticizer was subjected in advance to treatment at 90° C. under a reduced pressure of 1 torr or less for 3 hours for sufficient drying and crystallization. If the plasticizer has a melting point of 90° C. or lower, the sample plasticizer was subjected to measurement without the drying and crystallization treatment. About 5 mg of the sample was precisely weighed, was charged into a predetermined sample pan and was subjected to temperature elevation from -30° C. to 220° C. at a rate of 20° C./min in an atmosphere of nitrogen using a differential scanning calorimeter (DSC) RDC 220 available from Seiko Instruments Inc. The heat of crystal fusion derived from a poly(lactic acid) segment of the plasticizer was read out from the resulting thermograph.

(6) Tensile Modulus of Elasticity [MPa]

A sample film piece 10 mm wide and 150 mm long was subjected to moisture conditioning at a temperature of 23° C. and relative humidity of 65% for one day or longer in advance. The resulting film piece was subjected to a tensile test at 23° C. and at a distance between clamps of 50 mm and a tensile speed of 300 mm/min., using a Tensilon universal tester Model UTC-100 (ORIENTEC CO.) to determine a tensile modulus of elasticity. The measuring procedure was repeated a total of ten times, namely, five times in a longitudinal direction and five times in a widthwise direction per one level. In this procedure, the tensile modulus of elasticity was defined as the average of ten measurements.

(7) Heat Resistance [° C]

A test sample pressed sheet or film was attached under a tension without wrinkle to an aluminum frame having an inside size of 150 mm square, was fixed to the frame using a plurality of alligator clips for stationary, and was left in a hot-air oven held at a set temperature for 5 minutes. The sample was then taken out from the oven and was visually observed. The test procedure was repeated while changing the set temperature of the hot-air oven in steps of 5° C. In this procedure, the temperature indicating the heat resistance was defined as a highest temperature at which the sample did not show a change such as breakage or fusion to the frame.

(8) Film Haze [%]

The thickness of a sample film was determined in advance, and the haze of the sample film as an index of transparency thereof was determined using a Haze meter Model HGM-2DP (a product of Suga Test Instruments). The measurement procedure was repeated a total of five times per one level, and the film haze (%) was determined in terms of a film 10 µm thick based on the average of the five measurements.

(9) Adhesion [N/cm²]

A pair of two film pieces 10 mm wide and 100 mm long was prepared and was subjected to humidity conditioning at a temperature of 23° C. and relative humidity of 65% for one day or longer. Subsequently, a portion 10 mm in a longitudinal direction from the edge of one film piece was laid over a portion 10 mm in a longitudinal direction from the edge of the other film piece under the same atmosphere so that the longitudinal direction of one film piece met with that of the other. A load of 50 g/cm² was applied to the overlaid portion for one minute to thereby yield a test sample for measurement of adhesion. The adhesion was determined using a Tensilon universal tester Model UTC-100 (ORIENTEC CO.). The above-mentioned test sample was set into the tester so that the overlaid portion stood substantially at the center between clamps. A tensile test was carried out at a distance between the clamps of 50 mm and a tensile speed of 300 mm/min. in an atmosphere of 23° C., and a stress immediately before the overlaid portion peeled off was measured. When the film pieces had a relatively low tensile strength and another portion than the overlaid portion was broken before the overlaid portion peeled off, each two thicknesses were fully overlaid to give test pieces, and a pair of two overlaid test pieces were subjected to the above mentioned test procedure. The

measurement procedure was repeated a total of five times per one level, and the adhesion was defined as an average of the five measurements.

Poly(lactic acid) polymers and plasticizers were prepared in the following manner.

Poly(lactic acid) polymer (P1): A total of 0.02 part by weight of tin octylate was added to 100 parts by weight of L-lactide, followed by polymerization at 190° C. in an atmosphere of nitrogen for 15 minutes in a reactor equipped with a stirrer. The reaction mixture was formed into chips using a double-screw kneader-extruder, followed by solid-phase polymerization at 140° C. in an atmosphere of nitrogen for 3 hours to thereby yield a poly(lactic acid) polymer P1. P1 was subjected to DSC measurement and was found to exhibit crystallinity and to have a crystallization temperature of 128° C. and a melting point of 172° C.

Poly(lactic acid) polymer (P2)

A total of 0.02 part by weight of tin octylate was added to 65 parts by weight of L-lactide and 35 parts by weight of DL-lactide, followed by polymerization at 190° C. in an atmosphere of nitrogen for 40 minutes in a reactor equipped with a stirrer. The reaction mixture was formed into chips using a double-screw kneader-extruder to yield a poly(lactic acid) polymer P2. P2 was subjected to DSC measurement and was found that P2 did not exhibit crystallinity and that no crystallization temperature and melting point were observed.

Poly(lactic acid) polymer (P3)

A total of 0.02 part by weight of tin octylate was added to 86 parts by weight of L-lactide and 14 parts by weight of DL-lactide, followed by polymerization at 190° C. in an atmosphere of nitrogen for 40 minutes in a reactor equipped with a stirrer. The reaction mixture was formed into chips using a double-screw kneader-extruder to yield a poly(lactic acid) polymer P3. P3 was subjected to DSC measurement and was found to exhibit crystallinity and to have a melting point of 141° C.

Plasticizer (S1)

A total of 0.025 part by weight of tin octylate was added to 40 parts by weight of a poly(1,3,-butanediol adipate) having an average molecular weight of 8,000 and 60 parts by weight of L-lactide, followed by polymerization at 190° C. in an atmosphere of nitrogen for 60 minutes in a reactor equipped with a stirrer, to yield a block copolymer Si

between poly(1,3-butanediol-adipate) and poly(lactic acid). The block copolymer had poly(lactic acid) segments each having an average molecular weight of 6000 at both ends. S1 was found to have a ΔH_{po} of 23.3 J/g and a peak temperature in ΔH_{po} of 145.0° C.

