Copolyesters. VII. Thermal Transitions of Poly(butylene terephthalate-co-isophthalate-co-adipate)s

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SYNOPSIS

The copolyesters of 1,4-butanediol, terephthalic acid, isophthalic acid, and adipic acid with different compositions were prepared by melt polycondensation. The intrinsic viscosity of the copolyesters was controlled to be about 0.7–1.0 dL/g. Their second-run thermal properties were determined by DSC. The composition was found to be a major factor in the determination of the thermal transitions. The effect of the composition on the glass transition temperature and melt transition temperature was interesting. The glass transition temperature was found to be dependent mainly on the content of adipic acid. As the content of adipic acid increased, the glass transition decreased. When the content of terephthalic acid was not less than 35 mol % based on the total diacid monomers, the melting temperature was dependent mainly on the content of terephthalic acid and increased with increase of the content of terephthalic acid. When the content of terephthalic acid was less than 35 mol %, the melt temperature of the copolyesters did not follow a simple rule. However, the effect of the composition on their melting enthalpy showed no simple trend. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

The performance of a hot melt adhesive can be controlled by its thermal transitions including glass transition temperature (T_g), melting temperature (T_m), and melting enthalpy.[1,2] A lower T_g ameliorates flexibility and thus gives better low-temperature performance. A higher T_m increases the heat resistance, but always gives a higher melt viscosity, which will influence the processability. A higher melting enthalpy improves the heat resistance and the lap shear strength, but may give poorer adhesion.

The copolyesters of 1,4-butanediol and two different diacids have been considered to be used as hot melt adhesives.[2-8] The thermal transitions can be controlled by the chemical composition to some extent. However, it will be more flexible to incorporate a third diacid component to regulate the properties. Based on this observation, the copolyesters of 1,4-butanediol, terephthalic acid, isophthalic acid, and adipic acid have been used as hot melt adhesives.[9-13] In our laboratory, some poly(butylene terephthalate-co-isophthalate-co-adipate)s with a molar composition of 1,4-butanediol : terephthalic acid : isophthalic acid : adipic acid = 1 : 0.45 : 0.30 : 0.25 were prepared as hot melt adhesives.[14] These copolyesters were designed to have a T_m of about 110°C to fit a typical hot melt gun for the shoe sole application. In the screening of the suitable copolyesters, we also found that the T_g and the melting enthalpy were also important in determining their performance in addition to the T_m.

There are many different applications for copolyester-type hot melt adhesives. To optimize the performance for different applications, it is important to understand the factors influencing the thermal transitions of the copolyesters. In this article, various poly(butylene terephthalate-co-isophthalate-co-adipate)s with a wide composition range were prepared. Their thermal transitions were determined to investigate the effect of the composition.

EXPERIMENTAL

The homopolyesters and copolyesters were prepared by a typical melt polycondensation method as described previously.[14] The intrinsic viscosity of each copolyester was controlled within 0.7–1.0 dL/g by the reaction condition according to our experience. The samples were heated to 250°C and then cooled to −100°C at a cooling rate of 10°C/min so that the thermal history would be similar. Afterward, the thermal transitions were determined by a DuPont 910 DSC at a heating rate of 10°C/min under nitrogen. The midpoint of the inflection of the DSC heating curves was taken as the T_g, the peak temperature of the melting endotherm was taken as the T_m, and the melting enthalpy was determined from the area of the endothermic peak by comparing with that of indium (melting enthalpy = 6.8 cal/g).

RESULTS AND DISCUSSION

Three homopolyesters, six poly(butylene terephthalate-co-isophthalate)s, six poly(butylene terephthalate-co-adipate)s, six poly(butylene isophthalate-co-adipate)s, and 38 poly(butylene terephthalate-co-isophthalate-co-adipate)s were prepared. The compositions of the copolyesters are listed in Table I and noted in mol % of terephthalic acid (TPA), isophthalic acid (IPA), and adipic acid (AA) based on the total concentration of diacid monomers.

