Reverse Temperature Injection Molding of Biopol™ and Effect on Its Properties

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ABSTRACT: A novel reverse temperature profile for the injection molding of Biopol™ was studied. It was found that both the mechanical properties and the part quality of Biopol™ were improved with this new reverse temperature process. When injection molded, most conventional thermoplastic polymers are processed at 30 to 70°C above the melting temperature; under these conditions, Biopol™ degraded rapidly and the resulting material showed poor mechanical properties. In contrast, when using a reverse temperature molding process, where Biopol™ was melted in the first zone and then was conveyed through the barrel with a decreasing temperature pathway and was injection-molded at a temperature below its melting point, the resulting material showed higher mechanical properties. The processing of Biopol™ was also greatly improved. The reverse temperature process uses the characteristically slow crystallization rate of Biopol™, which can be easily injected as hot melt even below its normal melting point. DSC analysis suggested that the reverse temperature process resulted in a more homogeneous crystalline phase than the conventional process. GPC analysis also indicated that thermal degradation of Biopol™ was largely reduced in the reverse temperature injection-molding process compared with conventional methods. © 2004 Wiley Periodicals, Inc. J Appl Polym Sci 94: 483–491, 2004

Key words: biodegradable; thermal properties; molecular weight distribution/molar mass distribution; ageing; injection molding

INTRODUCTION

Poly(3-hydroxybutyrate) (PHB) and related copolymers, such as poly(3-hydroxybutyrate-*co*-3-hydroxyvalerate) under the trade name Biopol™, have long been the subjects of study for biodegradable and biomedical materials. However, some have displayed embrittlement shortly after processing, which remains as the major hurdle for commercial applications. More evidence indicates that the embrittlement is a result of secondary crystallization during storage[1,2] and irrelevant to the physical aging process.[3] A low temperature melting peak around 75°C was observed to accompany the secondary crystallization of PHB, which occurred during storage. The secondary crystallization was also investigated by following the density changes of PHB with time after molding.[1] Many efforts have been attempted to resolve this aging phenomenon of PHB and related copolymers. These include copolymerization of 3-hydroxybutyrate with 3-hydroxyvalerate (PHBV),[4,5] blending with other polymers,[6–9] subsequent annealing of the molded articles,[1] etc. In addition, the poor thermal stability of polyhydroxyalkanoates under conventional processing temperature conditions may present operational limitations for processing such as injection molding, extrusion, and compression molding. In this study, the authors found that, even at 170°C, the viscosity of Biopol™ decreased continuously with residence time, indicating the occurrence of molecular weight reduction, which may contribute to the poor performances of the materials. It is believed that the thermal degradation of PHB is dominated by a random *cis*-elimination reaction, and this is attributed to the activated C–H bond neighboring the carbonyl involved in a favorable six-member ring transition state.[10–14]

In this paper, the effect of processing temperature on the mechanical properties and aging process of molded Biopol™ was investigated. Injection molding of Biopol™ was performed under different temperature profiles. In the first case, like injection molding for most other polymers, Biopol™ was injection molded at the temperature above its melting point. In the second case, Biopol™ was melted in the first heating zone of the barrel then conveyed through the barrel with a decreasing temperature profile and was finally injection molded at a temperature well below its crystalline melting point. The practice of injection molding Biopol™ at temperature below its crystalline melting

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TABLE I
Setting of the Major Parameters for Injection Molding[a]

	Reverse temperature	Normal temperature
Temperature (°C)		
Zone 1	180	160
Zone 2	155–160	180
Zone 3	140–145	180
Nozzle	140	170
Mold	50	50
Injection (psi)		
P_{max}	2,000	2,000
Speed 1	50	50
Speed 2	30	30
Packing (psi)[2]		
P_{max}	600	500
P1	400–450	300
P2	300	200
Time (s)		
T1	5	5
T2	3	3
Cooling	20	20

[a] The cycle time is approximately 32 s.

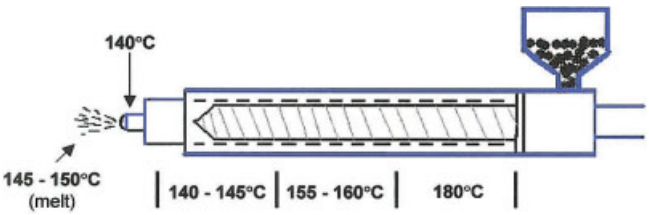

Figure 1 Illustration of zone temperature setting for reverse temperature injection molding. The resulting polymer melt is ~ 145–150°C.

point utilizes the characteristically slow crystallization growth rate of the PHBV copolymers. It is found that the maximum of spherulite growth rate of PHB-7%HV occurs at approximately 90°C, and the growth rate decreases rapidly at higher temperatures.[15] Therefore, after the temperature drops below its crystalline melting temperature, but still stays far above the maximum of its crystalline growth temperature, the supercooled Biopol™ melt will be in the molten flow state for a short period.

