

CHAPTER 6

THERMAL PROPERTIES

This chapter describes the thermal properties such as cure reaction behaviour, glass transition temperature (T_g), thermal degradation temperature and heat distortion temperature of epoxy, siliconized epoxy, bismaleimides (BMI-1, BMI-2, BMI-3 and BMI-4) modified epoxy and bismaleimides modified siliconized epoxy systems.

6.1 CURE REACTION BEHAVIOUR

The siloxane (HTPDMS) modification of epoxy resin in the presence of γ -APS proceeds in two steps. The first step involves the reaction between $-NH_2$ groups of γ -APS and oxirane rings of epoxy resin. From the DSC thermogram (Figure 6.1), it is evident that the reaction starts at $100^\circ C$ and reaches peak maximum at $120^\circ C$. Further, the reaction between $-OCH_2CH_3$ groups of γ -APS and the hydroxyl groups of HTPDMS also occurs simultaneously and is accelerated during degassing process. In the second step, the $-NH_2$ groups of DDM react with the remaining oxirane rings of epoxy resin. The epoxy-DDM reaction starts at $120^\circ C$ and reaches peak maximum at $167^\circ C$ (Figure 6.2). The large exotherm obtained for the epoxy-DDM system is due to the following reactions (i) oxirane ring opening reaction with active amine hydrogens of DDM (ii) autocatalytic reaction of oxirane ring with pendent hydroxyl groups of epoxy resin and hydroxyl groups formed during the reaction

(i) (Figure 6.3). Exotherm obtained for the reaction of epoxy resin with mixture of γ -APS and DDM shows unimodel behavior (Figure 2.4b). The exotherm starts at 70°C and reaches peak maximum at 165°C and it suggests that the reaction proceeds in a homogeneous path.

DSC thermograms of epoxy resin modified with 5%, 10% and 15% of bismaleimides BMI-1, BMI-2, BMI-3 and BMI-4 are presented in Figures 6.4, 6.5, 6.6 and 6.7 respectively. From Figures (6.4 - 6.7), it is observed that all the bismaleimides modified epoxy systems show unimodel reaction exotherm due to the presence of lower concentrations of bismaleimides. For all the bismaleimides incorporated systems, the reaction commences at 120°C. The peak maximum temperatures for 5%, 10% and 15% of BMI-1 incorporated systems are 169°C, 172°C and 175°C respectively (Figure 6.4), for BMI-2 incorporated systems are 173°C, 177°C and 179°C respectively (Figure 6.5), for the BMI-3 incorporated systems are 175°C 177°C and 180°C respectively (Figure 6.6) and for BMI-4 incorporated systems are 165°C, 163°C and 159°C respectively (Figure 6.7). The large exothermic peak obtained for the bismaleimides incorporated systems is due to the following reactions. (iii) Addition reaction of $-NH_2$ groups of DDM with double bonds of bismaleimides (Michael addition) and (iv) bismaleimides homopolymerization reaction in addition to reactions (i) and (ii) (Figure 6.3). Earlier, (Musto *et al.*, 1998) it was reported that the reaction (iv) is least possible due to requirement of higher activation energy (higher temperature) to initiate homopolymerization reaction of bismaleimides. For example the temperature required to start the homopolymerization reaction for BMI-1, BMI-2, BMI-3 and BMI-4 are 180°C, 202°C, 198°C and 227°C respectively (Figures 6.8 – 6.11). However, according to Musto *et al.* (1998) in the presence of epoxy resin, the same reaction (homopolymerization of BMI) starts at much lower temperature (120-140°C),

(Figures 3.17 – 3.20) because of the zwitter ion adduct formation between the oxirane ring and double bonds of bismaleimides. The slight increase in peak maximum temperature with increasing bismaleimides (BMI-1, BMI-2 and BMI-3) (Figures 6.4 – 6.6) concentration confirms the observation made by Musto *et al.* (1998), whereas the slight decrease in the peak maximum temperature with increase in BMI-4 concentration (Figure 6.7) indicates that the Michael addition reaction is predominant in the BMI-4 modified systems. Since homopolymerization reaction of BMI-4 requires high activation energy when compared to other bismaleimides, it occurs only at 227°C (Figure 3.20).

6.2 GLASS TRANSITION TEMPERATURE

6.2.1 Effect of siloxane

The glass transition temperature of epoxy and siliconized epoxy systems are presented in Table 6.1. The glass transition temperature obtained for epoxy-DDM system is 165°C (Figure 6.12a). Incorporation of HTPDMS into epoxy resin has no significant effect on Tg. However, a slight decreasing trend is observed with increasing HTPDMS concentration. For example, the Tg values for 5%, 10% and 15% HTPDMS modified systems are 163°C, 162°C and 160°C (Figure 6.12) respectively and this may be due to the presence of flexible and free rotation of –Si-O-Si- linkage. The single Tg value obtained for the siliconized epoxy systems indicates that the siloxane is chemically incorporated into the systems.

6.2.2 Effect of bismaleimides

The value of Tg (glass transition temperature) increases with introduction of BMI-1(Woo *et al.*, 1987; Kim *et al.*, 1995; Han *et al.*, 1998;

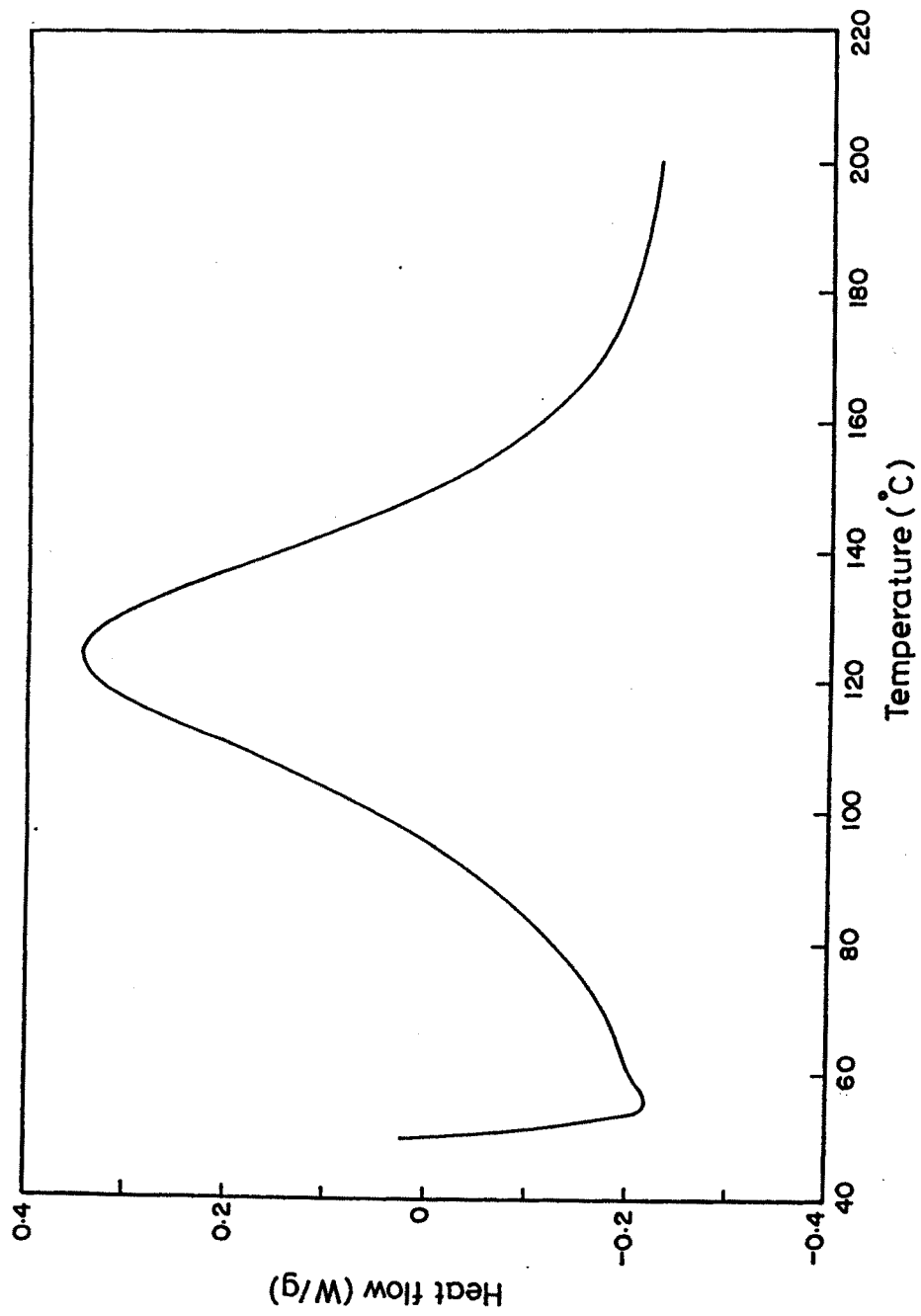


Figure 6.1 DSC thermogram of epoxy- γ -APS mixture during cure

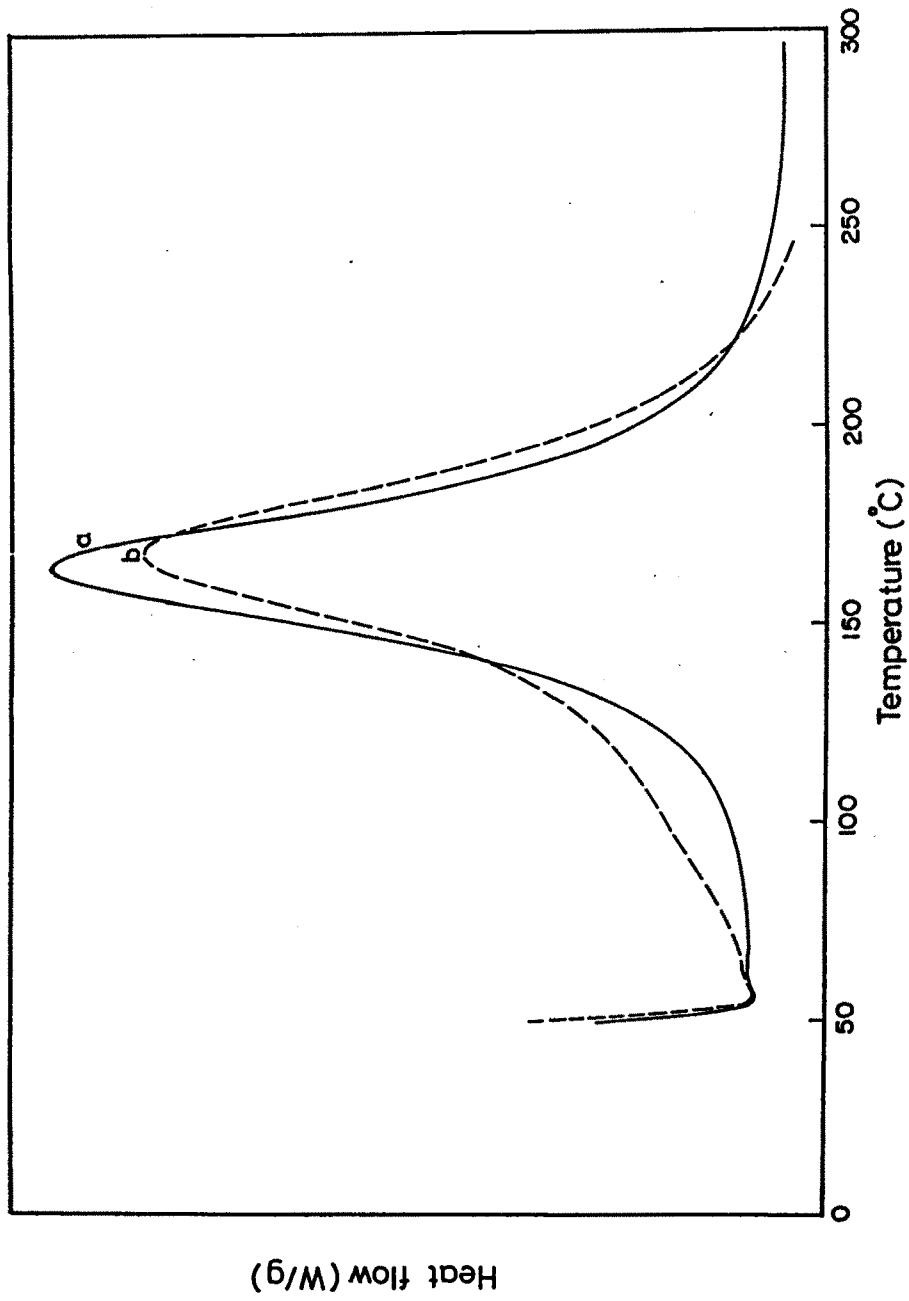


Figure 6.2 DSC thermograms of (a) epoxy-DDM and (b) mixture of epoxy-DDM- γ -APS system during cure

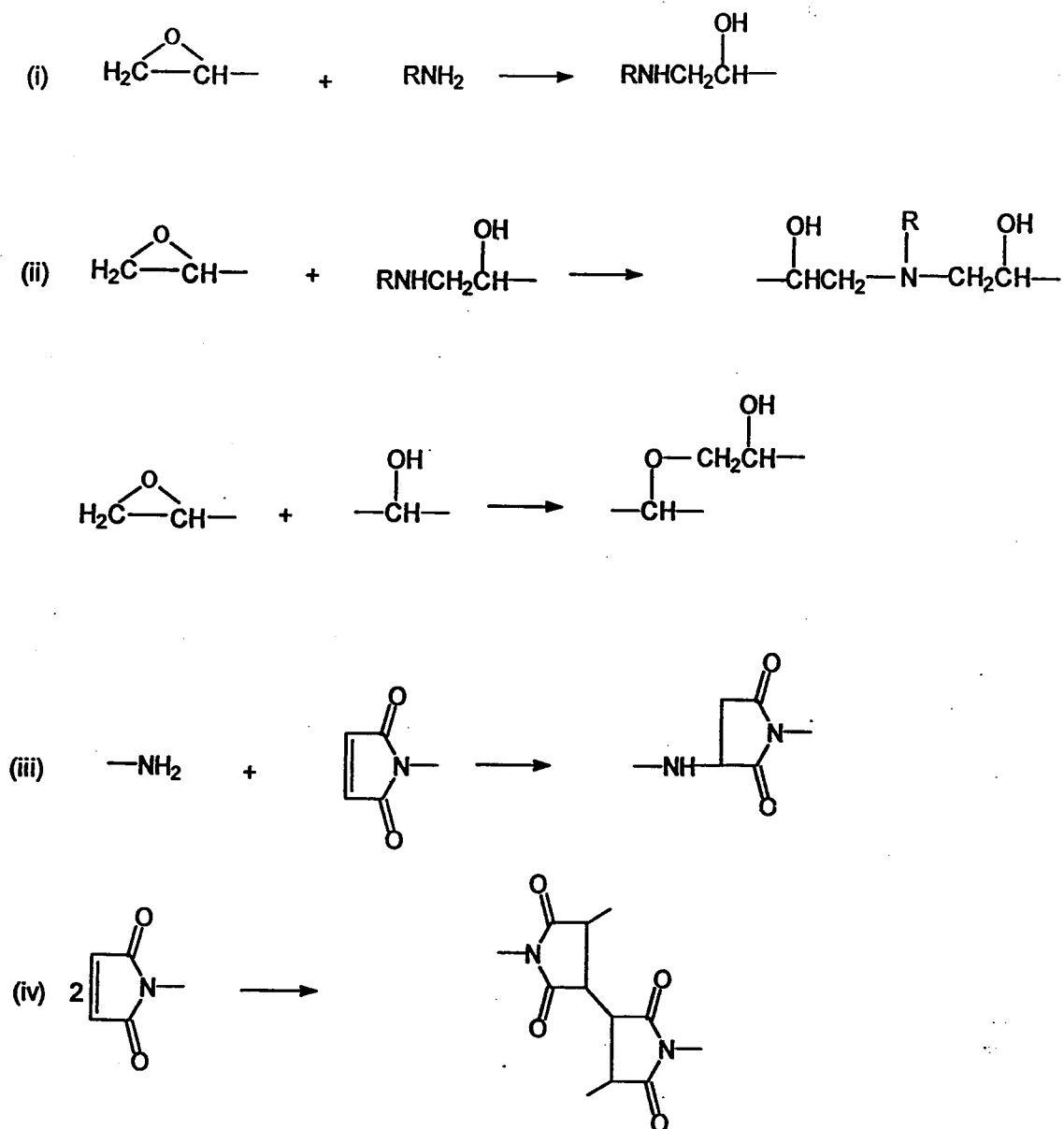


Figure 6.3 Reactions involved during the curing process of bismaleimides modified epoxy systems