Typical DSC heating curves of the copolyesters are shown in Figure 1. The measured T_g, T_m, and melting enthalpy (ΔH_m) of the polyesters and copolyesters are listed in Table I.

Glass Transition Temperature

In general, the T_g of the copolyesters would be affected by their composition, chemical structure, and molecular weight. Due to the transesterification reaction taking place in melt polycondensation, the copolyesters have a random structure. The chemical structure of copolymers can be characterized by the degree of randomness.[15] For completely random copolymers, the degree of randomness is equal to 1; for block copolymers, the degree of randomness is close to 0; and the alternative copolymers show a degree of randomness of 2. Some of the copolyesters showed a degree of randomness of about 1 and were, thus, random copolymers based on the proton NMR analyses as described in a previous article.[16] The intrinsic viscosity of the copolyesters lays between
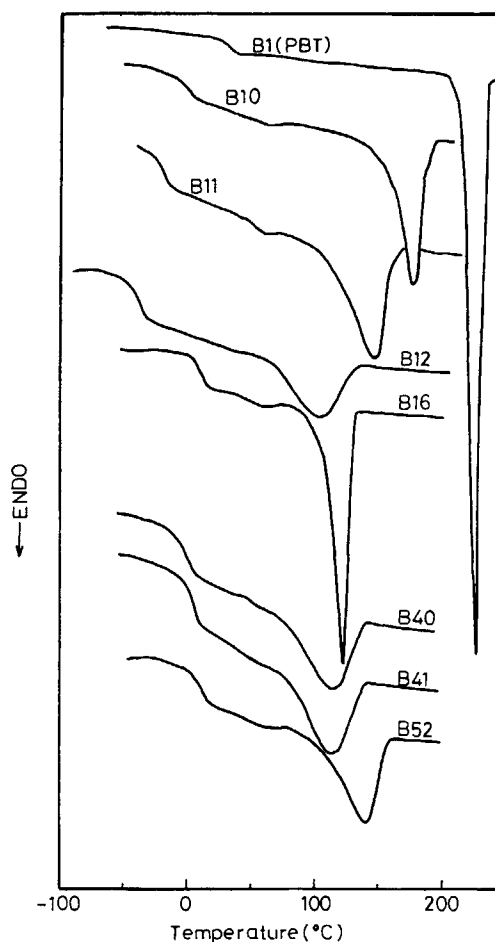

Figure 1 Heat flow diagrams of some copolyesters.

0.7 and 1.0 dL/g so that they will exhibit proper properties such as enough lap shear strength for the use as hot melt adhesives.[14] In this range of intrinsic viscosity, the variation in molecular weight would not greatly affect the T_g of the copolyesters, namely, less than 5°C.[14] Thus, the chemical composition would be the major factor affecting the T_g of the copolyesters.

The T_g's of poly(butylene terephthalate) (PBT), poly(butylene isophthalate) (PBI), and poly(butylene adipate) (PBA) were found to be 31, 18, and −50°C, respectively. As shown in Table I, the T_g of poly(butylene terephthalate-co-isophthalate)s was between those of PBT and PBI and showed a decreasing trend as the IPA content increased. For poly(butylene terephthalate-co-adipate)s and poly(butylene isophthalate-co-adipate)s, the T_g decreased considerably as the AA content increased. Overall, the T_g of the copolyesters of 1,4-butanediol and two diacids increased as the content of the more rigid unit increased, as expected.

Table I   The Composition, Glass Transition Temperature (T_g), Melting Temperature (T_m), and Melting Enthalpy (ΔH_m) of the Copolyesters