EXPERIMENTAL

Materials

Biopol™ XB 407 was obtained from Metabolix Inc, Cambridge, Massachusetts. The polymer had been compounded and was received as pellets. It is composed of poly(3-hydroxybutyrate-*co*-7% 3-hydroxyvalerate) (PHBV), a plasticizer, and a nucleating agent. Gel permeation chromatography (GPC) analysis shows that the molecular weight of Biopol™ XB 407 is ~ 574,000 M_w, and its polydispersity is ~ 1.69. Differential scanning calorimetry (DSC) analysis shows that its melting point is 159.2°C (maximum of endotherm), and the melting endotherm enthalpy is 62.5 J/g.

Injection molding

Injection molding was performed on a Battenfeld BA 1000/315 CDC injection molding machine. Table I lists the major parameters for the injection molding of Biopol™. Two different barrel temperature settings were used for the injection molding of Biopol™. In the first case, referred to as normal temperature setting (NT), the barrel temperature setting was similar to the conventional injection processing, with the first zone (convey section) temperature set at around the melting temperature of Biopol™, and melting zone, metering zone, and nozzle temperatures set above the melting temperature. With normal temperature setting, the temperature of melt injected from the nozzle was ~ 190°C and well above its melting point. In the second case, referred to as reverse temperature setting

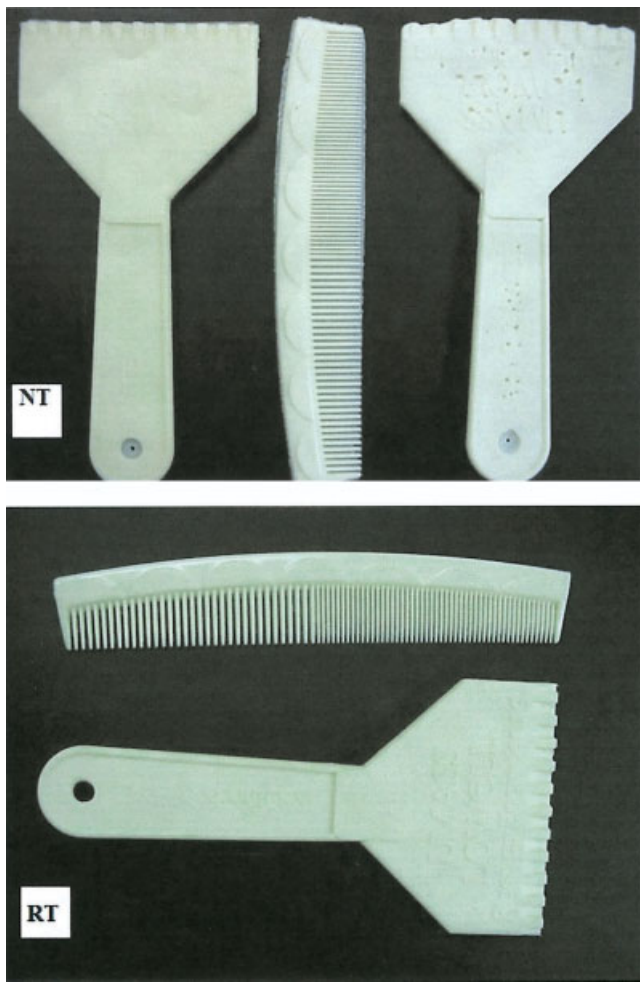

Figure 2 Parts molded at normal temperature (NT) and reverse temperature (RT).