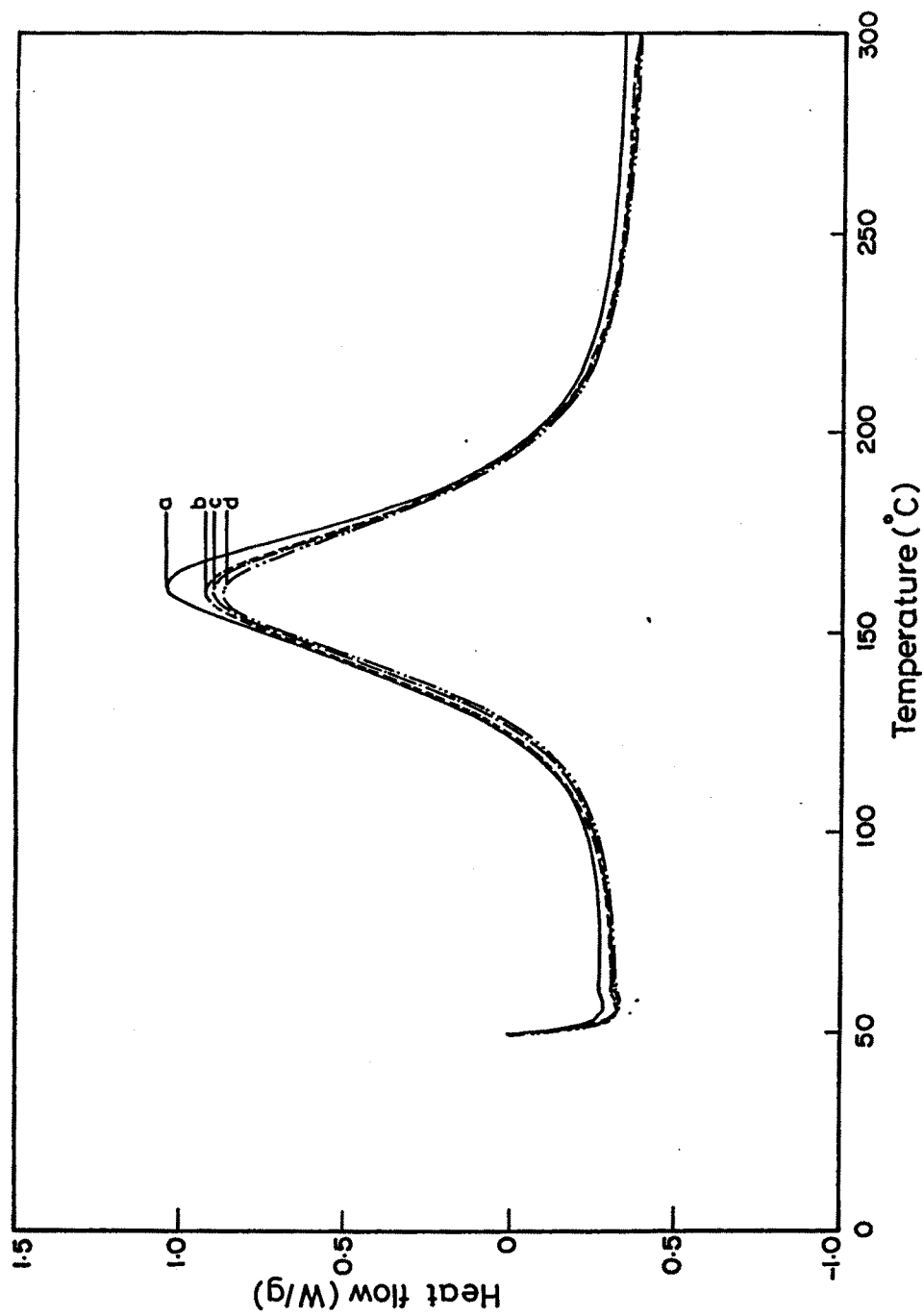


Figure 6.4 DSC thermograms of epoxy-BMI-1 systems during cure
(a) epoxy-DDM, (b) epoxy-DDM-5%BMI-1, (c) epoxy-DDM-10%BMI-1
and (d) epoxy-DDM-15%BMI-1

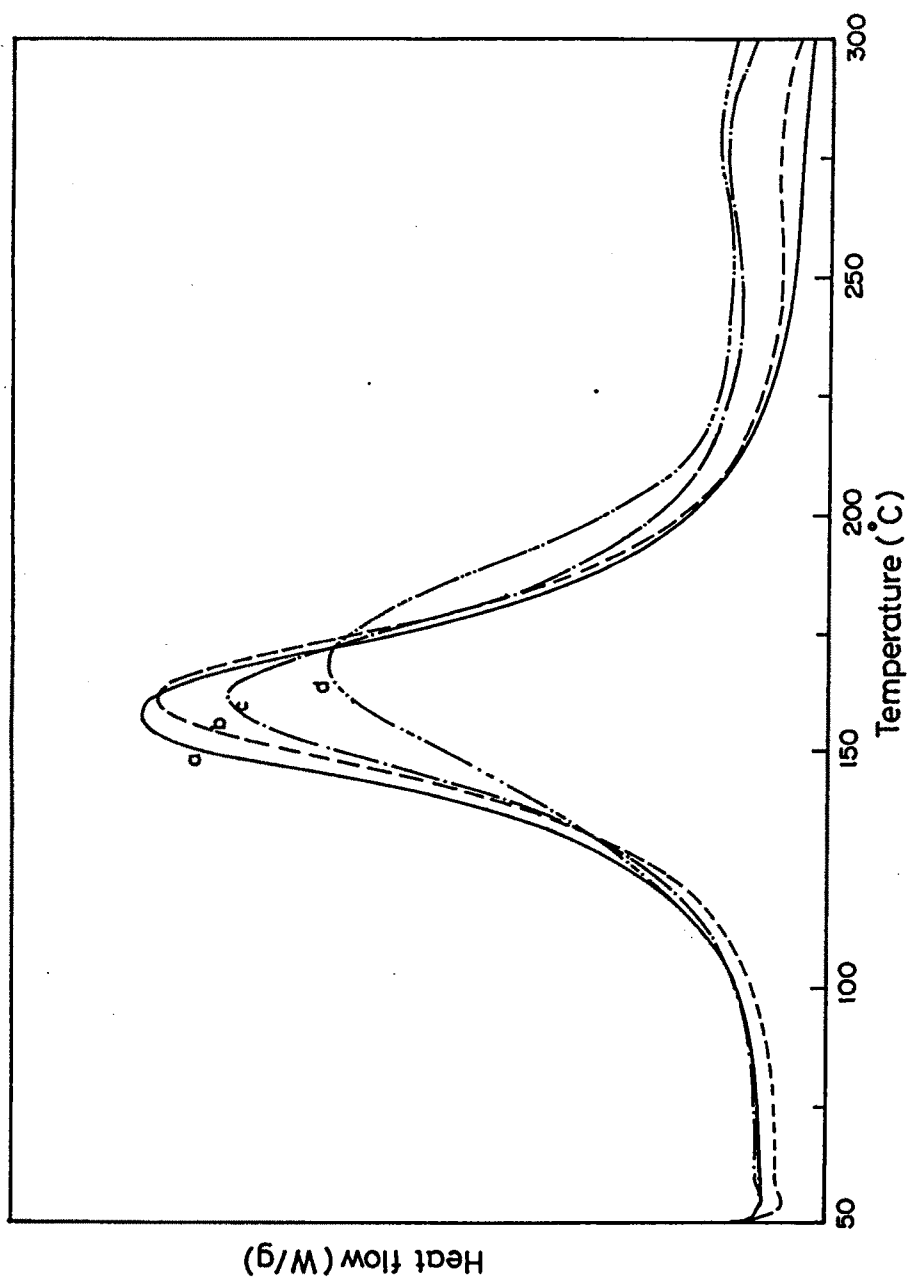


Figure 6.5 DSC thermograms of epoxy-BMI-2 systems during cure
(a) epoxy-DDM, (b) epoxy-DDM-5%BMI-2, (c) epoxy-DDM-10%BMI-2
and (d) epoxy-DDM-15%BMI-2

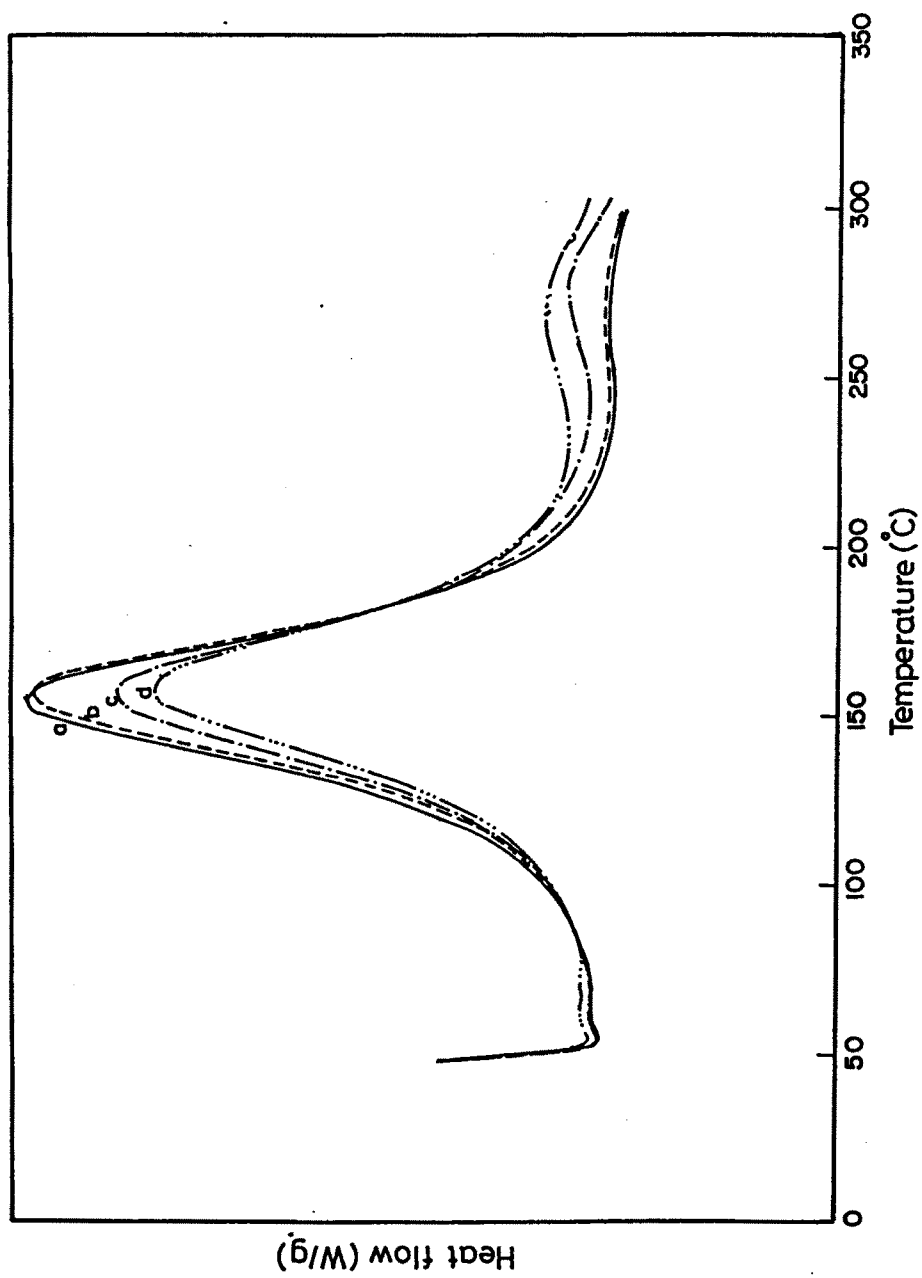


Figure 6.6 DSC thermograms of epoxy-BMI-3 systems during cure
(a) epoxy-DDM, (b) epoxy-DDM-5%BMI-3, (c) epoxy-DDM-10%BMI-3
and (d) epoxy-DDM-15%BMI-3

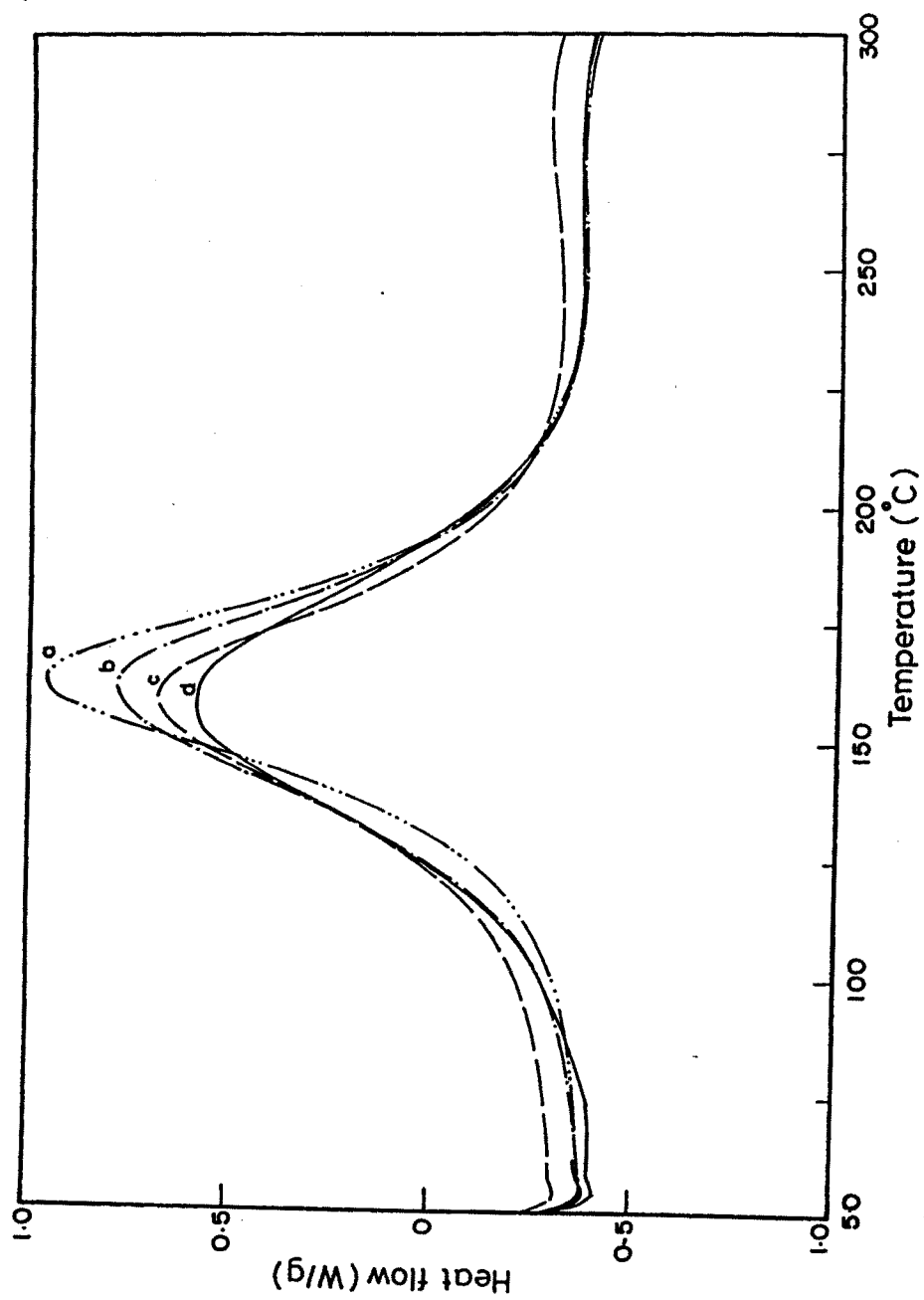


Figure 6.7: DSC thermograms of epoxy-BMI-4 systems during cure
(a) epoxy-DDM, (b) epoxy-DDM-5%BMI-4, (c) epoxy-DDM-10%BMI-4
and (d) epoxy-DDM-15%BMI-4

