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論 文 要 約

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Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) is one of the PHB based co-polymers known as a melt-processable aliphatic co-polyester. Melt processing of this polymer is not easy because the glass transition temperature of PHBH is below the room temperature whereas the crystallization rate of this polymer is extremely low. Accordingly, it is difficult to form fibers, films and other products from PHBH because the polymer can be still in a rubbery state after it is cooled down to the room temperature in the melt processing. In this research, attempts were made to overcome the low crystallizability of PHBH in the melt processing by applying the high-speed melt spinning process.

Firstly, the PHBHs with high and low 3HH compositions were subjected to the high-speed melt spinning process, and the spinning behavior and fiber properties were investigated. Secondly, PHBHs with four different melt flow indices, i.e. four different molecular weights, were used, and mechanical properties as well as the structure of the prepared as-spun fibers were investigated. The introduction of 3-hydroxyhexanoate (3HH) results in reductions of crystallization rate and degree of crystallinity. Therefore, thirdly, sheath-core bicomponent spinning was carried out using the low and high 3HH composition PHBHs as the sheath and core components, respectively.

In chapter 2, PHBHs with high and low 3HH compositions of 10.4 mol% (PHBH-H) and 5.4 mol% (PHBH-L) were subjected to the high-speed melt spinning process. Considering that the PHBHs are susceptible to the thermal degradation, wide range of extrusion conditions were adopted, and the spinning behavior as well as the structure and properties of the resultant as-spun fibers were investigated. For the PHBH-H fibers, low oriented α-form crystals were formed at high take-up velocities, however sticking among fibers could not be avoided because of the low crystallizability of the polymer. On the other hand, enhancement of crystallization at high take-up velocities was confirmed in the high speed melt spinning of PHBH-L fibers. Thermal decomposition caused significant effects on spinning and structure development behaviors. Accordingly, fiber structure development was promoted under the extrusion conditions of low extrusion temperature and high through-put rate. Applying the high-speed melt spinning process, separated fibers were obtained even at high extrusion temperature of 180 °C, the temperature higher than the melting temperature of pure PHB where crystalline nucleus of PHB is known to disappear. Wide-angle X-ray diffraction (WAXD) analysis of the as-spun fibers showed that the crystalline orientation of α-form crystals increased with an increase in the take-up velocity. A small amount of β-form crystals started to appear at high take-up velocities. This was another evidence for the occurrence of crystallization under high tensile stress in the spin-line. Lowering of the melting peak temperature observed in the DSC analysis of as-spun fibers of high take-up velocities also corresponded to the starting of orientation-induced crystallization in the spin-line.

In chapter 3, detailed analysis on the structure of high-speed spun PHBH fibers was carried out paying a particular attention to the formation of β-form crystals.

Enhancement of crystallization at high take-up velocities was confirmed in the high-speed melt spinning of PHBH-L fibers, and the crystalline orientation of α-form crystals increased with increasing take-up velocity. On the other hand, development of ß-form crystals was noted from the reflection on the equator in the WAXD patterns of the fibers prepared at high take-up velocities. The fraction of ß-form crystals appeared to increase under the spinning conditions with higher spin-line stress. PHBH fibers showed negative birefringence because of the negative intrinsic birefringence of the α-form crystal. With the increase of take-up velocity, absolute value of birefringence increased and then started to decrease from the take-up velocity where the β-form crystals started to appear. This was considered to be due to the positive intrinsic birefringence of the β-form crystal. During the in-situ measurement of WAXD patterns in the heating process of as-spun fibers, melting of the ß-form crystals was observed in the temperature range from 90 to 130 °C, which is lower than the melting temperature of the α-form crystal. Mechanical properties of as-spun fibers increased with an increase in the take-up velocity. The highest tensile strength and tensile modulus of 156 MPa and 2.43 GPa were obtained under the conditions of take-up velocity 6 km/min, extrusion temperature 180 °C and total through-put rate for four filaments 10 g/min. In addition, the tensile strength of the as-spun fibers showed positive correlation with the ß-form fraction.

In chapter 4, with the aim of investigating the effect of thermal decomposition in the extrusion process in detail, low 3HH composition PHBHs of four different melt flow indices (MI) were subjected to the high-speed melt spinning process. Temperature dependence of rate constant for the thermal decomposition showed similar tendency for polymers of different MIs. On the other hand, condition for obtaining separated fibers shifted to higher take-up velocities with increasing MI. It is worth noting that the effect of throughput rate on the structure development behavior showed opposite tendency for the polymers of high and low MIs. With the decrease of throughput rate, structure development of the low MI polymer was suppressed whereas that of the high MI polymer was enhanced. It was considered that the effect of enhanced viscosity reduction dominated the structure formation behavior in the former case, whereas the effect of the increase of draw-down ratio in the spinning process dominated the structure formation behavior in the latter case.

In chapter 5, high-speed melt spinning of sheath-core bicomponent fibers was carried out using the PHBH-L and PHBH-H as the sheath and core components, respectively. Molecular orientation of the sheath component of PHBH-L was high while that of the core component of PHBH-H was extremely low even at high take-up velocities especially when extrusion temperature was high. This was considered to be due to the orientation relaxation of PHBH-H component in the spin-line after the orientation-induced crystallization and subsequent solidification of PHBH-L. In comparison with the single component spinning of PHBH-H, advantages of applying the bicomponent spinning with PHBH-L were confirmed to be the collecting of well separated fibers at high take-up velocities as well as the increasing of the attainable highest take-up velocity.