

Thermal Properties of Unfilled Cast Cured Sheets of Polyesters Based on Bisacid A2

R. S. LENK, *Polytechnic of the South Bank, London, SE1 0AA, England*

Synopsis

The synthesis of bisacid A2 in a high state of purity, the preparation of unsaturated copolyesters therefrom, the preparation of solutions of the latter in suitable monomers, followed by casting of those solutions after addition of catalysts and curing of the material to obtain crosslinked polyester sheet, has been described in earlier communications.¹⁻³ This paper deals with the heat distortion temperatures⁴ and the (modified) Vicat softening points⁵ of the cast sheets of various copolyesters at various monomer contents.

INTRODUCTION

The heat distortion temperatures (HDT) of maleic/phthalic and fumaric/phthalic polyesters were reported by Parker and Moffett⁶ at a fiber stress of 264 psi ($1.82 \times 10^6 \text{ Nm}^{-2}$) and were stated to be about 40°C and 70°C, respectively. The present work is based on maleic copolyesters only, but the saturated acids were either mixtures of phthalic and bisacid A2 or bisacid A2 alone. The monomer used by Parker and Moffett was styrene, while in the present investigation methyl methacrylate and equimolar mixtures of styrene/methyl methacrylate were also included. The effect of varying the monomer content is also investigated. The heat distortion temperatures are reported at both 0.010 in. and 0.100 in. deflection (2.54×10^{-4} and 2.54×10^{-3} m, respectively) in order to gain an insight into the rates of change of rigidity of the polyesters with temperature once they have reached a leathery condition. The difference between the two deflection points in terms of temperature is noted in separate columns of Tables I, II, and III.

Vicat softening points (VSP), extensively used in the characterization of thermoplastics, indicate the temperature at which a steel cylinder of 1-mm² cross-sectional area indents the specimen to a depth of 1 mm under a standard applied load of 1 kg at a heating rate of approximately 50°C per hr. The determination of VSP is described in detail in ref. 5. With thermosetting materials, it is not usual to determine VSPs because an indentation of 1 mm is not usually attainable; but it has been known to be used for phenolic moldings at 0.1 mm indentation. In the present work, the "tenth-Vicat" figures and in some cases "twentieth-Vicat" figures have been determined, using the standard load but a constant heating rate of

TABLE I
Heat Distortion Temperatures of Maleic/(Bisacid A2-Phthalic) Copolyesters^a

Code no.	Bisacid A2/phthalic, molar ratio	Acid value	No. of unsatura- tion points per 1000 MW	30% Monomer		35% Monomer		45% Monomer		
				0.010 in.	Differ- ence	0.010 in.	Differ- ence	0.010 in.	Differ- ence	
				deflec- tion	deflec- tion	deflec- tion	deflec- tion	deflec- tion	deflec- tion	
6.2	0	9.5	2.77	68	91	23	—	76	97	21
6.1	0	9.0	2.77	—	—	—	89	105	—	—
6.1	MMA	9.0	2.77	—	—	—	47	54	—	—
9	0.143	7.7	2.59	86	100	14	84	104	—	—
8	0.333	9.6	2.47	59	77	18	—	—	—	—
7	0.6	10.9	2.42	62	80	18	—	—	—	—
4.2	7	13.3	1.94	71	83	12	—	—	—	—

^aMolar ratio of maleic to combined saturated acids constant at 1:1. Phthalic/bisacid A2 molar ratios variable (Monomer = styrene, unless otherwise indicated. MMA = methyl methacrylate). Acid Values all about 10.

TABLE II
Heat Distortion Temperatures of Maleic/Bisacid A-2 Copolyesters at Various Molar Ratios of Unsaturated/Saturated Acids^a

Code no.	Maleic/ bisacid A2 ratio	No. of unsatu- ration points per 1000 MW	30% Monomer		35% Monomer		45% Monomer		50% Monomer		55% Monomer	
			in. deflec- tion	in. deflec- tion	in. deflec- tion	in. deflec- tion	in. deflec- tion	in. deflec- tion	in. deflec- tion	in. deflec- tion	in. deflec- tion	in. deflec- tion
17	1	1.86	77	87	10	78	90	12	—	—	—	—
17.1	1	1.86	—	—	—	—	—	—	69	84	15	70
17.2	1	1.86	—	—	—	—	—	—	71	86	15	69
16	1.08	1.97	74	88	14	68	83	15	—	—	—	—
15	1.17	2.07	73	87	14	69	84	15	—	—	—	—
14	1.25	2.17	81	96	15	81	95	14	—	—	—	—
13	1.33	2.26	82	102	20	74	89	15	—	—	—	—
12	1.5	2.44	78	96	22	83	100	17	—	—	—	—
11	1.75	2.54	64	89	25	73	98	25	84	103	19	89
11 ST/MMA	1.75	2.54	—	—	—	—	—	—	75	89	14	80
10	2	2.85	89	106	17	84	99	15	95	110	15	—
10.2	2	2.85	—	—	—	—	—	—	96	108	12	93
20	3	3.52	—	—	—	—	—	—	104	130	26	104
21	3	3.52	—	—	—	—	—	—	102	130	28	103
19	4	3.97	—	—	—	—	—	—	105	131	28	102