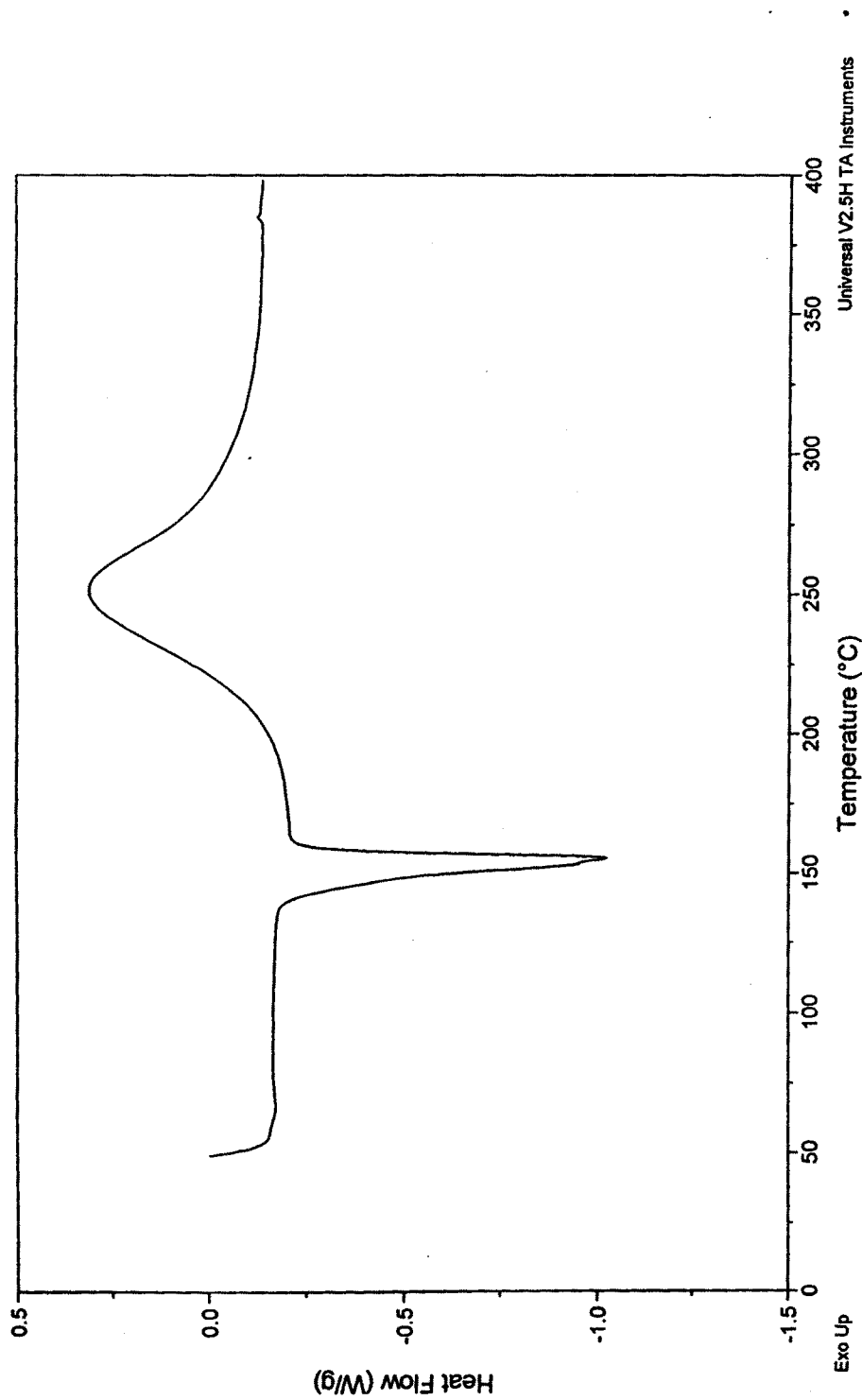


Figure 6.8 DSC thermogram of BMI-1 during cure

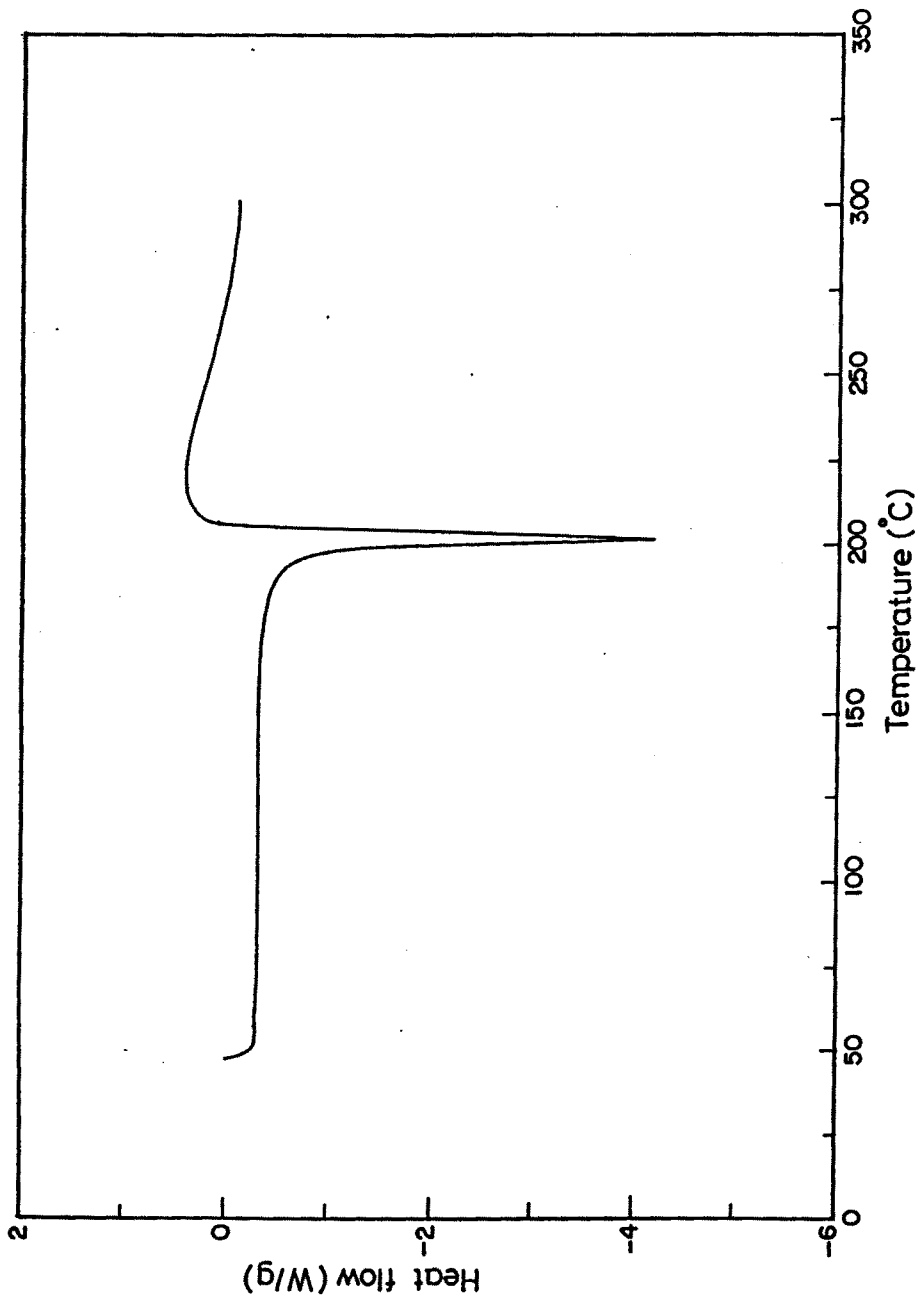


Figure 6.9 DSC thermogram of BMI-2 during cure

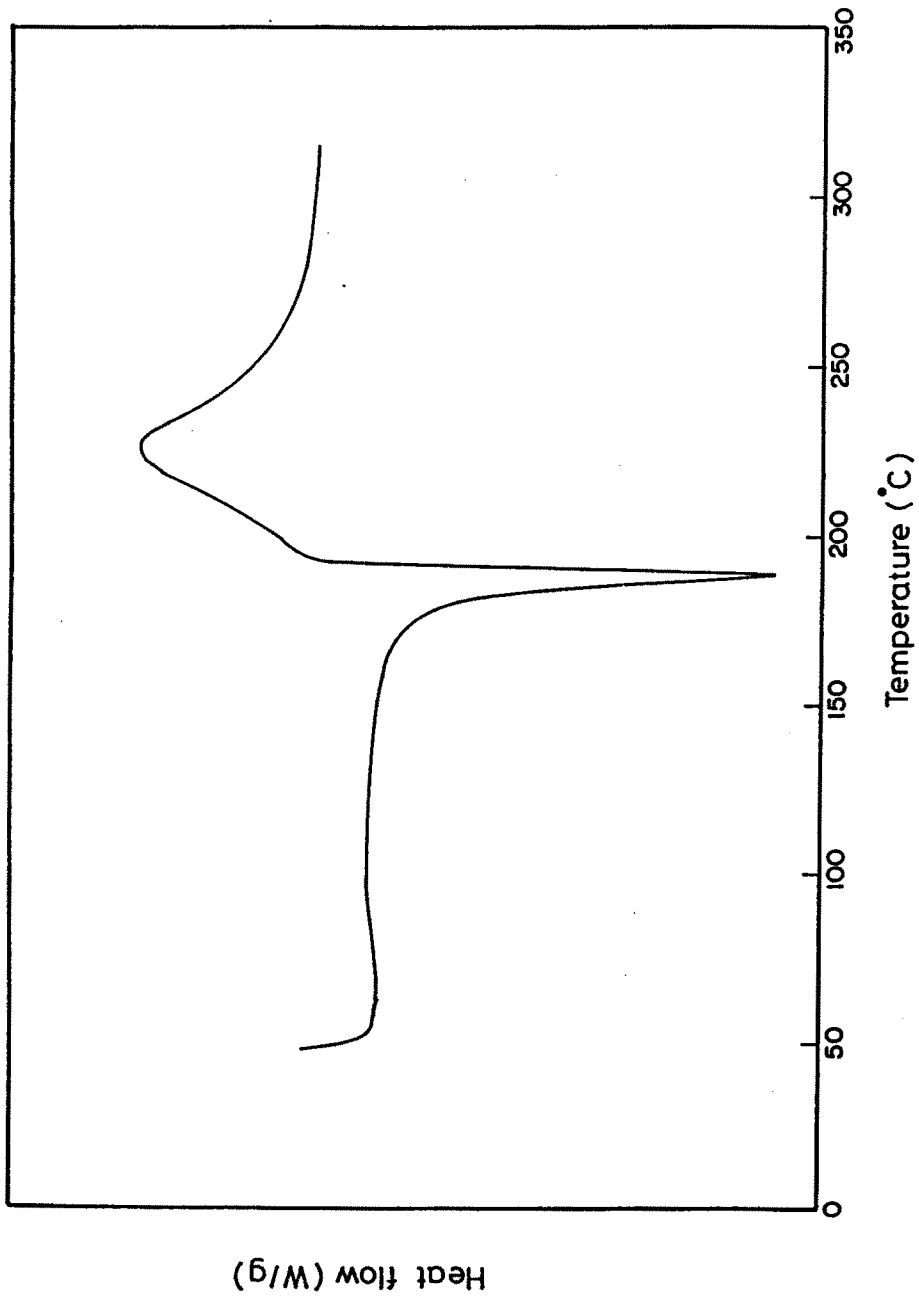


Figure 6.10 DSC thermogram of BMI-3 during cure

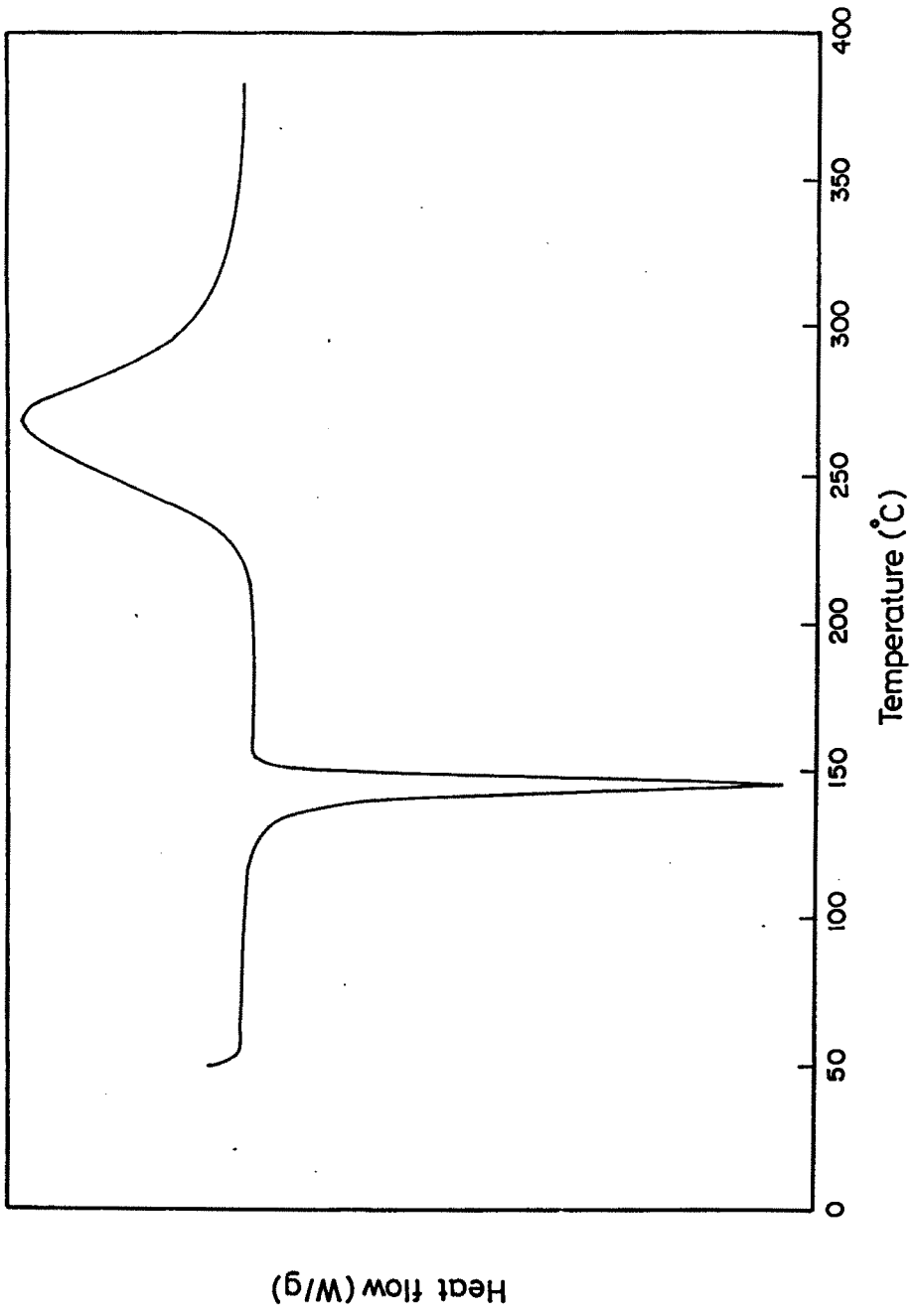


Figure 6.11 DSC thermogram of BMI-4 during cure

Han *et al.*, 1998a), BMI-2, and BMI-3 into epoxy (Figures 6.13 - 6.15) and siliconized epoxy systems (Figures 6.17 - 6.19), whereas the introduction of BMI-4 (Figure 6.16 and Figure 6.20) decreases the T_g values. The reduction in the values of T_g in the case of BMI-4 modified systems may be explained due to the presence of long aliphatic chain, which imparts flexibility to the systems. Further, in the case of BMI-4 modified systems the rate of partial Michael addition reaction is slightly higher than that of homopolymerization reaction, as high temperature (Figure 6.11) is required for the homopolymerization reaction of BMI-4 (227°C).

The increase in T_g values of bismaleimides BMI-1, BMI-2 and BMI-3 modified epoxy and siliconized epoxy systems are due to the homopolymerization of bismaleimides rather than Michael addition reaction (Figure 6.3 iii) confirmed from IR spectra (Figures 3.18 - 3.19). Since Michael addition reaction leads to the formation of thermally weak amine linkage and ultimately reduces the crosslink density due to chain extension (Melissaris *et al.*, 1998). Moreover, if Michael addition reaction predominates, that will reduce the number of available hydrogen to cure epoxy resin since, only stoichiometric amount of amine curative (with respect to epoxy group) is added to the systems. In such a case, the reaction mixture will not be cured and T_g will be reduced. The rise in T_g for BMI-1, BMI-2 and BMI-3 (Figures 6.13 - 6.15, Tables 6.1 - 6.3)) confirms that the homopolymerization reaction of bismaleimides is predominant rather than that of Michael addition reaction. In addition, homopolymerization reaction of bismaleimides leads to the formation of thermally stable -C-C- linkage. Further, the improvement in T_g lends support to the earlier observation made by Musto *et al.* (1998) that in the presence of epoxy resin, homopolymerization reactions of bismaleimides starts even below at 130°C. The single T_g value obtained for all the bismaleimides