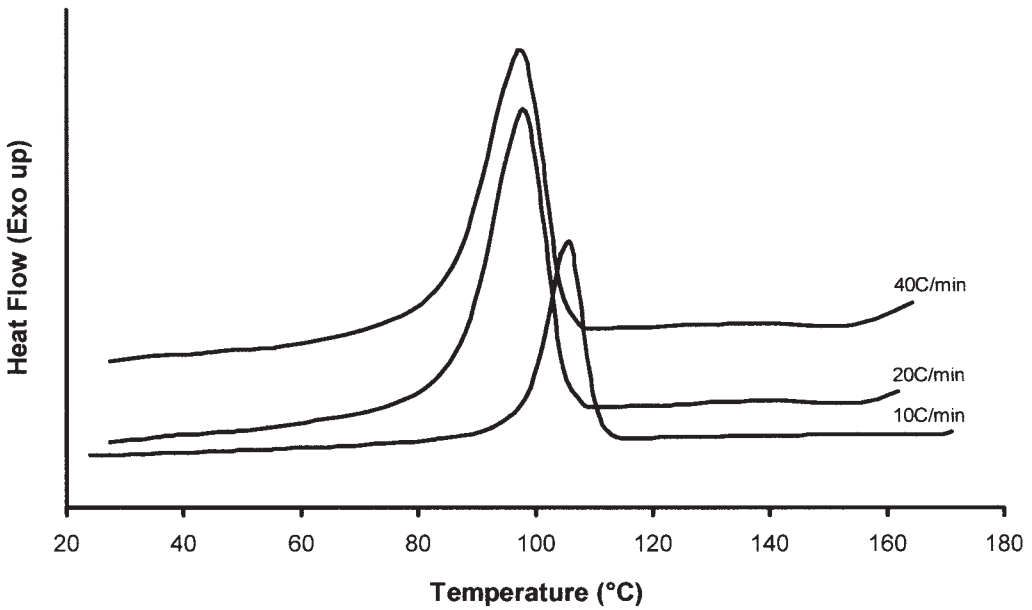

Figure 3 DSC cooling thermograms of Biopol™ XB 407 melt at different rates. The sample was heated up to 185°C at 20°C/min, kept isothermally for 1 min, and then cooled at the specific rate.

(RT), the temperature of the first zone was set at 180°C where Biopol™ was melted, and the temperatures at the following sections and nozzles were set in an order of decreasing temperature. Figure 1 gives an illustration of the barrel temperature setting for the reverse temperature process. With reverse temperature setting, the temperature of melt injected from nozzle was about 145–150°C and well below its melting temperature.

Thermal analysis

Crystallization and melting behavior of Biopol™ XB 407 was studied by DSC. The analysis was carried out using a TA Instruments DSC 2010, with nitrogen as the purge gas. The sample size was 5 ± 0.5 mg, and heating or cooling rate was 20°C/min unless stated otherwise.

Molecular weight measurements

Molecular weight of the polymer samples was measured by GPC. The GPC system was equipped with a Hitachi L-6200A gradient pump, a Polymer Labs PL-Gel 5 μm mixed column, and a Hitachi L-3350 RI detector. Chloroform was used as the eluent at a flow rate of 1 mL/min. The GPC system was calibrated using monodisperse polystyrene standards.

Rheology

The viscosity of Biopol™ was measured using a Kayeness Inc. capillary rheometer Galaxy V. The diameter of the die was 0.0197 in., and L/D ratio was 40. The material was heated for 3 min under certain force in the barrel at the test temperature before the measurement began, and viscosity was measured with the shear rate ranging from 100 to 10,000 s^{-1}.

Mechanical properties test

The tensile test was conducted on an Instron 6025 system following the procedures described in ASTM D638–98. The crosshead speed was 5 mm/min. Izod pendulum impact resistance was conducted on a TMI impact tester following ASTM D256–97, and a two-pound pendulum was used and the samples were not notched. All the data were an average of six repeats.

TABLE II
The Molecular Weight of Biopol™ XB 407 Versus Processing Temperature[a]

	M_w	M_n	PDI
Control (resin)	574,558	339,807	1.69
170°C	480,573	275,311	1.75
180°C	421,321	242,506	1.74
190°C	396,549	220,585	1.80
200°C	323,347	182,365	1.77
205°C	298,615	169,797	1.76
220°C	81,030	24,508	3.31

[a] Experiment was conducted in a capillary rheometer. After melting for 4 min at the specific temperature, the viscosity at shear rate of 1,000 s^{-1} was measured, and the molecular weight of the extruded material was analyzed.

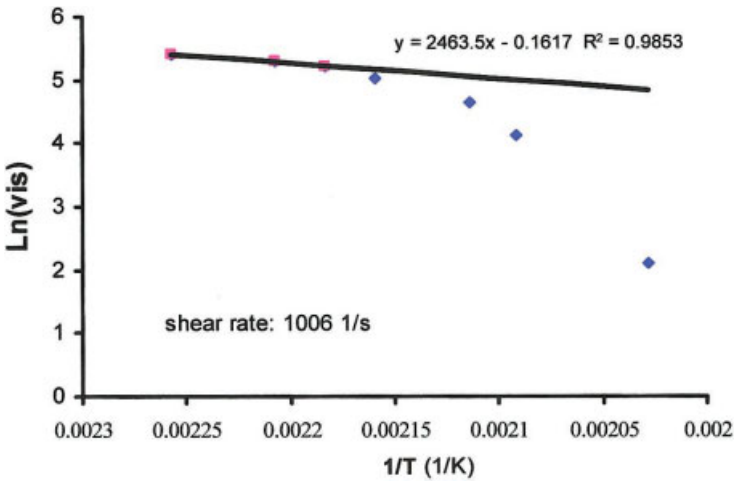

Figure 4 Viscosity of Biopol™ XB 407 versus temperature. The sample was melted at the specific temperature for 4 min before measurement started.