^a Monomer = styrene, unless otherwise indicated (ST/MMA = equimolar mixture of styrene and methyl methacrylate). Acid values all about 10, except in code no. 21, where it was 23.5.

TABLE III
Heat Distortion Temperatures of Some Commercial Polyesters^a

Code	No. of unsaturation points per 1000 MW	31% Monomer			48% Monomer		
		0.010 in. deflection	0.100 in. deflection	Difference	0.010 in. deflection	0.100 in. deflection	Difference
		A	5.05		—	—	
B	5.05	—	—	—	93	111	18
C	5.05	—	—	—	100	114	14
D	2.77	58	80	22	—	—	—
E	2.77	61	82	21	—	—	—

^a Monomer = styrene. A: A polyester of bisphenol A glycol with maleic anhydride; styrene content 48%; acid value 11.8; made and cast by Scott Bader, Ltd., using a catalyst system with a very high amount of cobalt octoate accelerator. B: The same resin as A, also cast by Scott Bader, but using the usual quantities of peroxide/cobalt naphthenate catalyst system. C: The same resin and catalyst system as in B, but cast by the writer. D: An equimolar maleic/phthalic polyester of propylene glycol made by Scott Bader to a low degree of condensation (acid value 34), styrene content 31%; cast and cured by the manufacturers using the standard catalyst system. E: The identical resin as D, but cast and cured by the writer, using the same catalyst system.

120°C per hour (i.e., 2°C per minute) instead of the 50°C per hour stipulated in ref. 5.

RESULTS

Two sets of tables are given. Tables I, II, and III give heat distortion temperatures, and Tables IV, V, and VI give modified VSPs. Table I and IV cover copolyesters with equimolar ratio of maleic/saturated acids, but

TABLE IV
Tenth-Vicat Softening Points of Maleic/(Bisacid-Phthalic) Copolyesters^a

Code no.	Molar ratio of bisacid A2/phthalic	No. of unsaturated points per 1000 MW	30%	35%	45%
			Monomer	Monomer	Monomer
			1/10 VSP, °C	1/10 VSP, °C	1/10 VSP, °C
6.2	0	2.77	102	—	106 ^b
6.1	0	2.77	—	100	—
6.1 MMA	0	2.77	—	58	—
9	0.143	2.59	100	96	—
8	0.333	2.47	83	—	—
7	0.6	2.42	72	—	—
4.2	7	1.94	87	—	—

^a Molar ratio of maleic to combined saturated acids constant at 1:1. Phthalic/bisacid A2 molar ratios variable. (Monomer = styrene, unless otherwise indicated; MMA = methyl methacrylate). Acid values all about 10.

^b 1/20 VSP gave 101°C.

TABLE V
 Twentieth- and Tenth-Vicat Softening Points of Maleic/Bisacid A2 Copolyesters at Various Molar Ratios of Unsaturated/Saturated Acids^a

Code no.	Molar ratio of maleic/bisacid A2	No. of unsaturation points per 1000 MW	30% Monomer		35% Monomer		45% Monomer		50% Monomer		55% Monomer	
			1/10 VSP, °C	1/10 VSP, °C	1/10 VSP, °C	1/10 VSP, °C	1/20 VSP, °C	1/10 VSP, °C	1/20 VSP, °C	1/10 VSP, °C	1/20 VSP, °C	1/10 VSP, °C
17	1	1.86	93	88	—	—	—	—	—	—	—	—
17.1	1	1.86	—	—	—	91	—	—	—	90	—	91
17.2	1	1.86	—	—	—	90	—	—	—	90	—	93
16	1.08	1.97	87	85	—	—	—	—	—	—	—	—
15	1.17	2.07	83	86	—	—	—	—	—	—	—	—
14	1.25	2.17	91	94	—	—	—	—	—	—	—	—
13	1.33	2.26	100	95	—	—	—	—	—	—	—	—
12	1.5	2.44	102	96	—	—	—	—	—	—	—	—
11	1.75	2.54	93	101	—	—	—	—	—	—	—	—
11 ST/MMA	1.75	2.54	—	—	—	—	—	—	—	—	—	—
10	2	2.85	115	84	—	116	—	—	—	—	—	—
10.2	2	2.85	—	—	105	112	—	—	—	98	—	98
20	3	3.52	—	—	126	>150 (1) ^b	121	>150 (4)	119	>164 (6)	—	—
21	3	3.52	—	—	132	>150 (2)	128	>160	—	>160	—	113
19	4	3.97	—	—	122	>150 (3)	124	>150 (5)	119	>164 (7)	—	—