modified epoxy and siliconized epoxy systems further confirm the formation of intercrosslinking network (Figures 6.13 – 6.20).

Among the bismaleimides modified epoxy and siliconized epoxy systems, the aromatic bismaleimide modified systems (Tables 6.1 – 6.2) show higher improvement in Tg than that of aliphatic bismaleimides modified systems (Tables 6.3 – 6.4) due to the presence of rigid aromatic skeleton.

In the case of aromatic bismaleimides modified epoxy and siliconized epoxy systems, the BMI-2 modified systems (Table 6.2) show higher improvement in Tg than BMI-1 (Table 6.1). For example, the Tg values for 10% BMI-2 modified epoxy (system O2) and 10% BMI-2 modified 10% siliconized (10%) epoxy (system I2) are 188°C and 184°C respectively, whereas the Tg values for the same percentage of BMI-1 incorporated systems are 173°C (system O1) and 168°C (system I1) respectively. This may be explained due to the presence of higher crosslinking density in the BMI-2 modified systems than that of BMI-1 modified systems, because of more number of available reactive molecules in the former. Further, the presence of methylene linkage in BMI-1 imparts flexibility to the systems and hence, lesser improvement in Tg is observed for BMI-1 modified systems.

In the case of aliphatic bismaleimides modified epoxy and siliconized epoxy systems, the BMI-3 modified systems show improvement in Tg (Figures 6.15 – 6.19 and Table 6.3), whereas BMI-4 modified systems exhibit decreasing trend. For example, the values of Tg for 10% BMI-3 modified epoxy (system O3) and 10% BMI-3 modified siliconized (10%) epoxy systems (system I3) are 170°C and 167°C respectively, whereas the values of Tg for the same percentage of BMI-4 modified systems are (system O4) 162°C and

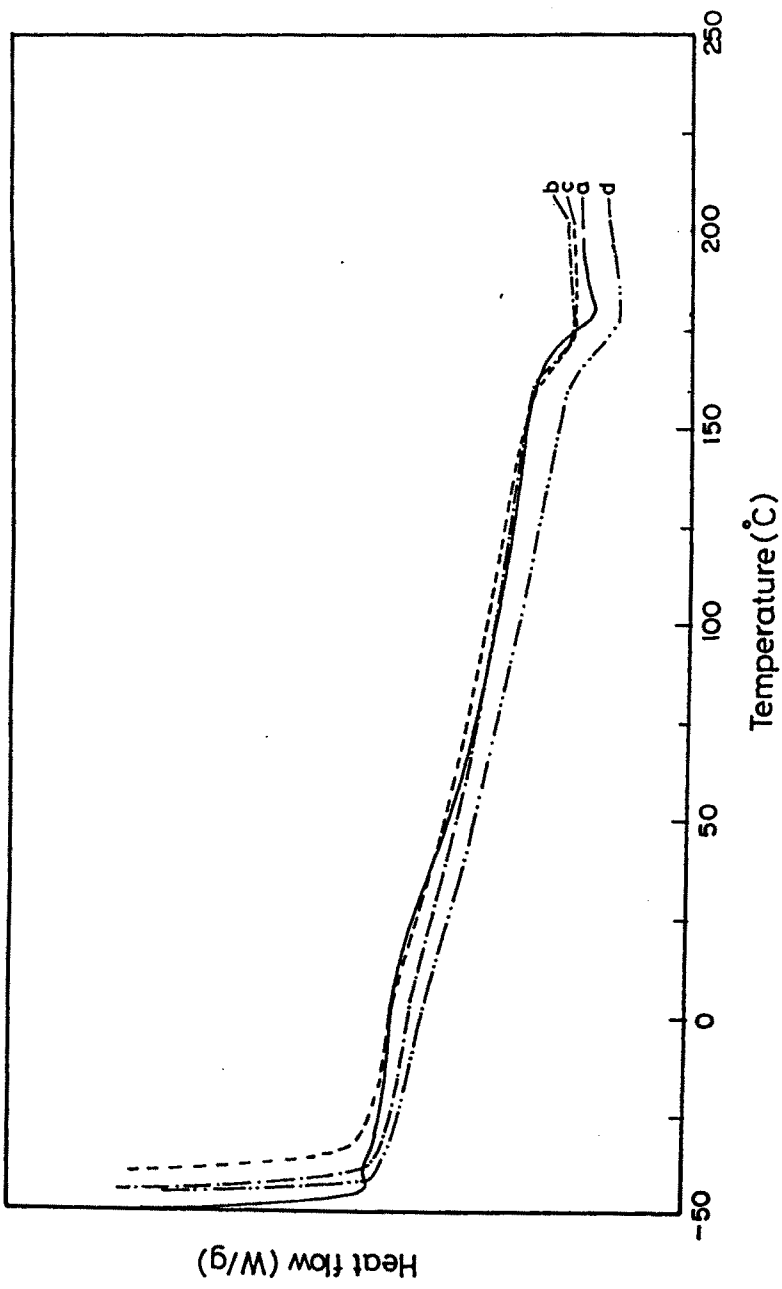


Figure 6.12 DSC traces of epoxy and siliconized epoxy systems
(a) unmodified epoxy, (b) 5%, (c) 10% and (d) 15% siloxane modified epoxy systems

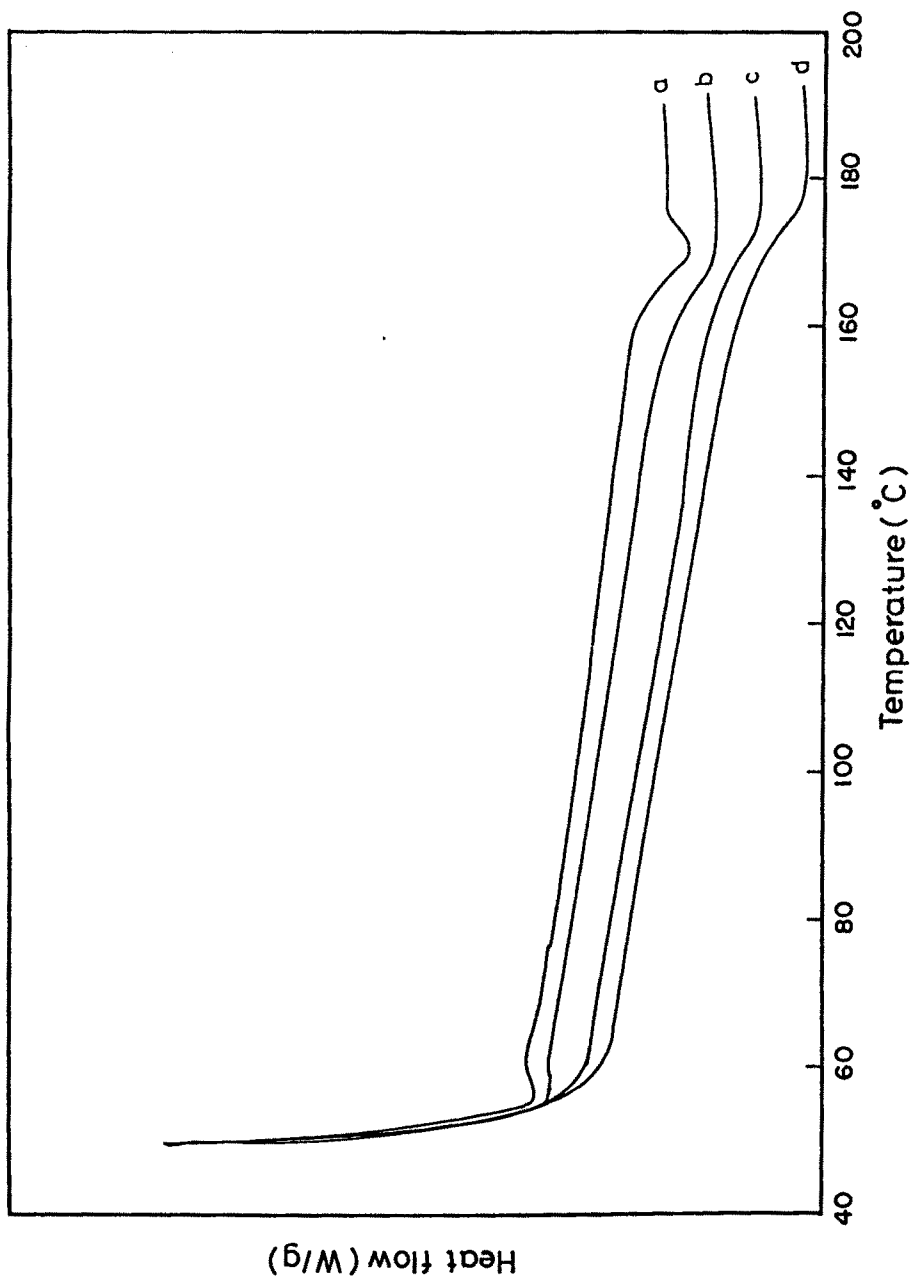


Figure 6.13 DSC traces of BMI-1 modified epoxy systems
 (a) unmodified epoxy, (b) 5%, (c) 10% and (d) 15% BMI-1 modified epoxy systems

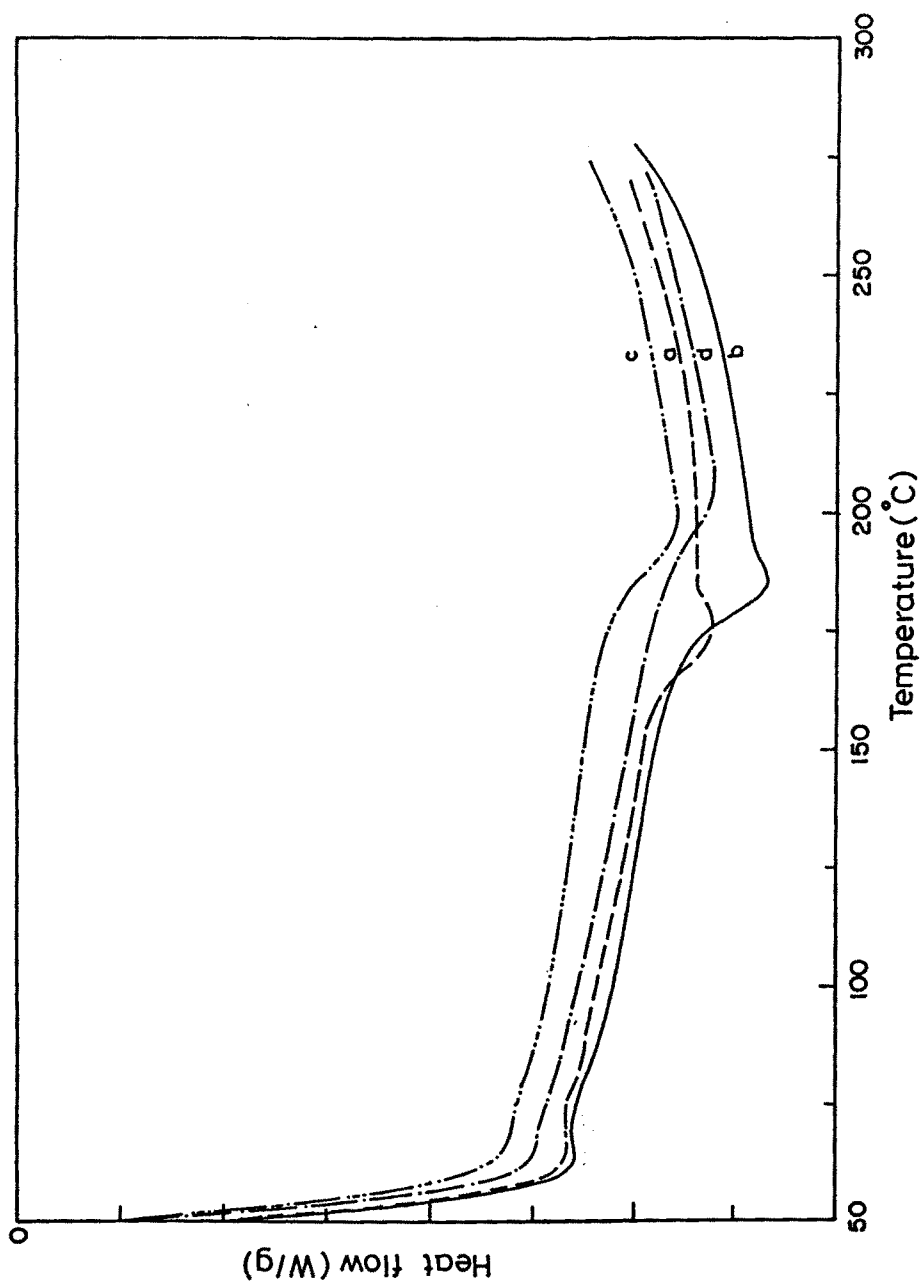


Figure 6.14 DSC traces of BMI-2 modified epoxy systems
(a) unmodified epoxy, (b) 5%, (c) 10% and (d) 15% BMI-2 modified epoxy systems