Batch	TPA	IPA	AA	T_g (°C)	T_m (°C)	ΔH_m (cal/g)	Batch	TPA	IPA	AA	T_g (°C)	T_m (°C)	ΔH_m (cal/g)
1	100	0	0	31	227	12.6	31	35	45	20	5	89	0.7
2	85	15	0	28	201	10.0	32	40	20	40	-21	99	4.0
3	70	30	0	24	174	6.7	33	40	25	35	-17	101	4.7
4	55	45	0	24	141	4.4	34	40	30	30	-10	101	3.3
5	40	60	0	21	105	1.1	35	40	35	25	-9	104	4.0
6	25	75	0	22	110	4.5	36	40	40	20	6	104	3.2
7	15	85	0	18	124	6.9	37	40	45	15	8	98	2.7
8	0	0	100	-50	62	19.8	38	45	20	35	-14	112	4.1
9	85	0	15	14	204	8.8	39	45	25	30	-9	112	4.1
10	70	0	30	-1	176	8.2	40	45	30	25	-4	113	4.4
11	55	0	45	-21	144	6.8	41	45	35	20	4	110	4.8
12	40	0	60	-39	98	5.3	42	45	40	15	7	114	5.2
13	25	0	75	-44	42	8.0	43	45	45	10	14	109	5.3
14	15	0	85	-47	47	15.0	44	50	20	30	-7	128	5.5
15	0	100	0	17	147	9.4	45	50	25	25	-3	128	4.5
16	0	85	15	8	120	7.6	46	50	30	20	3	130	5.3
17	0	70	30	-12	97	5.8	47	50	35	15	11	130	5.2
18	0	55	45	-26	66	4.8	48	50	40	10	11	128	4.1
19	0	40	60	-39	48	1.9	49	55	15	30	-9	144	4.4
20	0	25	75	-45	27	6.8	50	55	20	25	-3	142	4.8
21	0	15	85	-45	45	11.5	51	55	25	20	7	143	4.6
22	5	90	5	17	125	7.8	52	55	30	15	7	141	4.7
23	10	15	75	-40	40	7.6	53	55	35	10	13	144	4.9
24	10	30	60	-36	50	1.7	54	60	20	20	4	155	5.3
25	10	45	45	-26	54	2.7	55	60	25	15	10	154	5.4
26	35	20	45	-28	87	4.2	56	60	30	10	10	155	4.7
27	35	25	40	-24	90	4.2	57	65	20	15	9	165	5.0
28	35	30	35	-13	92	1.9	58	65	25	10	17	163	5.6
29	35	35	30	-9	87	1.2	59	70	15	15	8	179	6.0
30	35	40	25	-3	88	1.1							

For the copolyesters of 1,4-butanediol and three diacids, their T_g also increased as the content of the more rigid units increased, as shown in Table I. The T_g of PBT (31°C) was not considerably different from that of PBI (18°C), and the T_g of PBA (−50°C) was considerably lower than those of PBT and PBI. Thus, the AA content would be a major factor affecting the T_g of poly(butylene terephthalate-co-isophthalate-co-adipate)s. Based on this, the copolyesters with the same AA content were examined. The AA content of Batches 29, 34, 39, 44, and 49 was 30 mol %, and their T_g's were −9, −10, −9, −7, and −9°C, respectively. Although the contents of TPA and IPA were different, they showed a T_g close to −9°C. The variation in T_g was small. At an AA content of 20 mol %, Batches 31, 36, 41, 46, 51, and 54 showed T_g's of 5, 6, 4, 3, 7, and 4°C, respectively. The variation was also small. Within the composition range of the poly(butylene tere-phthalate-co-isophthalate-co-adipate)s that we prepared, the T_g was mainly dependent on the AA content. At a given AA content, the T_g's of the copolyesters were averaged. It was found that the difference in T_g of a measured value from the average was not greater than 3°C for most cases. A plot of the average T_g as a function of the composition is shown in Figure 2, wherein the number of a straight line with solid circles indicates the average T_g, and the number of the open circles indicates the measured T_g of other polyesters. This average T_g was taken as a value for discussion.