^a Monomer = styrene, unless otherwise indicated (ST/MMA = equimolar mixture of styrene and methyl methacrylate). Acid values all about 10, except in no. 21, where it was 23.5.

^b The following data lists the maximum indentation, mm, and the temperature at which it was reached. (1) 0.06 at 140°C; (2) 0.06 at 150°C; (3) 0.07 at 143°C; (4) 0.08 at 140°C; (5) 0.07 at 143°C; (6) 0.09 at 133°C; (7) 0.09 at 142°C.

TABLE VI
Twentieth- and Tenth-Vicat Softening Points of Some Commercial Polyesters*

Code	No. of unsaturation points per 1000 MW	31% Styrene		48% Styrene	
		1/10 VSP, °C	1/20 VSP, °C	1/10 VSP, °C	1/10 VSP, °C
A	5.05	—	—	—	127
B	5.05	—	108	—	118
C	5.05	—	116	—	122
D	2.77	82	—	—	—
E	2.77	84	—	—	—

* Monomer = styrene. For key to code letters see Table III.

with the saturated acids consisting of various molar ratios of phthalic/bisacid A2. Tables II and V deal with copolyesters of maleic and bisacid A2 only, but at varying molar ratios of maleic/bisacid A2, thus covering a wide range of potential crosslink density as expressed by the number of unsaturation points per 1000 molecular weight. Tables III and VI report results on some commercial polyesters cast by the resin manufacturers and by the author, and they thus afford a comparison of reproducibility of results in different laboratories. Tables I through VI also show the effect of varying monomer contents in cast, cured sheet based on otherwise identical solid polyesters.

The heat distortion temperature specimens were 3.06 ± 0.1 mm thick and were milled to give smooth, parallel, rectangular bars of 12.2 ± 0.1 mm width and not less than $11\frac{1}{2}$ cm length, the distance between supports being 10.16 cm.

DISCUSSION

Heat Distortion Temperatures

In the series containing phthalic acid, there is an indication that the heat distortion temperature (HDT) rises slightly with increasing bisacid A2/phthalic acid ratio, but appreciable changes in acid value (i.e., in the degree of condensation or the chain length of the polyester chains prior to crosslinkage) also seem to be reflected. Thus, resin 9, which had a somewhat lower acid value than standard (7.7 as against the normal 10 ± 1), had a relatively high HDT in spite of quite a low bisacid A2 content, while resin 4.2, with a very high bisacid A2 content, had an HDT which was not particularly high, considering its composition, probably because resin 4.2 had a rather higher acid value (13.3) compared to the normal run of resins. It should, however, be remembered, that an increase in bisacid A2 also implies a lower crosslink density. If that acid raises HDT, then the lower number of unsaturation points per 1000 MW will tend to produce a compensating opposite effect. Substantial changes in monomer content did not seem to have a very strong influence on the HDT, but the type of monomer

used is evidently of the greatest importance, as shown by the figures appertaining to the styrene-crosslinked and the MMA-crosslinked resin 6.1 (a straight 1:1 maleic/phthalic resin). MMA-crosslinked resins have much the lower HDTs.