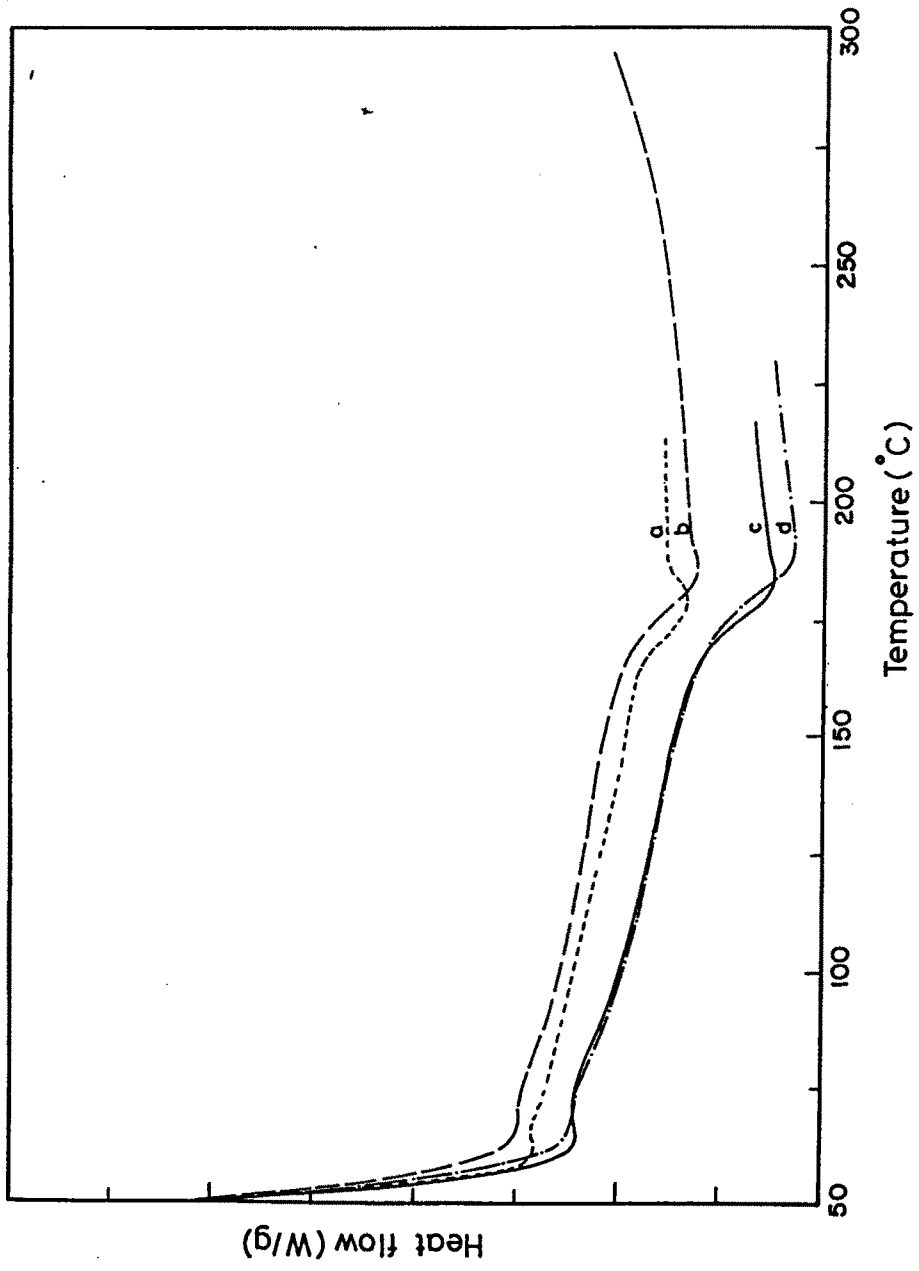


Figure 6.15 DSC traces of BMI-3 modified epoxy systems
(a) unmodified epoxy, (b) 5%, (c) 10% and (d) 15% BMI-3 modified epoxy systems

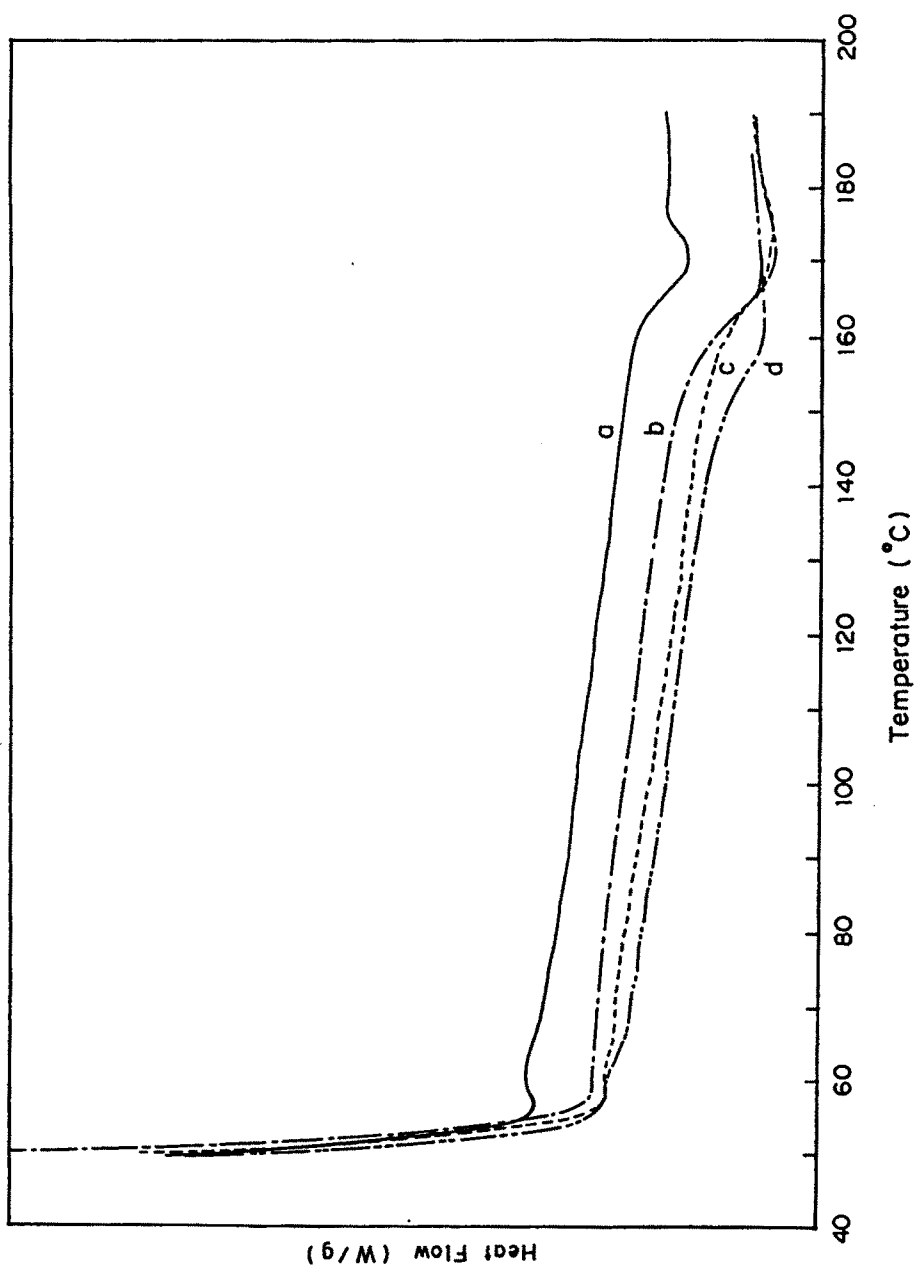


Figure 6.16 DSC traces of BMI-4 modified epoxy systems
(a) unmodified epoxy, (b) 5%, (c) 10% and (d) 15% BMI-4 modified epoxy systems

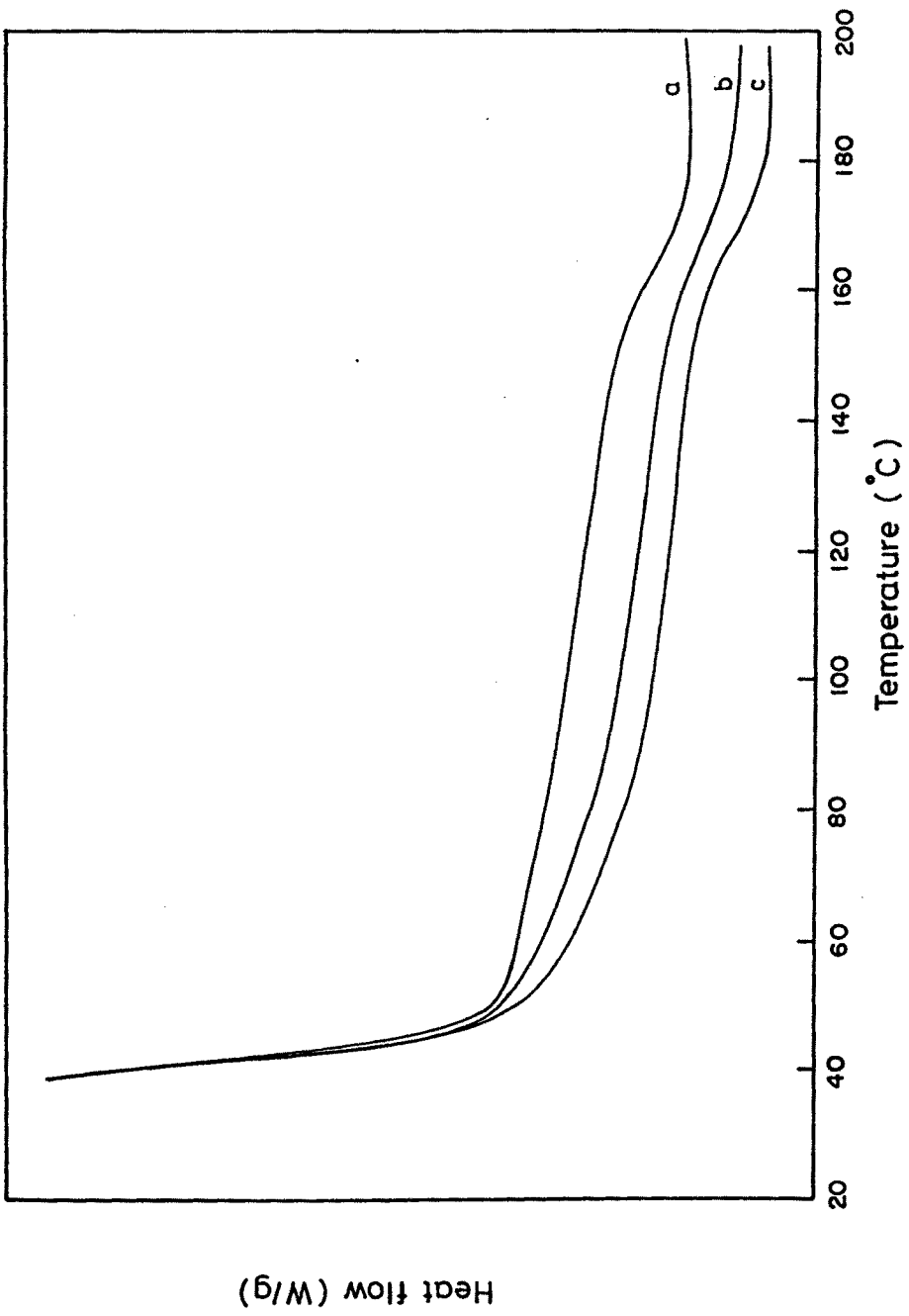


Figure 6.17 DSC traces of 10% siliconized epoxy / BMI-1 systems
(a) 5%, (b) 10% and (c) 15% BMI-1 modified 10% siliconized epoxy systems

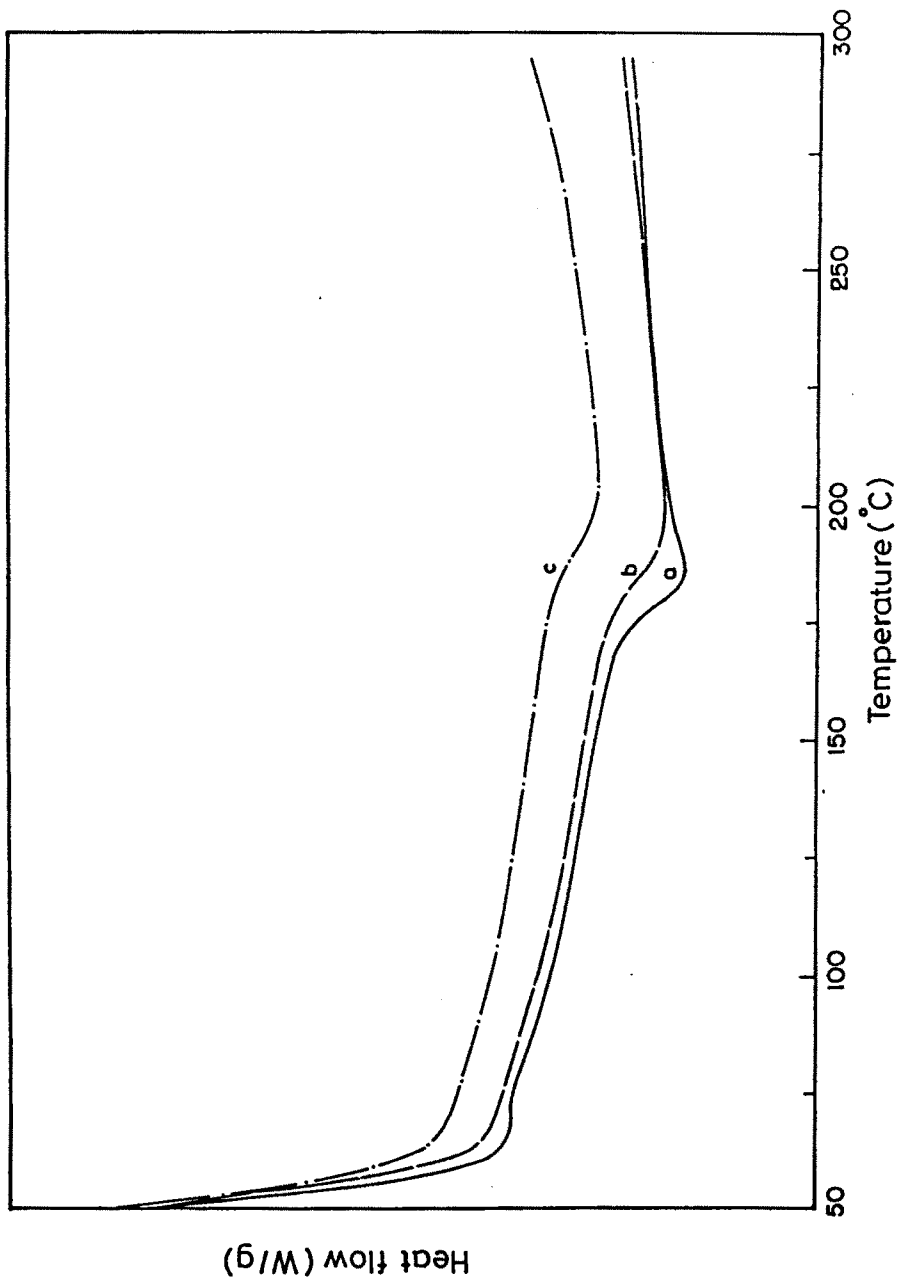


Figure 6.18 DSC traces of 10% siliconized epoxy / BMI-2 systems
(a) 5%, (b) 10% and (c) 15% BMI-2 modified 10% siliconized epoxy systems

