Melting Behaviour of Poly (butylene succinate) during Heating Scan by DSC

E. S. Yoo and S. S. Im,

Dept. of Textile Engineering, Engineering College, Hanyang University

1. Introduction

Recently, biodegradable polymers have received much attention from industry. It is well known that some synthetic aliphatic polyesters such as poly (butylene succinate) (PBS) show excellent biodegradability. In order to promote relatively low physical properties, many investigation on the modifiaction of this aliphatic polyester by means of physical blending or chemical treatment such as copolymerization have been reported. In spite of much demands from industrial fields, however, little work has been done on the processing of PBS. And the preceding of the study on the melting behaviour of polymers is inevitable to investigate about polymer processing.

Melting behaviour during differential thermal analysis is of interest because of the multiple endotherm[1] for so many semicrystalline polymers including flexible polymers such as polyethylene (PE)[2] and polypropylene (PP)[3], and semistiff polymers such as poly(ether ether ketone) (PEEK)[4], poly(ethylene terephthalate) (PET)[5], polyamide (PA) and polystyrene (PS). But as for PBS which is one of the flexible polymers, there is no work about it's melting behaviour.

The interpretation of melting endotherms, particularly of the double melting peaks, has been dependent upon researcher and polymer as a sample. In annealed PE, double melt endotherms were interpreted by Bassett[6] as an artefact of the measurement technique rather than a characteristic of the original polymer, even though some other workers proved the real presence of a double population of crystallites in linear PE by SAXS and TEM experiments. In the semistiff polymers, especially in PEEK, three types of morphological model have been suggested to analyze crystallization and melt behaviour which were shown in DSC, real-time SAXS and WAXD experiments. The dual lamellar stack model, and lamellar insertion model were proposed by some workers who insist the double population of lamellar result in double or multiple endotherms in DSC. The third one is a homogeneous lamellar thickness model as the melting recrystallization theory. It is thought that these three model system need not be limited to semistiff polymer, though they have been proposed on the basis of the results from PEEK. In fact, it is seem to be hard to suggest the totally different model with above

three types.

We observed a little different results in melting process of isothermally crystallized PBS during heat scan comparing to that of other semicrystalline polymers. So in this paper, we tried to interpret the multiple endotherms of PBS on the basis of all the possible models, by using some technique with DSC.

2. Experimentals

2.1 Source of materials

PBS chip was obtained from Jeil synthetics Inc. The reported Mn and Mw are 15,000 and 33,200, respectively. It is known that the T_g is ca, -30℃ and T_m is about 114℃. PBS was recrystallized from 1wt% o-dichlorobenzene solutions so as to remove the impurities. Recrystallized PBS was filtered and dried for 3 days at room temperature under vaccum. Dried PBS was melted at 150℃ for 5 min in the hot press with the pressure of 2000 psi, and then quenched in the ice water. Quenched PBS film cut into small slice about 5~6 mg which is used for thermal experiments in the DSC and into the slices about 1×2cm for WAXD experiments.

2.2 Thermal analysis and X-ray measurement

Differential scanning calorimetry was carried out for most samples in a Perkin-Elmer DSC 7. All thermal experiments in DSC were done in a nitrogen atmosphere to prevent oxidation of the specimen. The sample were quickly heated to 150℃, held for 5 min to destroy anisotropy, and then cooled to the selected crystallization temperature at rate of 200℃/min. After isothermal crystallization is completely finished, i.e., there is no more changes of heat flow, then the crystallized sample was quenched to 10℃ at a rate of 200℃/min. It took about 2 min to complete the isothermal crystallization at 70℃ and about 15 min at 85℃, 30 min at 90℃, respectively. More than 2 h was needed to complete the crystallization at 100℃. And, at 105℃ , it took more than 4 h(see Table 1).

The amorphous state sample for cold crystallization were prepared in DSC by rapid cooling(-200℃/min) to -100℃, from the melt(150℃ for 5 min). And this quenched sample was heated to 10℃ at a rate of 200℃/min, holding at 10℃ for 10 min and the heat scanning was performed.

In the all heat scanning experiments, a 10℃/min scan rate was selected unless otherwise indicated. Melting points were calibrated by scanning standard melting point substances, Indium and Zinc, at the selected rate.

In order to prepare the PBS film for X-ray scattering experiments, melt and cold crystallization were conducted in the oil bath as the same procedure as used in the DSC. WAXD measurment were carried out, using Cukα radiation(Rigaku Denki

RAD-C) operated at 35 kv and 40 mA.

2.3 PBS single crystals

Single crystals of PBS were grown from a 0.5 wt% 0 - dichlorobenzene solution. at the temperature of 30, 39, 48, 52, 57 and 62℃, respectively. The time for growing of single depended on the temperature, increasing from 1 h to 36 h as the crystallization temperature increas from 30℃ to 65℃. Single crystals in solution were filtered and made into mat form. Then the single crystal mat were dried at room temperature for 24 h prior to DSC measurement.

3. Results and Discussion

The melting behaviour of isothermally crystallized poly(butylene succinate)(PBS) has been investigated using differential scanning calorimetry (DSC) and wide angle X-ray scattering. At the crystallization temperature under 80℃, each sample usually showed two endotherms (low temperature endotherm T_{m1} and high temperature endotherm T_{m2}) and one exotherm, T_{ex} (Table 1).