RESULTS AND DISCUSSION

Processing and products quality

To achieve consistent and homogeneous melt property, the semicrystalline polymer is usually processed at temperature well above its melting point. In conventional injection molding or extrusion process, the polymer runs through convey, melting, and metering zones with temperatures set in an increasing order, and finally exits with a temperature above its melting temperature. When PHB copolymers are melt processed in this manner, the characteristic low viscosity of PHB copolymers brings many difficulties and problems during process. For example, the extrudate strand is very easy to break during extrusion upon pulling due to its low melt strength. In the injection molding process, flash, jet, drool, and sink marks are often the problems. Furthermore, thermal degradation of PHB copolymers starts at a temperature slightly above their melting points, resulting in discoloration of the materials. These problems make the processing of Biopol™ very difficult. However, when injection molded at reverse temperature (RT), as illustrated in Figure 1, these problems were mostly avoided, and the processing window became larger. Figure 2 shows the parts molded at normal and reverse temperatures. In the reverse temperature process, though the Biopol™ polymer left the nozzle at a temperature (~ 145–150°C) well below its melting point, it still existed in hot molten state and was injection molded easily. This is due to its very slow crystallization rate in the neighborhood of this temperature. From previous studies of isothermal crystallization of polyhydroxyalkanoate, it has been well known that the maximum of the spherulite growth rate of PHB occurs at ~ 90°C, and the growth rate slows down rapidly with increasing 3-hydroxyvalerate content in the copolymers and the maximum shifts to lower temperatures.[15–17] Chen et al.[18] studied the nonisothermal crystallization of PHB and found that crystallization temperature decreased drastically with an increase in cooling rate. We have observed that the Biopol™ can exist in the molten state for a long period after the melt temperature was decreased to a temperature below its melting point. Figure 3 gives the thermogram of Biopol™ XB 407 melt at different cooling rates. At a cooling rate of 10°C/min, Biopol™ XB 407 crystallization started at 110.6°C, while at cooling rates of 20 and 40°C/min, the crystallization started at 105.6 and 105.2°C, respectively. In another experiment, Biopol™ XB 407 was loaded into a melt flow indexer heated at 185°C; the heat was then turned off. It was found that the melt retained its flowability until the temperature reached 127°C, 40 min later, when it froze.

Molecular weight and processing temperature

Our study of the viscosity of Biopol™ using a capillary rheometer showed that the shear viscosity continuously decreased with residence time even at a temperature right above its melting point, indicating thermal degradation had taken place at this temperature level. This is in agreement with Aoyagi and coworkers'[10] study on PHB thermal degradation, which concluded that thermal degradation of PHB even started at a temperature below its melting point. However, the molecular weight analysis showed that the reverse temperature injection molding greatly reduced the degree of thermal degradation compared to the injection molding at normal temperature, where the melt temperature was up to 190°C. In the molding of tensile and flexural test plaques, the molecular weight decreased from 574,000 to 437,000 (M_w) in reverse temperature process, an approximately 24% drop in mo-