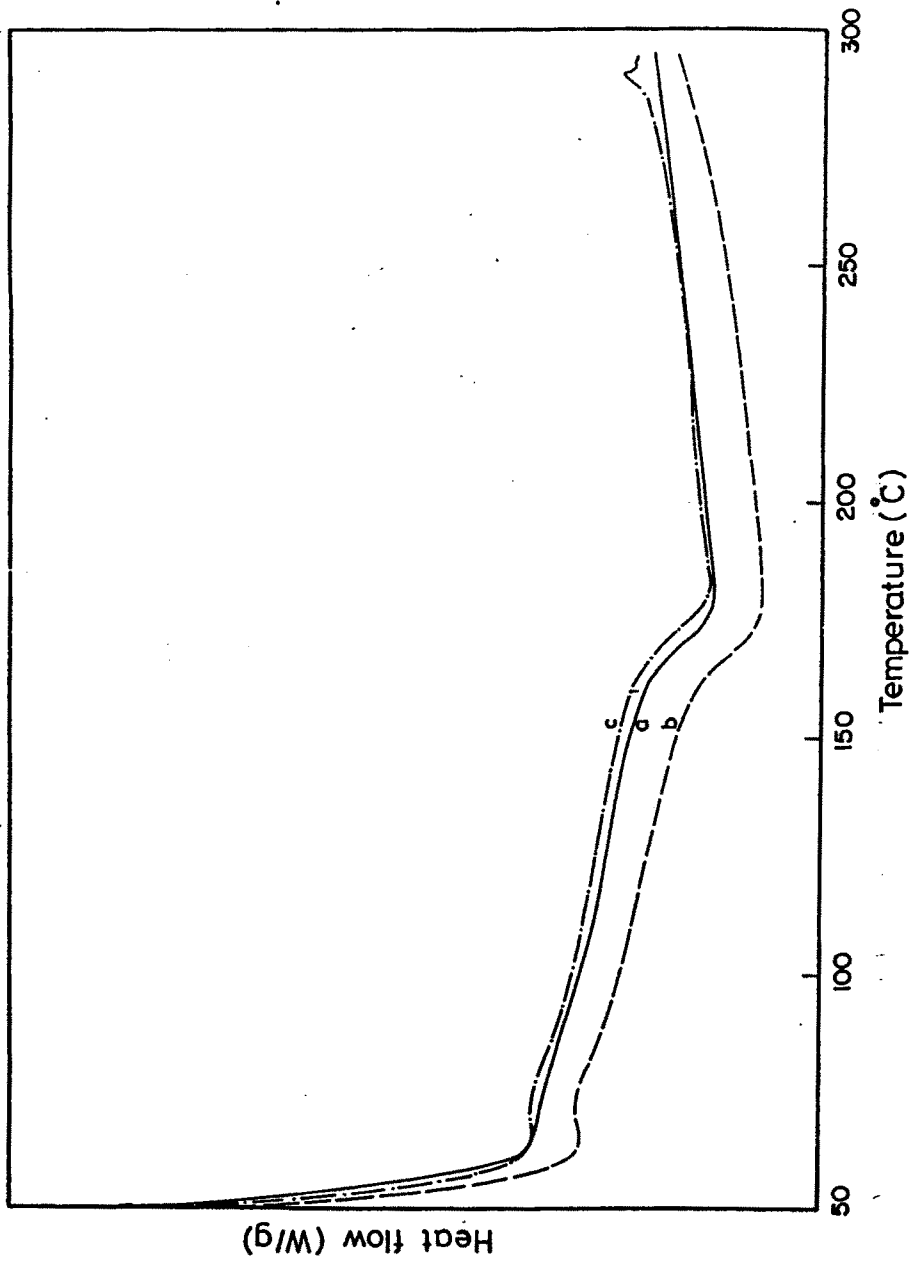


Figure 6.19 DSC traces of 10% siliconized epoxy / BMI-3 systems
(a) 5%, (b) 10% and (c) 15% BMI-3 modified 10% siliconized epoxy
systems

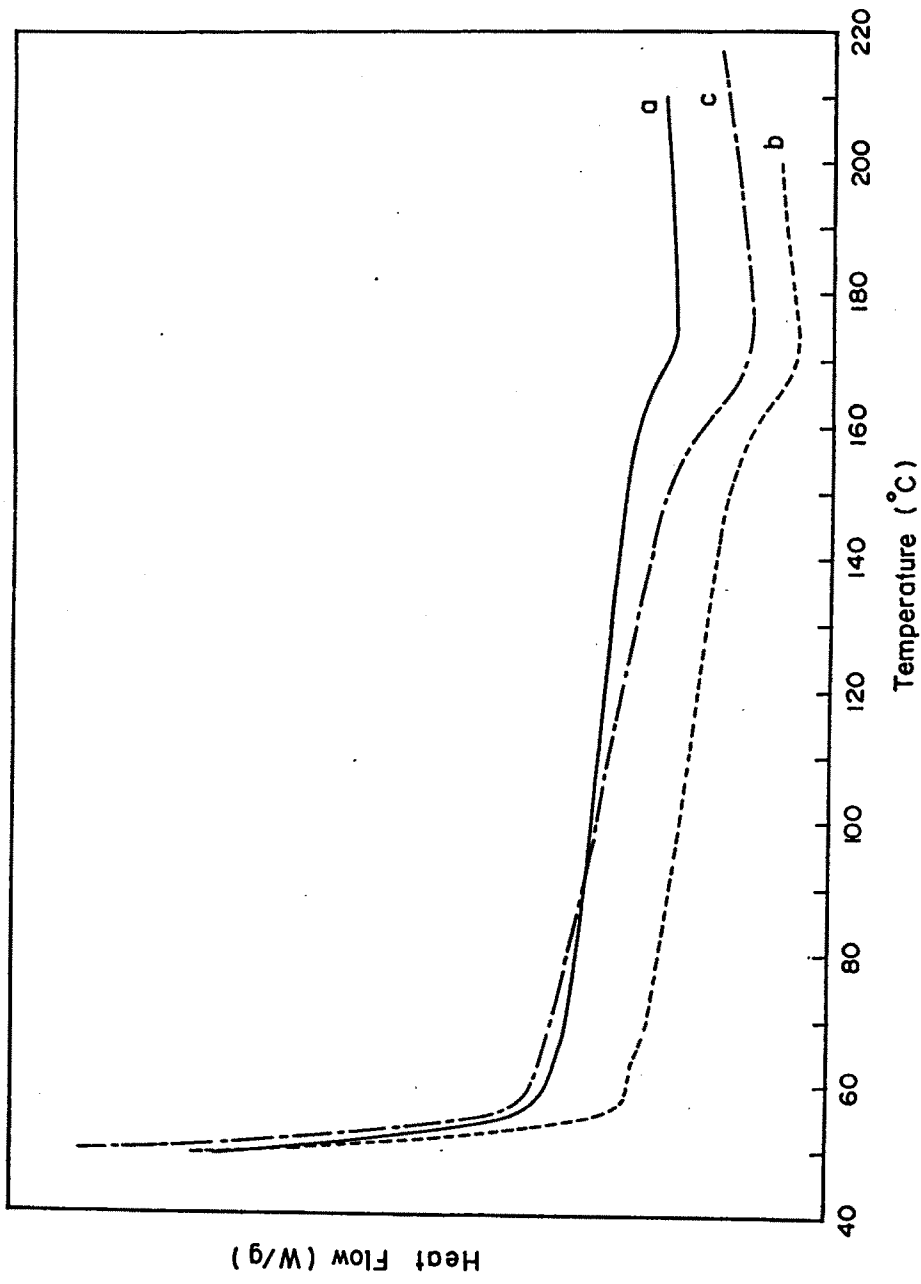


Figure 6.20 DSC traces of 10% siliconized epoxy / BMI-4 systems
(a) 5%, (b) 10% and (c) 15% BMI-4 modified 10% siliconized epoxy systems

(system I4) 158°C respectively (Table 6.4 and Figures 6.16 and 6.20). The increase in T_g value for the BMI-3 modified systems is due to the presence of higher number of reactive molecules. Further, the presence of long aliphatic chain in the BMI-4 and chain extension due to Michael addition reaction, imparts flexibility to the systems and hence molecular relaxation has taken place at lower temperature.

6.3 THERMOGRAVIMETRIC ANALYSIS

Incorporation of siloxane into epoxy resin improves thermal stability and enhances the degradation temperature according to its percentage concentration (Figures 6.21 – 6.22). The presence of siloxane skeleton in the epoxy system delays the degradation process and high thermal energy is required to attain the same percentage weight loss than that required for unmodified epoxy system. The delay in degradation caused by the siloxane moiety may be attributed to its partial ionic nature and high bond energy of -Si-O-Si- linkage.

For example, the temperature required for 10%, 30% and 50% weight losses of unmodified epoxy-DDM systems are 365°C, 383°C and 392°C (Figure 6.21), whereas the temperature required to attain the same percentage weight losses for 15% HTPDMS modified systems are increased to 388°C, 408°C and 415°C respectively (Figure 6.21). A similar trend is observed for 5% and 10% HTPDMS modified epoxy systems. From Figures 6.23-6.38), it is observed that the thermal degradation temperature of all the bismaleimides (BMI-1, BMI-2, BMI-3 and BMI-4) modified epoxy systems are raised with increasing bismaleimides concentration. The plots of degradation temperature against bismaleimide concentrations are presented in Figures 6.23-6.30. From

Figures 6.23-6.30, it is evident that the degradation temperature increases with increasing BMIs concentrations as observed in the case of HTPDMS modified systems and this may be due to the formation of intercrosslinking network between epoxy and bismaleimides and rigid heterocyclic ring structure of bismaleimides.

Among the bismaleimides modified epoxy systems, the aromatic bismaleimides (BMI-1 and BMI-2) modified systems (Figures 6.23-6.26) show higher thermal degradation temperature when compared with that of aliphatic bismaleimides (BMI-3 and BMI-4) modified systems (Figures 6.27-6.30) and this may be due to the presence of thermally stable aromatic-heterocyclic structure.

In the case of aromatic bismaleimides modified epoxy systems, the BMI-2 modified systems (Figures 6.25-6.26) exhibit higher thermal degradation temperature when compared to the same percentage of BMI-1 modified systems (Figures 6.23-6.24). For example, thermal degradation temperature for 10%, 30% and 50% weight losses of 15% BMI-2 modified epoxy systems are 391°C, 421°C and 435°C respectively, while the degradation temperature for the same percentages weight losses of 15% BMI-1 modified epoxy systems are 386°C, 400°C and 417°C respectively.

In the case of aliphatic bismaleimides (BMI-3 and BMI-4) modified epoxy systems (Figures 6.27-6.30), the BMI-3 modified systems (Figures 6.27-6.28) exhibit higher thermal degradation temperature than that of BMI-4 modified systems (Figures 6.29-6.30). For example, the thermal degradation temperature for the 10%, 30% and 50% weight losses of 15% BMI-3 modified systems are 382°C, 395°C and 410°C respectively, whereas

the degradation temperature for the same percentages weight losses of 15% BMI-4 modified systems are 378°C, 394°C and 407°C respectively.

Similar trend is observed in the case of aromatic and aliphatic bismaleimides modified siliconized epoxy systems. However, the thermal stability of bismaleimides (both aromatic and aliphatic) modified siliconized epoxy systems are slightly higher than that of bismaleimides (both aromatic and aliphatic) modified epoxy and HTPDMS modified epoxy systems. For example, the temperature required for 50% weight loss of 15% siliconized epoxy and 15% BMI-1 modified epoxy systems are 415°C and 417°C respectively, whereas the temperature required to attain the same 50% weight loss for 15% BMI-1 modified siliconized (10%) epoxy system is 420°C. This enhancement is mainly due to synergistic effect of bismaleimides and HTPDMS. Similar trend is observed for the rest of systems.