Plasticizer (S2): A total of 0.025 part by weight of tin octylate was added to 71 parts by weight of a poly(1,3-butanediol adipate) having an average molecular weight of 10000 and 29 parts by weight of L-lactide, followed by polymerization at 190° C. in an atmosphere of nitrogen for 60 minutes in a reactor equipped with a stirrer, to yield a block copolymer S2 between poly(1,3-butanediol adipate) and poly(lactic acid). The block copolymer had poly(lactic acid) segments each having an average molecular weight of 2,000 at both ends. S2 was found to have a ΔH_{po} of 11.4 J/g and a peak temperature in ΔH_{po} of 124.1° C.

Plasticizer (S3)

A poly(propylene glycol)/(ethylene glycol) block copolymer having a molecular weight of 10000 was prepared by adding ethylene oxide to both ends of a poly(propylene glycol) having an average molecular weight of 2000. A total of 0.025 part by weight of tin octylate was added to 71 parts by weight of the block copolymer and 29 parts by weight of L-lactide, followed by polymerization at 190° C. in an atmosphere of nitrogen for 60 minutes in a reactor equipped with a stirrer, to yield a block copolymer S3 between poly(propylene glycol)/(ethylene glycol) and poly(lactic acid). The resulting block copolymer had poly(lactic acid) segments each having an average molecular weight of 2000 at both ends. S3 was found to have a ΔH_{po} of 15.8 J/g and a peak temperature in ΔH_{po} of 131.8° C.

Plasticizer (S4)

A total of 0.025 part by weight of tin octylate was added to 71 parts by weight of a poly(ethylene glycol) having an average molecular weight of 10000 and 29 parts by weight of L-lactide, followed by polymerization at 190° C. in an atmosphere of nitrogen for 60 minutes in a reactor equipped with a stirrer, to yield a block copolymer S4 between poly(ethylene glycol) and poly(lactic acid). The block copolymer had poly(lactic acid) segments each having an average molecular weight of 2000 at both ends. S4 was found to have a ΔH_{po} of 17.0 J/g and a peak temperature in ΔH_{po} of 135.0° C.

Plasticizer (S5)

An ether ester plasticizer “RS-1000” (liquid at room temperature), a product of Asahi Denka Kogyo K. K., was used as a plasticizer S5.

Plasticizer (S6)

A poly (ethylene glycol) having an average molecular weight of 8000 was used as a plasticizer S6.

Plasticizer (S7)

A total of 0.025 part by weight of tin octylate was added to 80 parts by weight of a poly(ethylene glycol) having an average molecular weight of 8000 and 20 parts by weight of L-lactide, followed by polymerization at 190° C. in an atmosphere of nitrogen for 60 minutes in a reactor equipped with a stirrer, to yield a block copolymer S7 between poly(ethylene glycol) and poly(lactic acid). The block copolymer had poly(lactic acid) segments each having an average molecular weight of 1000 at both ends. The ΔH_{po} of S7 was not observed.

Plasticizer (S8)

A total of 0.025 part by weight of tin octylate was added to 79 parts by weight of a poly(ethylene glycol) having an average molecular weight of 10000 and 21 parts by weight of L-lactide, followed by polymerization at 190° C. in an atmosphere of nitrogen for 60 minutes in a reactor equipped with a stirrer, to yield a block copolymer S8 between poly(ethylene glycol) and poly(lactic acid). The block copolymer had poly(lactic acid) segments each having an average molecular weight of 1300 at both ends. S8 was found to have a ΔH_{po} of 9.2 J/g and a peak temperature in ΔH_{po} of 122.0° C.

The number-average molecular weight of the poly(lactic acid) segment was found to be 1260 as determined by calculation according to the following equation:

$$\text{Number-average molecular weight} = \frac{1}{2} \times \frac{I_{\text{PLAX}} \times 72}{I_{\text{PEG}} \times 44/4} \times M_{\text{PEG}}$$

wherein I_{PEG} is the integrated intensity of signals derived from hydrogen of the methylene group of the principal chain of PEG; I_{PLA} is the integrated intensity of signals derived from hydrogen of the methine group of the principal chain of PLA; and M_{PEG} is the average molecular weight of the poly (ethylene glycol), based on a chart obtained by subjecting a solution of the plasticizer (S8) in deuterium chloroform to ¹H-NMR measurement. This value very

satisfactorily corresponded to a value calculated according to the formula:

$(\frac{1}{2}) \times (w_A/w_B) \times M_{PEG}$ wherein w_A is the parts by weight of L-lactide; w_B is the parts by weight of the poly (ethylene glycol); and M_{PEG} is the average molecular weight of the poly (ethylene glycol), based on the charged proportions of the raw materials.

Plasticizer (S9)

A total of 0.025 part by weight of tin octylate was added to 71 parts by weight of a poly(ethylene glycol) monomethyl ether having an average molecular weight of 10000 and 29 parts by weight of L-lactide, followed by polymerization at 190° C. in an atmosphere of nitrogen for 60 minutes in a reactor equipped with a stirrer, to yield a block copolymer S9 between poly(ethylene glycol) and poly(lactic acid). The block copolymer had a poly(lactic acid) segment having an average molecular weight of 4000 at one end. S9 was found to have a ΔH_{po} of 21.8 J/g and a peak temperature in ΔH_{po} of 134.8° C.

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