In the series containing bisacid A2 and maleic acid only (but at varying ratios), the indications are that an increasing maleic content tends to increase the HDT. This is to be expected in view of the implied increasing potential crosslink density, as indicated by the increasing number of unsaturation points per 1000 MW in the polyester chain prior to cure. It is also seen (nos. 10 and 11) that an increase in monomer content from 30–35% to 45–55% produces an increase in HDT, presumably owing to a more effective utilization of available crosslink sites with increasing monomer content. This would appear to reach a plateau at 45%, with no significant changes from 45% to 55%, a feature which is confirmed by all the data on resins that were cast at monomer contents within the latter range (17.1, 17.2, 10.2, 20, 21, and 19). MMA does not crosslink readily when bisacid A2 is a constituent of the system, but mixtures of styrene and MMA do crosslink, albeit tardily. The resulting HDT is, however, lower than that obtained from the same solid resin made into a casting solution with styrene alone. This is in line with observations made earlier. The effect of major differences in acid values at a very high maleic/bisacid A2 ratio was examined in resins 20 and 21, the former having an acid value of 10–12, the latter an acid value of 23.5. No significant difference was found, presumably because at high crosslink densities the molecular weight of the parent chain becomes relatively unimportant after cure. The repeats of 17 (17.1 and 17.2) were made because of insufficiency of material which prevented the casting of sheet at the higher monomer contents. The acid values were 10.1, 8.0, and 8.7, respectively, but resin 17.1 had been slightly overheated and was somewhat darker than resin 17.2. The effect of this is evidently not noticeable in the HDT results, which also proved to be highly reliable and reproducible.

The HDTs of the commercial resins quoted in Table III represent an exercise in the reproducibility of results of castings made on the same resins but in different laboratories, and good concordance was recorded. The rather special resin based on a bisphenol glycol/maleic system was included because of its obvious structural relationship to maleic/bisacid A2 systems condensed with propylene glycol. The heat distortion points of the bisphenol glycol/maleic polyesters are of the same order as those of maleic/bisacid A2 systems with maleic/bisacid A2 ratios of 2 to 3 at comparable styrene contents. It should, however, be noted that the bisphenol glycol/maleic resins have a substantially higher number of potential crosslinkage sites (bisphenol glycol/maleic resin, 5.05; resins 20 and 21, 3.52; resin 19, 3.97 per 1000 MW). This shows that in the first of these resins the crosslinkage potential is far from being fully utilized, possibly as a result of unfavorable steric factors or the build-up of strains during cure. Comparing resins D and E (straight 1:1 maleic/phthalic copolyesters) with a similar

resin made by the writer (6.1 and 6.2 of Table I), it is seen that resin D and E have lower HDTs at comparable monomer contents; resins D and E have also substantially higher acid values (34 compared with 9 to 10 for resins 6.1 and 6.2), so that the differences, at lowish potential crosslink densities, are fully as expected. Very pronounced changes in the catalyst concentration (resin A as against resins B and C) do not appear to have any significant effect on the HDT.

Vicat Softening Points

Tenth-vicat softening points ($1/10$ VSP) provide useful data which do, on the whole, correlate quite well with HDT data. All the factors discussed under the previous heading are likewise applicable here. Some of the differences, e.g., the effect of differences in acid value in straight 1:1 maleic/phthalic polyesters (samples D and E, Table VI, compared with sample 6.2, Table IV), or the effect of introducing MMA as a monomer in place of styrene, are thrown into even sharper relief. The need for a $1/20$ VSP arises where very high maleic contents and high degrees of effective crosslinkage make it impossible to achieve an indentation of even as little as 0.1 mm at temperatures of up to 150°C or beyond (resins 20, 21, and 19 of Table V). The $1/20$ VSP was also recorded for the bisphenol glycol/maleic type polyesters, because of their high potential crosslink density. Again, this potential is evidently not effectively realized since the VSPs are substantially lower than those of resins 20, 21, and 19. The last three resins, with a much lower number of unsaturation points per 1000 MW, have extremely high VSPs ($1/10$ VSP > 150°C, $1/20$ VSP \sim 120°–130°C), while the values for the bisphenol glycol/maleic resins are around 120°C and 110°C, respectively, at $1/10$ and $1/20$ Vicat indentation depths.

SUMMARY

The HDT and $1/10$ and $1/20$ VSP of unfilled cast, cured polyester sheet specimens containing bisacid A2 were determined. A high crosslink density naturally tends to raise these temperatures. Increasing the bisacid A2 content in itself seems to raise these temperatures; but since this increase implies a decrease in crosslink density, the two effects tend to counterbalance each other. An increase in styrene content from 30–35% to 45–55% tends to raise the HDT and VSP, presumably as a result of more efficient utilization of crosslink potential, but plateaus are reached at 45–55%. A high acid value tends to reduce both HDT and VSP, except where the number of unsaturation points per 1000 MW is very high, say about 3.5. Replacement or partial replacement of styrene with methyl methacrylate causes a sharp drop in HDT and VSP.

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