6.4 HEAT DISTORTION TEMPERATURE (HDT)

Heat distortion temperature is carried out to determine the thermo-mechanical behaviour of matrix systems. HDT values for epoxy, HTPDMS modified epoxy, bismaleimides (BMI-1, BMI-2, BMI-3 and BMI-4) modified epoxy and siliconized epoxy systems are presented in Tables 6.1-6.4. From Table 6.1, it is evident that HDT decreases with increasing HTPDMS concentration. This may be explained due to the presence of flexible -Si-O-Si- linkage. However, HDT increases for bismaleimides (BMI-1, BMI-2 and BMI-3) modified epoxy and siliconized epoxy systems with increasing BMIs concentration. The enhancement in the values of HDT for bismaleimides modified systems are due to high network and heterocyclic structure. Among the bismaleimides modified epoxy and siliconized epoxy systems, the aromatic

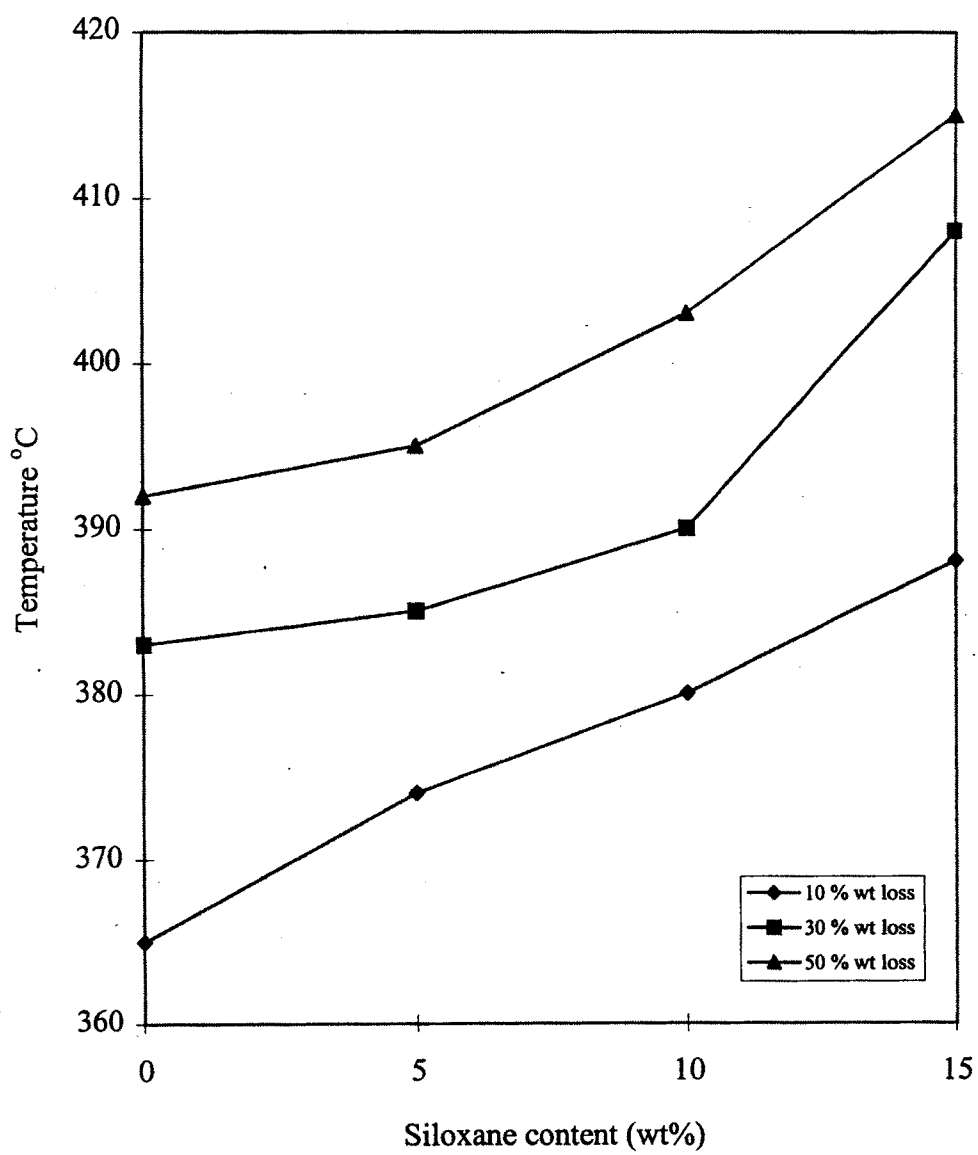


Figure 6.21 Effect of siloxane content on percentage weight loss of epoxy system

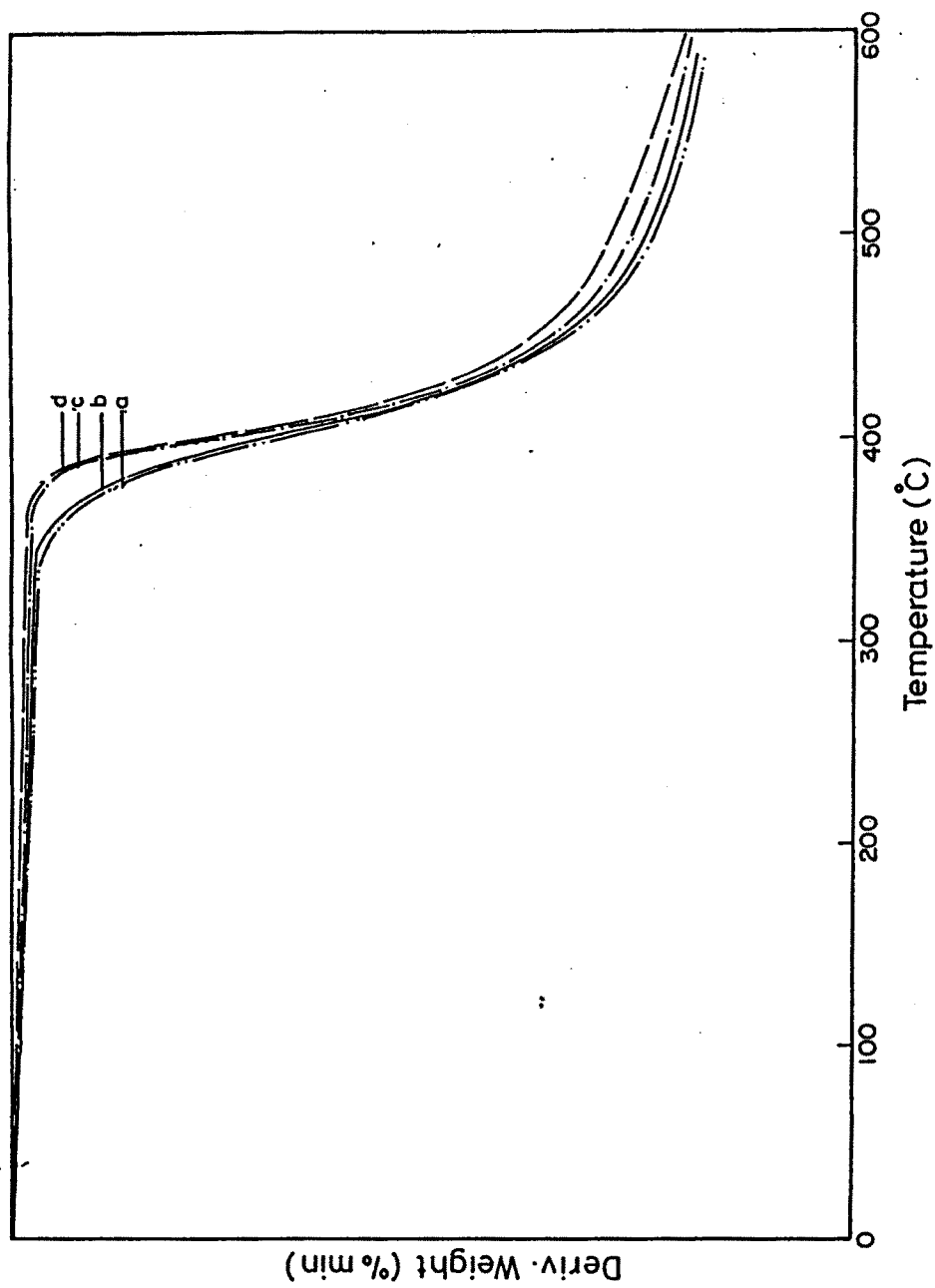


Figure 6.22 TGA curves of siliconized epoxy systems
(a) unmodified epoxy, (b) 5%, (c) 10% and (d) 15% siloxane modified epoxy systems

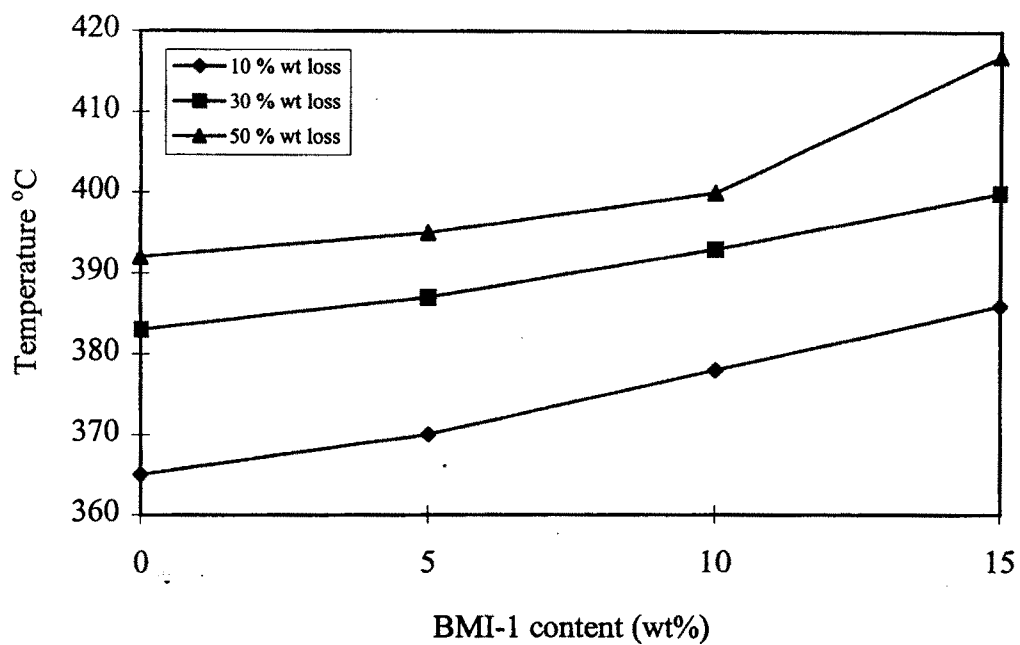


Figure 6.23 Effect of BMI-1 content on percentage weight loss of epoxy

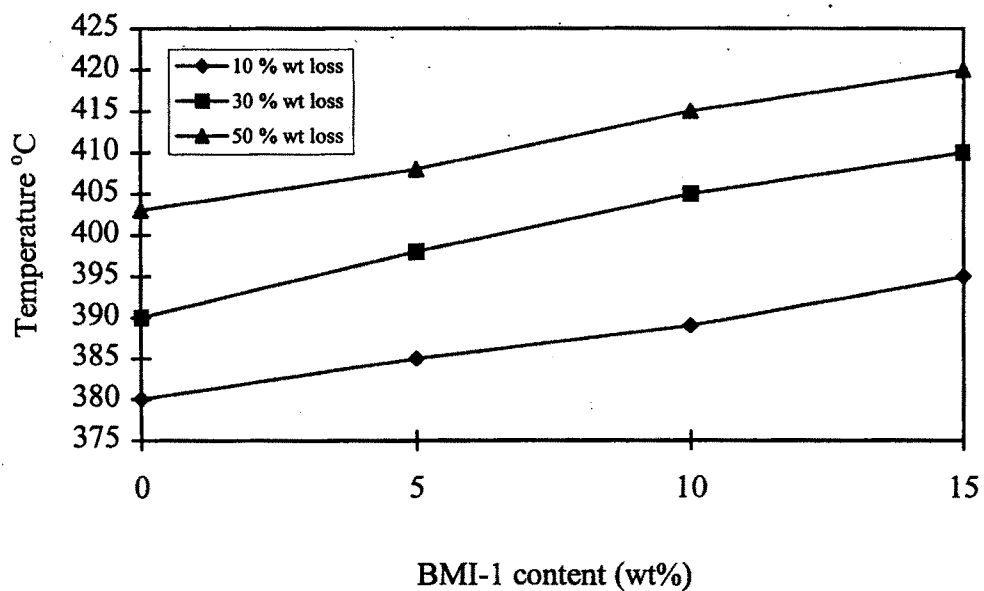


Figure 6.24 Effect of BMI-1 content on percentage weight loss of 10% siliconized epoxy system

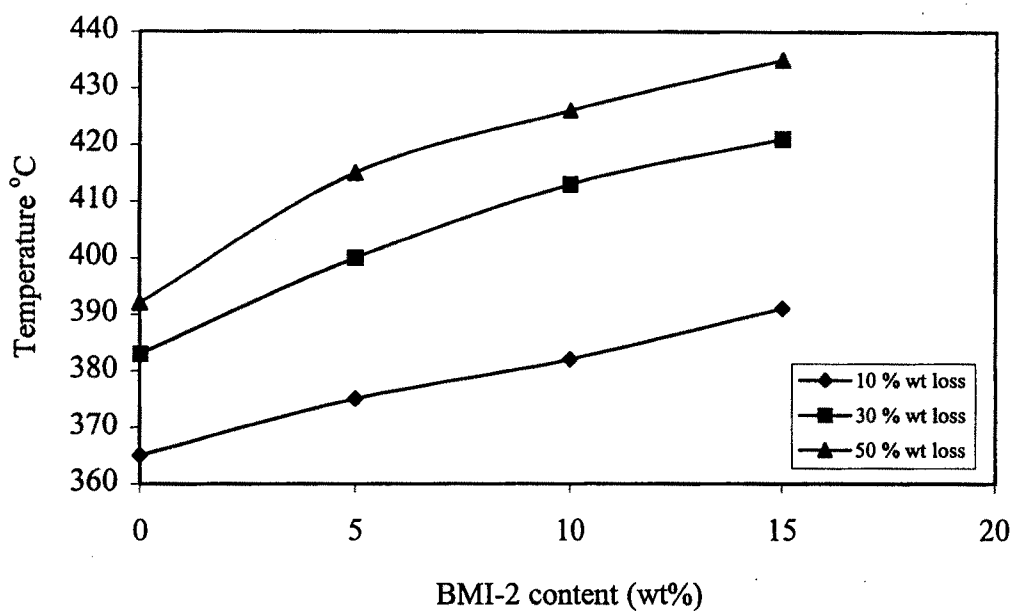


Figure 6.25 Effect of BMI-2 content on percentage weight loss of epoxy system

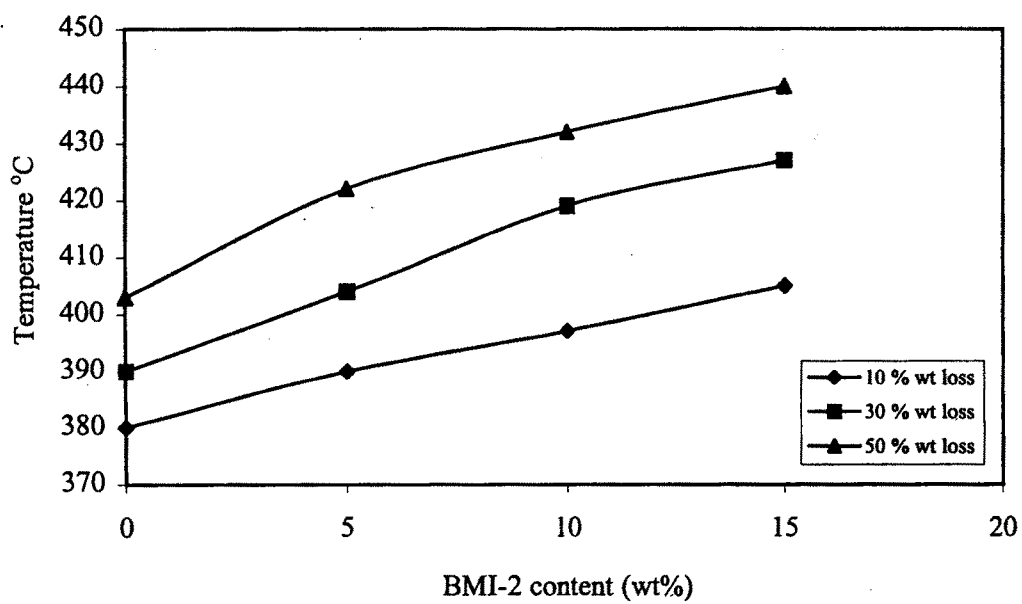


Figure 6.26 Effect of BMI-2 content on percentage weight loss of 10% siliconized epoxy system