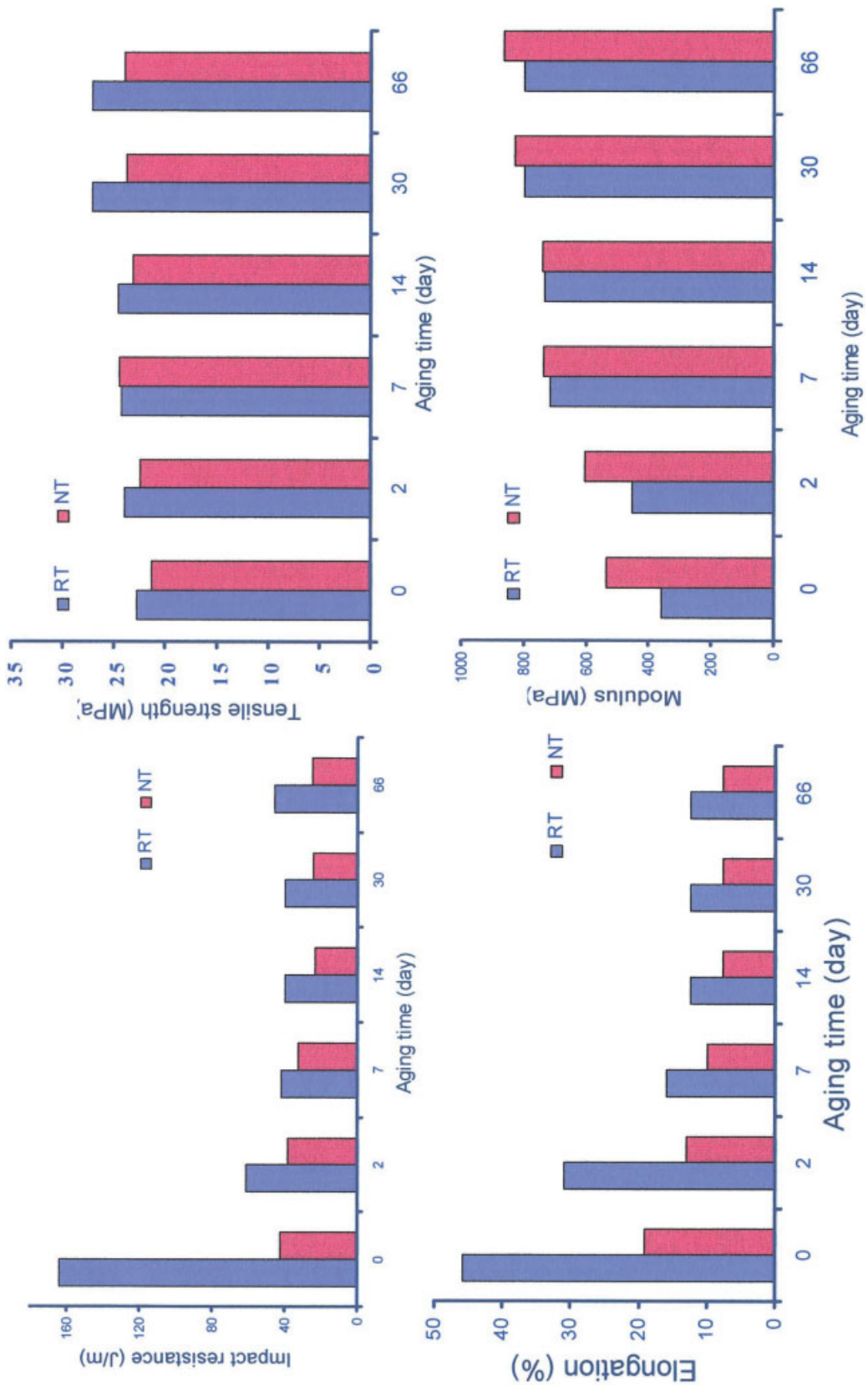

Figure 5 Mechanical properties of Biopol™ XB 407 versus storage time. NT, molded at normal temperature; RT, molded at reverse temperature.

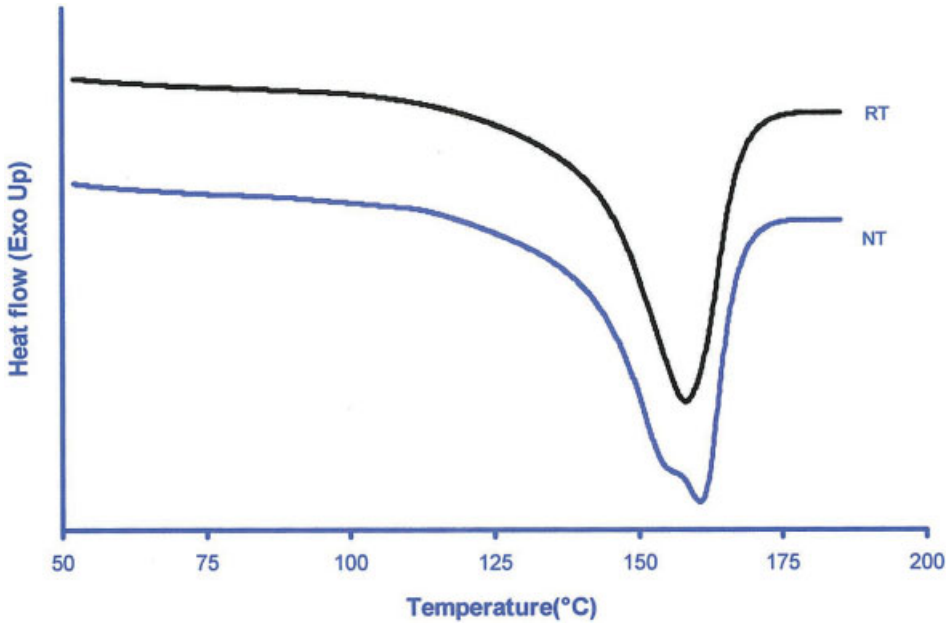

Figure 6 DSC melting thermograms of Biopol^{TM} XB 407 molded at normal temperature (NT) and reverse temperature (RT). The samples were aged for 2 days at room temperature after molding, and the heating rate was 20°C/min.