Table 1. PeaK Temperatures (T_{m1},T_{m1}',T_{ex},T_{m2}, respectively) for isothermaly melt- and cold-crystallized PBS

T_c(℃)	Time(min)	T_{m1}(℃)	T_{m1}'(℃)	T_{ex}(℃)	T_{m2}(℃)
		Cold-crystalllized PBS			
10	10	42	-	85	112.6
		Melt-crystallized PBS			
15	-	-	-	84.4	112.5
35	-	-	-	90.1	112.0
65	0.8	67.6	-	92.9	112.0
70	2	74.0	-	94.4	112.6
75	8	79.1	-	96.9	112.7
80	15	84.0	98.0	100.5	113.1
85	20	88.8	100.9	103.0	112.0
90	30	94.0	104.7	107.4	113.4
95	60	97.2	107.3	-	115.0
100	130	-	111.4	-	114.8
107	250	-	115.8	-	-
115	500	-	121.3	-	-

temperature depending on crystallization temperature T_c. In the rage of T_c from 80℃ to 100℃, new endotherm (middle endotherm T_{m1}'), which started to developed at the position just before the exotherms, grow in magnitude and shifted to higher temperature with T_c. From the results of the melting peak vs. crystallization temperature plot (Figure 1), it was suggested that this new developed endotherms was corresponded to the melt of original crystallites and the high endotherms to the melt of recrystallzied one. As the DSC heating rate increased, the peak temperature of the low and middle endotherms increased and that of high endotherm decreased, indicating that the low endotherm was due to the original crystallite as well as the middle endotherm. As for the origin of the low endotherm, it was observed in direct heating technique that the low endotherm started to develop at the last stage of the growth of the middle endotherm. This means that the low endotherm was attributed to the secondary population of crystallite. When the crystallization temperature was so high that the probability of forming secondary population was low, only one melt endotherm was observed, whose temperature moves to higher with T_c. Consequently, in the heating scan of PBS, the melting behaviour due to morphologically two kinds of crystallite and due to the melting and recrystallization were observed simultaneously. From the results of PBS and that of poly(ethylene),

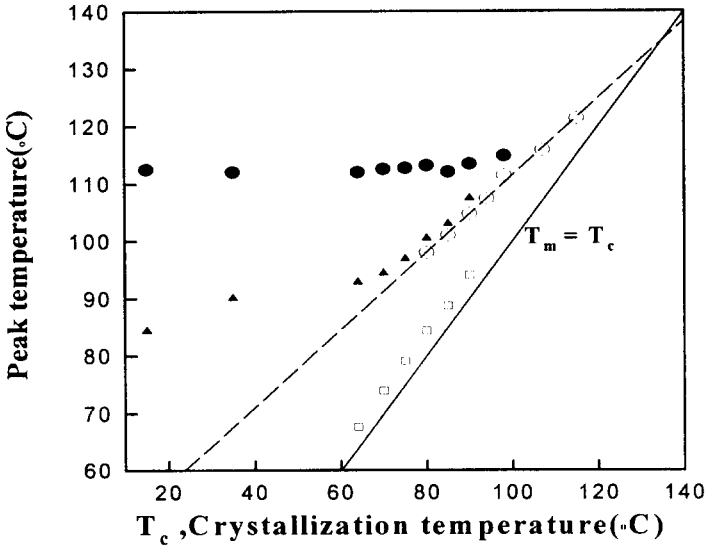

Figure 10. Peak temperature (at 10℃/min) of PBS crystallized from the melt vs. crystallization temperature: □; T_{m1}, ○; T_{m1}', ▲; T_{cx}, ●; T_{m2}. Solid line is for $T_m = T_c$.

poly(ethylene terephthalate) and poly(ether ether ketone) reported by others, we suggested that the multiple melting characters of semicrystalline polymers depend on the rate of recrystallization and the DSC heating rate.

4. Conclusion

Isothermally crystallized PBS from the melt has shown three of four peaks during DSC scans, depending on crystallization temperature, T_c.

In the cold-crystallized sample, the melt thermogram reveals three characteristic peak; low endotherm (T_{m1}) at 42℃ which was attributed to the melt of original crystallites, broad exotherms (T_{ex}) at around 85℃ which occurred from recrystallization and large high endotherms (T_{m2}) of melting of recrystallized crystallites.

The almost samples crystallized in the T_c range from 15℃ to 75℃ showed three characteristic peaks whose origin is similar to the cold crystallized one. The maximal position of T_{m1} shifted to higher temperature as T_c increase, while the T_{m2} was almost constant regardless of T_c. As the crystal size and degree of perfectness determined from the value of 1/A, showed increase trends depending on the T_c, the dependence of the low melt endotherm, T_{m1}, on T_c could be one of the evidences that T_{m1} is due to original crystallite.

The PBS crystallized at the T_c range form 80 to 100℃ showed three melt-endothermic peaks; T_{m1} which increased parallel to the increasement of T_c, T_{m1}' which was newly developed at the T_c = 80℃ increasing with T_c, and T_{m2} which is independent on T_c.

From the results of melting temperature vs. T_c, it was identified that T_{m1}' is attributed to the melt of original crystallites, and T_{m2} is due to the melt of recrystallized one. It was observed in the DSC result of PBS single crystals, that the low and high endotherms were corresponded to T_{m1}' and T_{m2} in melt-crystallized PBS, respectively.

The origin of T_{m1} was investigated by direct heating scan from crystallization temperature. As T_{m1} was developed at the second half of T_{m2} growth, T_{m1} could be due to the melt of the crystallites comprised of relatively low molecular weight chains which was excused during main crystallization like as studied in PE.

Consequently, in the PBS melting behaviour, the evidence of two kinds population of lamellae and of melt and recrystallization are observed, simultaneously. We thought that whether the melt and recrystallization phenomenon during DSC scans can be observed or not depends upon the rate of recrystallization during heating and the heating rate of DSC.

5. References

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