As shown in Figure 2, the T_g of the poly(butylene terephthalate-co-isophthalate-co-adipate)s was predictable from the AA content. As the AA content increased, the T_g decreased. However, a significant deviation from the value based on the rule of mixture was observed. When the AA content was increased from 15 to 30 mol %, the T_g was decreased from 9
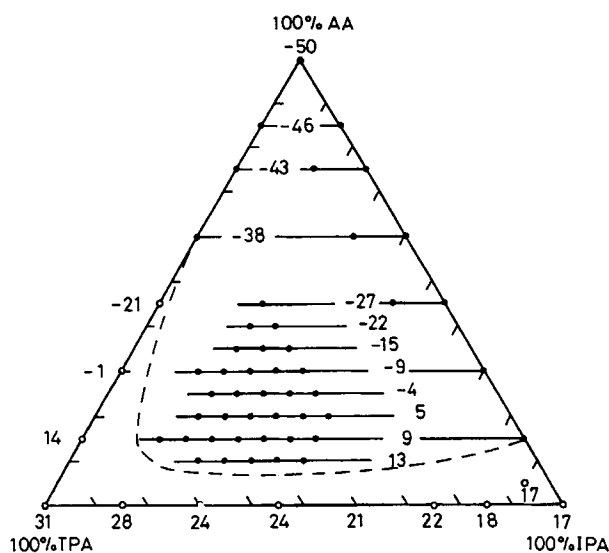
Figure 2 Effect of the copolyester composition on the T_g (the number indicates the T_g in °C).

to −9°C. A decrease in T_g by 18°C was observed. When the AA content was increased from 45 to 60 mol %, a decrease in T_g by 18°C from −9 to −27°C was also observed. However, the decrease in T_g was only 4°C from −46 to −50°C) when the AA content was increased from 85 to 100 mol %. Thus, at a high AA content, the T_g of the copolyesters decreased to a lesser extent as the AA content increased.

For the poly(butylene terephthalate-co-adipate)s and the poly(butylene isophthalate-co-adipate)s, the T_g's of some copolyesters fell above the straight lines. However, when the AA content of the poly(butylene terephthalate-co-adipate)s was 45 mol % or lower, they showed a T_g higher than that of the corresponding poly(butylene terephthalate-co-isophthalate-co-adipate)s at the same AA content. This would be due to the more rigid nature of the TPA unit. In Figure 2, the composition range wherein the T_g can be predicted from the AA content is indicated by the dashed line.

Melting Temperatures

The T_m of the copolyesters would also be affected by their composition, chemical structure, and molecular weight. In a previous article,[17] the block copolymers of poly(butylene terephthalate-co-adipate)s with a different degree of randomness and thus different sequence length were prepared. When the degree of randomness was less than 0.3, the block copolyesters showed two T_m's, corresponding to the melting of the PBT and PBA segments, respectively.

For the copolyesters with a degree of randomness between 0.8 and 1.0, the copolyesters showed only one T_m. The copolyesters in this paper would be random copolymers with a degree of randomness of about 1, and they would show only one T_m. It has been also shown that the molecular weight had little effect on the T_m of some poly(butylene terephthalate-co-isophthalate-co-adipate)s.[14] Thus, the composition would be a major factor in determination of the T_m of the copolyesters.

The T_m's of PBT, PBI, and PBA were found to be 227, 147, and 62°C, respectively. The melting behavior of the poly(butylene terephthalate-co-isophthalate)s showed a minimum T_m at an IPA content of about 60 mol %. The melting behavior of the poly(butylene terephthalate-co-adipate)s showed a minimum T_m at an AA content of about 60 mol %. The melting behavior of the poly(butylene isophthalate-co-adipate)s also showed a minimum T_m at an AA content of about 75 mol %. Therefore, the effect of the composition on the T_m of the poly(butylene terephthalate-co-isophthalate-co-adipate)s looks complex at first glance. However, a simple rule was found to apply in a wide composition range.