lecular weight. In contrast, the molecular weight decreased to 365,000 (M_w) in normal temperature process, about a 36% decrease. The residence time also had a significant effect on the relatively large molecular weight decrease in both cases, because the shot size for molding tensile and flexural bars was at the low end of the injection capacity, resulting in a residence time in the range of 3 to 4 min. The thermal degradation of Biopol^{TM} at different temperatures was further studied using a capillary rheometer. The changes of molecular weight and polydispersity of Biopol^{TM} with processing temperature are given in Table II. The molecular weight distribution gradually shifted toward the low molecular weight side with the increase in temperature. Above 190°C, Biopol^{TM} thermal degradation accelerated, and its molecular weight decreased drastically. A plot of shear viscosity versus $1/T$ also shows the accelerated degradation at temperature above 190°C (Fig. 4), and the linear relation was no longer retained. Below 185°C, though there was thermal degradation, a linear relation was still observed. Since the thermal degradation of Biopol^{TM} depends on not only temperature but also residence time in the barrel, thermal degradation will be reduced further by adjusting the shot size to the upper end of the injection capacity, which in turn will reduce the residence time of the resins in the barrel.

Mechanical properties

Figure 5 gives the comparison of mechanical properties of Biopol^{TM} injection molded at these two different temperature processes. It shows that the reverse temperature injection molding resulted in overall improvement in mechanical properties. Biopol^{TM} molded under a reverse temperature process showed higher impact, higher tensile strength, larger elongation, and more flexibility (low modulus) than that of Biopol^{TM} molded at a normal temperature process. Similar to Biopol^{TM} molded at normal temperature, the reverse temperature-molded Biopol^{TM} plastics also showed aging effect, and the stiffness and tensile strength increased with storage time while elongation and impact strength decreased. Since most changes in mechanical properties took place in the first few days after it was molded, it is believed that the major aging process occurred in the first week after parts were molded, though the properties changed with time up to 2 months. The higher molecular weight of Biopol^{TM} molded at reverse temperature definitely accounts for its improved mechanical properties. On the other hand, the difference in thermal history experienced by the polymer in these two processes may also have an effect.

Thermal properties

Figure 6 shows a DSC thermogram of Biopol^{TM} molded at two different processes. Biopol^{TM} injection molded at normal temperature showed a bimodal melting endotherm, and samples molded at reverse temperature showed a single melting endotherm. This result indicates that the reverse temperature processing leads to a more homogeneous crystalline phase. Based on the enthalpy of fusion, ΔH, both processes yielded almost identical crystallinity. These melting

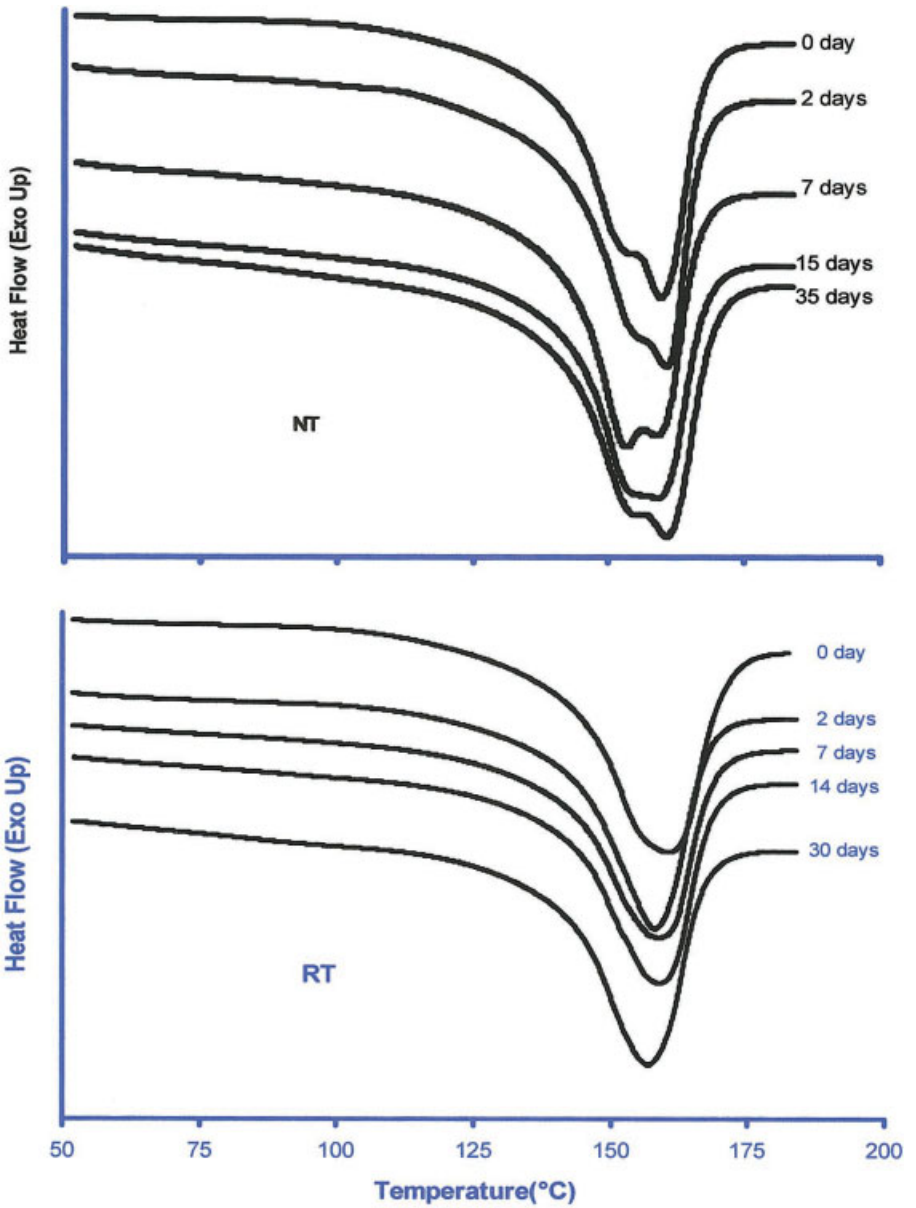

Figure 7 DSC melting thermograms of Biopol™ XB 407 molded at normal temperature (NT) and reverse temperature (RT) with different storage times. The heating rate was 20°C/min.

behaviors remained unchanged with storage time, as shown in Figure 7 and Table III, and the crystallinity did not show any obvious change with storage time, according to the integration of the major melting endotherm. In the reverse temperature process, the melt temperature at the front of the barrel was below the melting point of polymer but much higher than the temperature of maximum crystal growth rate, therefore more time was allowed for the nucleation process at a favorable temperature during each molding cycle, which could be the major reason for the homogeneous crystalline phase. In the normal temperature process, however, the melt temperature at the front of barrel was well above the melting point of Biopol™, where nucleation was not able to take place, and virtually both nucleation and crystallization took place in the mold. Furthermore, the temperature drop was much higher for the melt leaving the nozzle into the mold and a "quenching" effect might account for the less homogeneous crystalline structure of polymer molded at normal temperature. Chambers and coworkers[19] also found the dependence of crystalline homogeneity on processing thermal history, in their study of extrusion and compression molding of Biopol™ materials. The bimodal melting endotherm of Biopol™ molded at the normal temperature was not the result of melt/recrystallization process as observed in some PHBV by Yoshie and coworkers,[20] otherwise it would alsoap-

TABLE III
DSC Data for Biopol™ XB 407 Processed with Two Different Methods

RT				NT			
Aging (day)	T_m (°C) at onset	T_m (°C) at peak	ΔH (J/g)	Aging (day)	T_m (°C) at onset	T_m (°C) at peak	ΔH (J/g)
0[1]	142	160.4	62.6	0	139.8	156, 159.6	62.7
2	140.2	158.1	63.1	2	140.7	154.9, 160.6	63.3
7	140	158.6	59.7	7	141.1	153.3, 159	60.5
14	140	158.8	61	15	141	152.7, 159	58
30	140.3	157	63.5	35	139.2	155.1, 160.7	62.5

[a] Test on day 0 was conducted on plaques that were left to cool down at room temperature for 2 h after molding.

pear in the thermogram of Biopol™ molded at reverse temperature. Further study of DSC at different heating rates suggested the melt/recrystallization process would only take place at a slow heating pace (Fig. 8), for example, 5 or 10°C/min. In Figure 5, when the heating rate decreased to 10°C/min, a second peak