When the TPA content was not less than 35 mol %, the T_m of poly(butylene terephthalate-co-isophthalate-co-adipate)s was found to be dependent mainly on the TPA content. The TPA content of Batches 32–37 was 40 mol %, and their T_m's were 99, 101, 101, 104, 104, and 98°C, respectively. They exhibit a T_m close to 101°C. The TPA content of Batches 5 and 12, two copolyesters of 1,4-butanediol with TPA and IPA or AA, was 40 mol %, and their T_m's were 105 and 98°C, respectively, a value that is close to the average T_m (101°C). At a TPA content of 55 mol %, Batches 4, 11, and 49–53 showed T_m's of 141, 144, 144, 142, 143, 141, and 144°C, respectively. The variation in T_m was also small. For most cases, the difference in T_m of a measured value from the average was not greater than 3°C. A plot of the average T_m as a function of the composition is shown in Figure 3, wherein the number of a straight line with solid circles indicates the average T_m, and the number of the open circles indicates the measured T_m of other polyesters with a TPA content less than 30 mol %.

As shown in Figure 3, when the TPA content was not less than 35 mol %, the average T_m of the poly(butylene terephthalate-co-isophthalate-co-adipate)s was predictable from the TPA content. The T_m increased as the TPA content increased. However, the T_m's of the copolyesters with a TPA content less than 35 mol % showed no obvious trend.
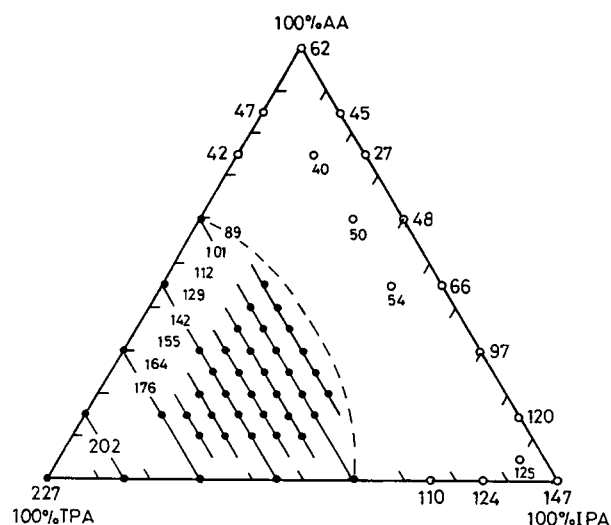
Figure 3 Effect of the copolyester composition on the T_m (the number indicates the T_m in °C).

Although the T_m's of PBT, PBI, and PBA differed significantly, the trend of the T_m's of the poly(butylene terephthalate-co-isophthalate-co-adipate)s followed a simple rule depending only on the TPA content when the TPA content was not less than 35 mol %. A deeper look into the effect of the composition on the T_m's of the poly(butylene terephthalate-co-isophthalate)s and the poly(butylene terephthalate-co-adipate)s can explain this. Figure 4 shows the effect of the TPA content on the T_m's of the poly(butylene terephthalate-co-isophthalate)s and poly(butylene terephthalate-co-adipate)s. Considering the effect of the incorporation of IPA or AA into the main chain of PBT, the presence of TPA and AA units decreased the T_m of PBT after copolymerization. Obviously, when the TPA content was greater than 40 mol %, IPA and AA units decreased the T_m of PBT almost to the same extent. Thus, in the poly(butylene terephthalate-co-isophthalate-co-adipate)s, the combination of IPA and AA units also decreased the T_m of PBT to the same extent. As a result, the effect of the TPA content on the T_m of poly(butylene terephthalate-co-isophthalate-co-adipate)s fell into the same trends, as the TPA content was not less than 35 mol %. When the TPA content was less than 35 mol %, the effect of the IPA and/or AA units on the T_m played an important role, and no simple trend in T_m was observed.

In Figure 3, the composition range in which the T_m of the copolyesters can be predicted from the TPA content is indicated by the dashed line. This predictable composition range is narrower than that of the T_g. However, there is an overlap range. From

the data given in Figures 2 and 3, it is possible to design a copolyester hot melt adhesive with suitable T_m and T_g.