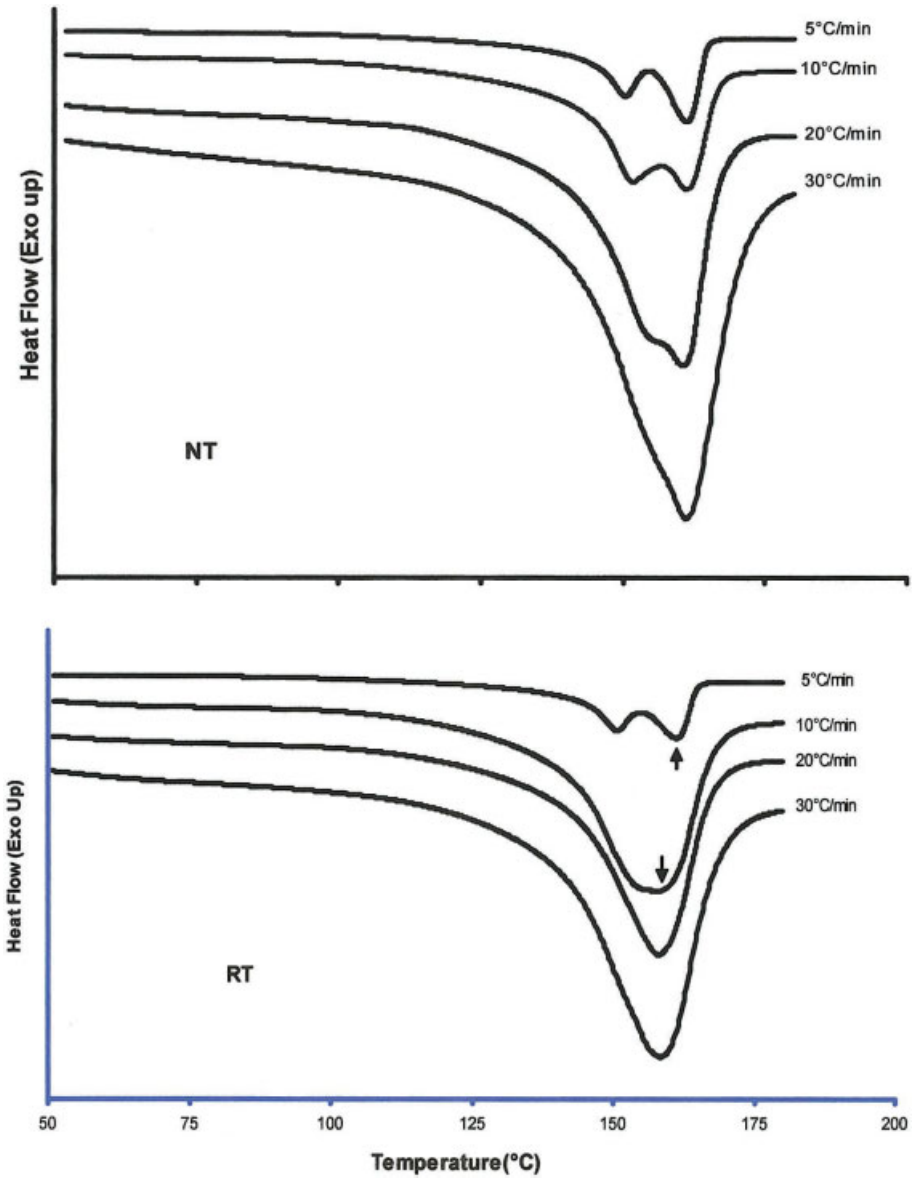

Figure 8 DSC melting thermograms of Biopol™ XB 407 molded at normal temperature (NT) and reverse temperature (RT) with different heating rates. The samples were aged for 2 days at room temperature after molding.

appeared at a higher temperature in the thermogram of the sample molded at reverse temperature. This peak was attributed to the melt/recrystallization process.

CONCLUSION

Compared with conventional injection-molding process, reverse temperature injection molding of Biopol™ results in plastics with improved mechanical properties, especially impact resistance and flexibility. However, the aging process still occurs. Reverse temperature injection molding leads to a more homogeneous crystalline phase than molding at normal temperature. The reverse temperature process improved not only the mechanical properties of the molded Biopol™, but also its processing and part quality. Because of its very low melt viscosity at temperatures above its melting point, Biopol™ injection molded at temperatures above its melting temperature likely has problems such as flash, sink marks, drool, etc. However, these problems are eliminated through molding at reverse temperature where the viscosity is significantly higher and more comparable to traditional thermoplastic materials. GPC data indicate that the thermal degradation of Biopol™ is significantly reduced compared with that molded at normal temperature. The improvement of mechanical properties by reverse temperature injection molding is attributed to the combination of less thermal degradation and homogeneous crystalline phase.

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