Melting Enthalpy

As shown in Table I, the three homopolyesters showed a high melting enthalpy greater than 9 cal/g. After copolymerization, the melt transition heat was decreased. The melt transition heat of each poly(butylene terephthalate-co-adipate) was greater than 5 cal/g. However, at a specific composition, a poly(butylene terephthalate-co-isophthalate) and a poly(butylene isophthalate-co-adipate) showed a very low melting enthalpy. The melting enthalpy of the poly(butylene terephthalate-co-isophthalate) with an IPA content of 60 mol % was only 1.1 cal/g and that of the poly(butylene isophthalate-co-adipate) with an AA content of 60 mol % was 1.9 cal/g. The presence of the IPA meta-substituted unit significantly hinders the crystallization of the copolyesters. This justify the very low melting enthalpy observed for the latter two series of copolyesters at some compositions.

The melting enthalpy of the poly(butylene terephthalate-co-isophthalate-co-adipate)s disclosed considerable variations. Considering Batches 26–31,
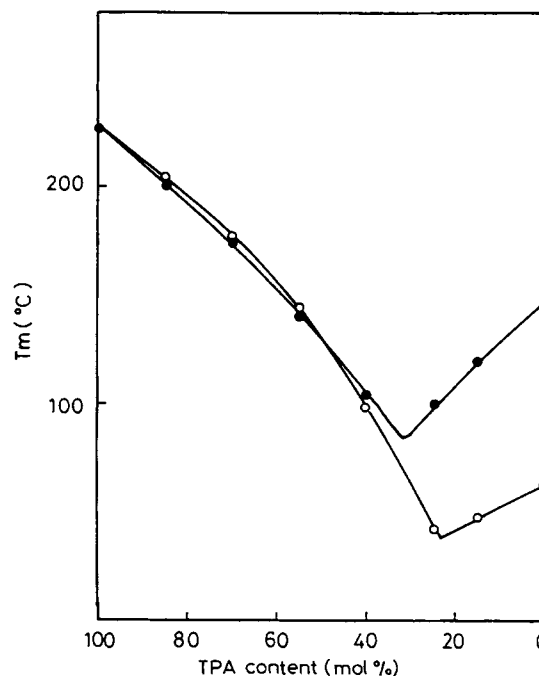

Figure 4 The effect of the TPA content on the T_m of the poly(butylene terephthalate-co-isophthalate)s (solid circles) and the poly(butylene terephthalate-co-adipate)s (open circles).

where the TPA content was 35 mol %, the melting enthalpy was found to be from 4.2 to 0.7 cal/g. For these six copolyesters, the melting enthalpy decreased as the IPA content increased. This should be due to the presence of the IPA unit, which might significantly hinder the crystallization at some compositions. When the TPA content was 40 mol %, this effect decreased and the melt transition heat of Batches 32–37 was in the range of 2.7–4.7 cal/g. When the TPA content was between 45 and 70 mol % (Batches 38–59), the melting enthalpy of the poly(butylene terephthalate-co-isophthalate-co-adipate)s fell into the range of 4–6 cal/g. However, no simple trend was observed for the effect of the composition on their melting enthalpy.

The homopolyesters showed a sharp melting peak. After copolymerization, the melting peak became broader as shown in Figure 1 for some copolyesters. When the TPA content was greater than 40 mol %, the melting peak of the poly(butylene terephthalate-co-isophthalate-co-adipate)s was as broad as that of the poly(butylene terephthalate-co-adipate)s at a given TPA content. This followed a similar trend as the effect of the TPA content on the T_m.

CONCLUSION

The effect of the composition on the thermal transitions of the random poly(butylene terephthalate-co-isophthalate-co-adipate)s with similar molecular weight was studied. The T_g was found to be dependent mainly on the AA content and decreased with increasing AA content. At a TPA content not less than 35 mol %, the T_m was dependent mainly on the TPA content, and the T_m increased with the increase of the TPA content. When the TPA content was less than 35 mol %, the T_m of the copolyesters did not follow a simple rule. However, the effect of the composition on their melting enthalpy showed no simple trend. Based on transition temperature variations, it is possible to design a copolyester hot melt adhesive with desirable T_m and T_g by varying the composition within a wide range.

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