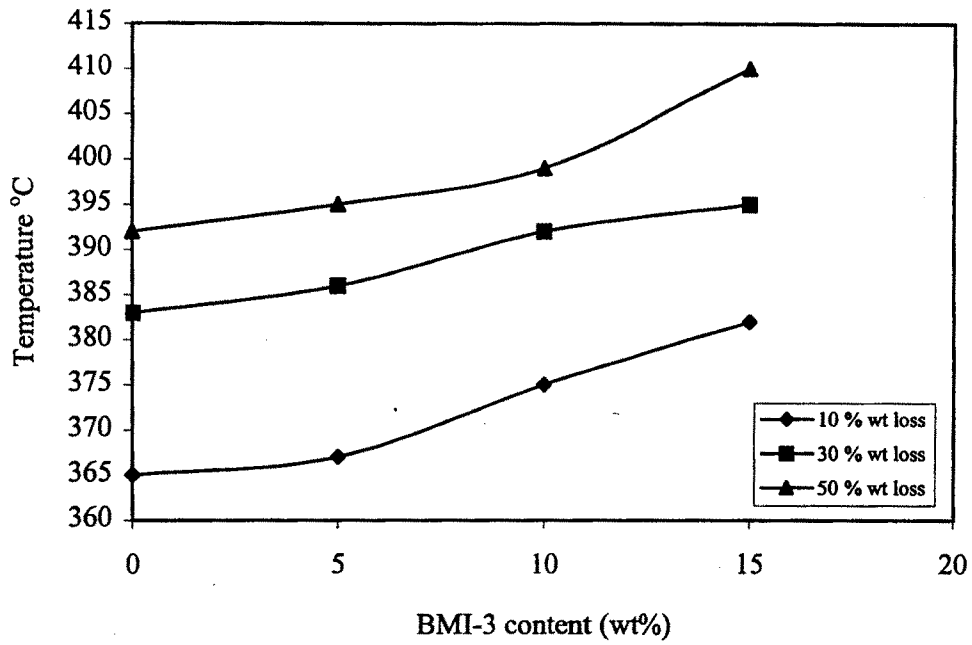


Figure 6.27 Effect of BMI-3 content on percentage weight loss of epoxy system

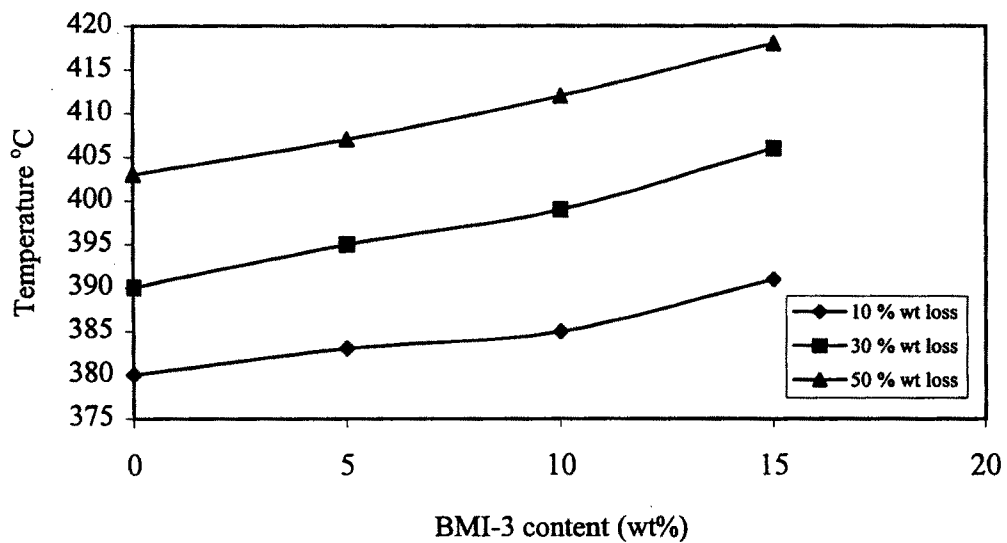


Figure 6.28 Effect of BMI-3 content on percentage weight loss of 10% siliconized epoxy system

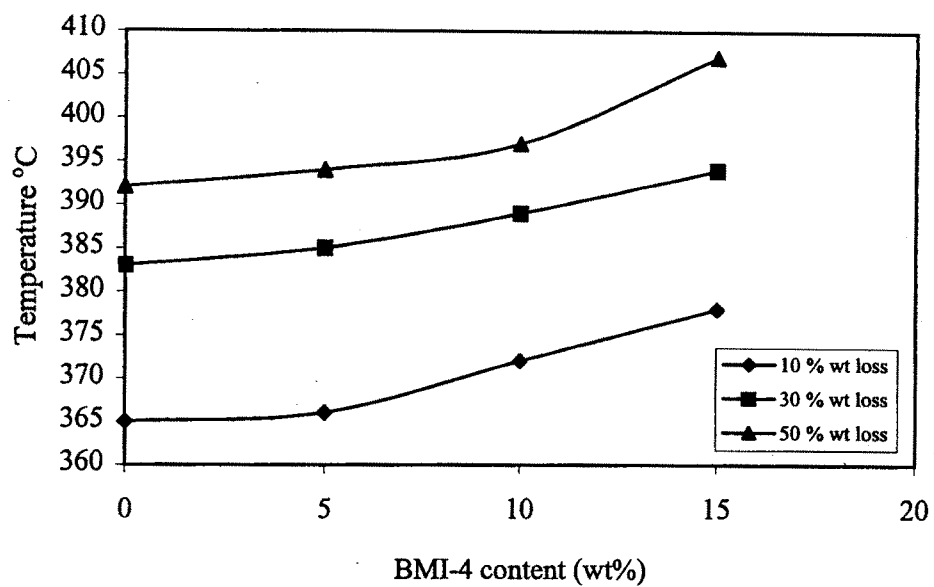


Figure 6.29 Effect of BMI-4 content on percentage weight loss of epoxy system

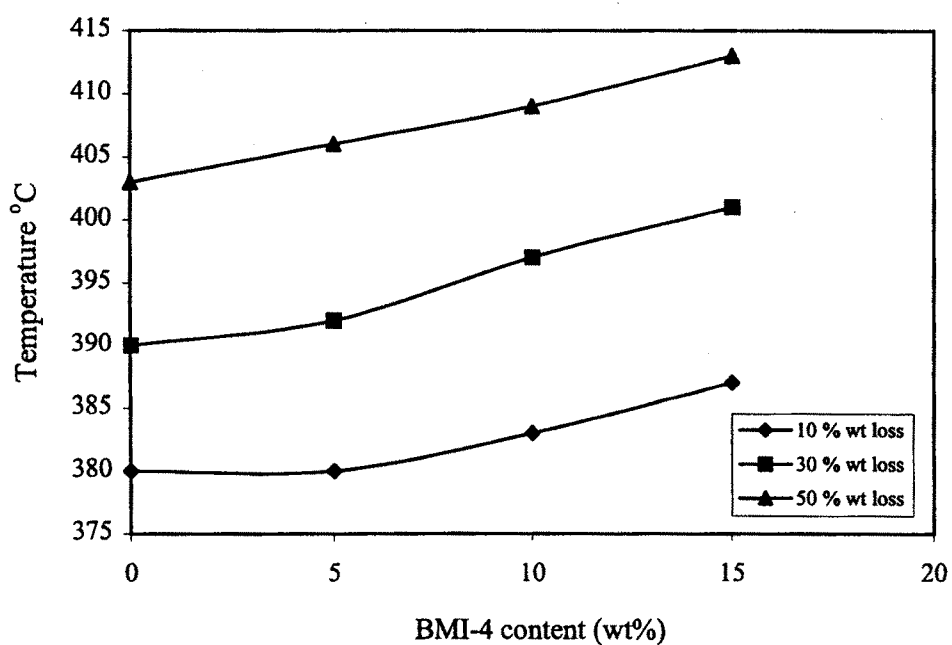


Figure 6.30 Effect of BMI-4 content on percentage weight loss of 10% siliconized epoxy system

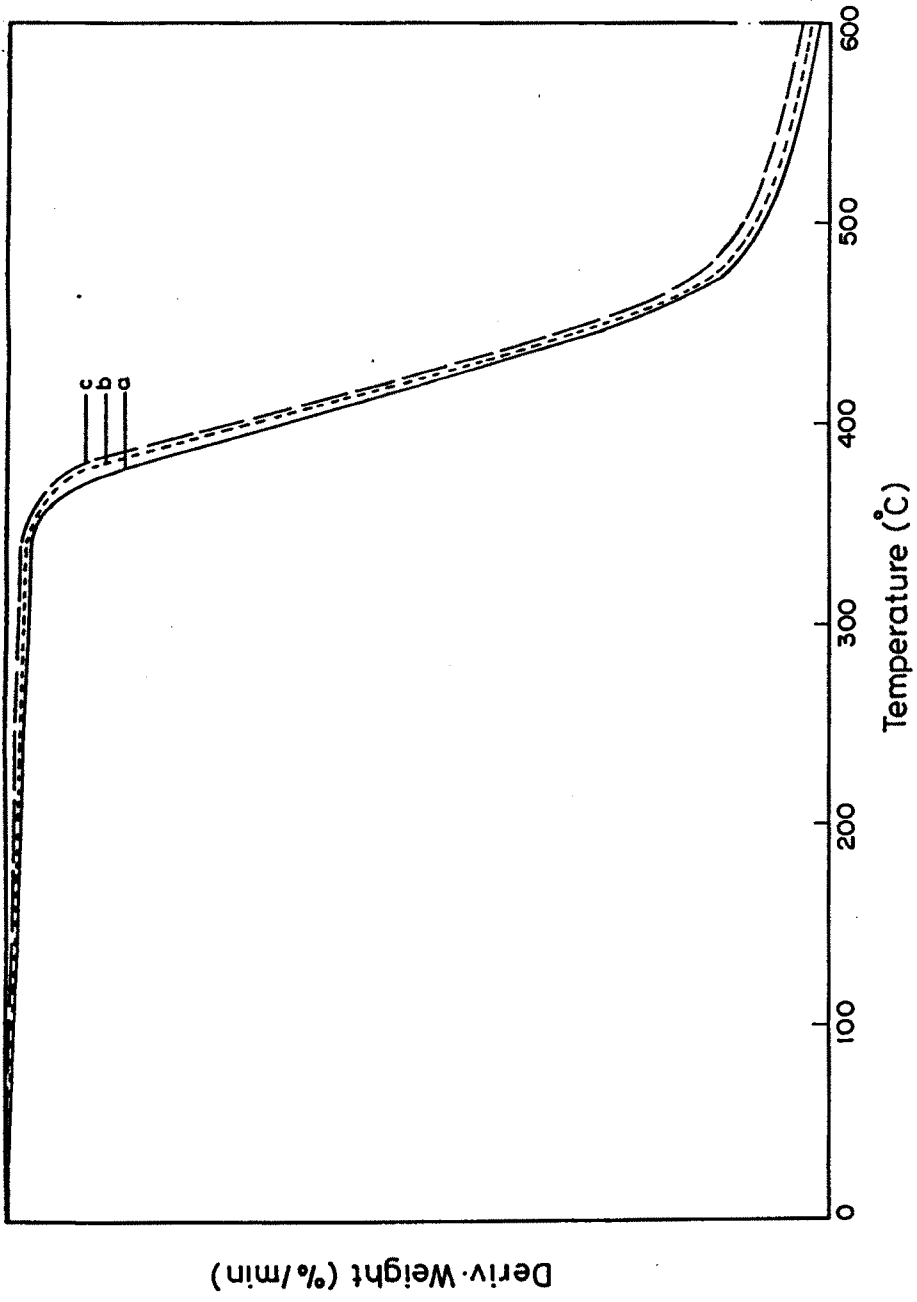


Figure 6.31 TGA curves of BMI-1 modified epoxy system (a) 5%, (b) 10% and (c) 15% BMI-1 modified epoxy systems

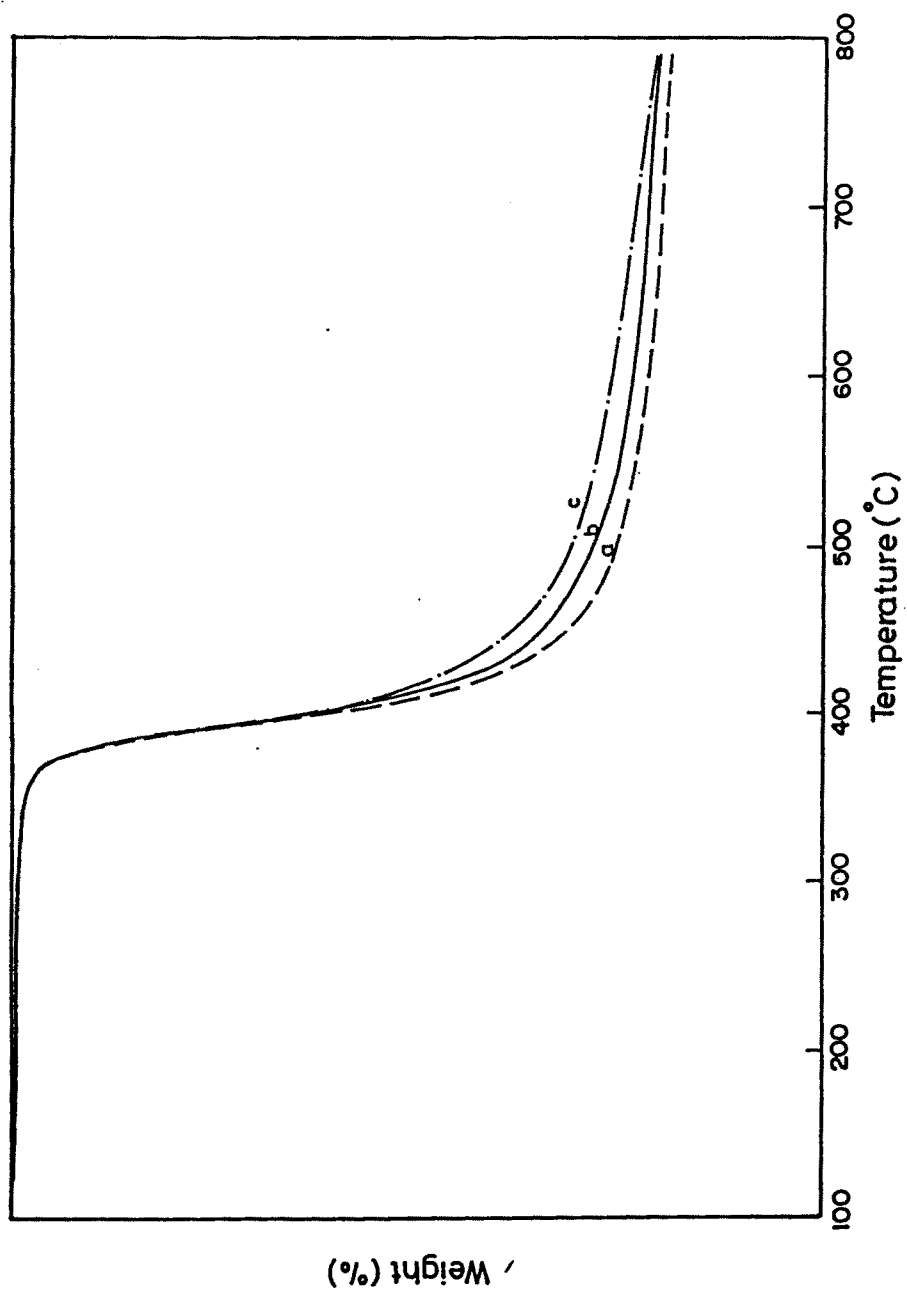


Figure 6.32 TGA curves of BMI-2 modified epoxy system
(a) 5%, (b) 10% and (c) 15% BMI-2 modified epoxy systems

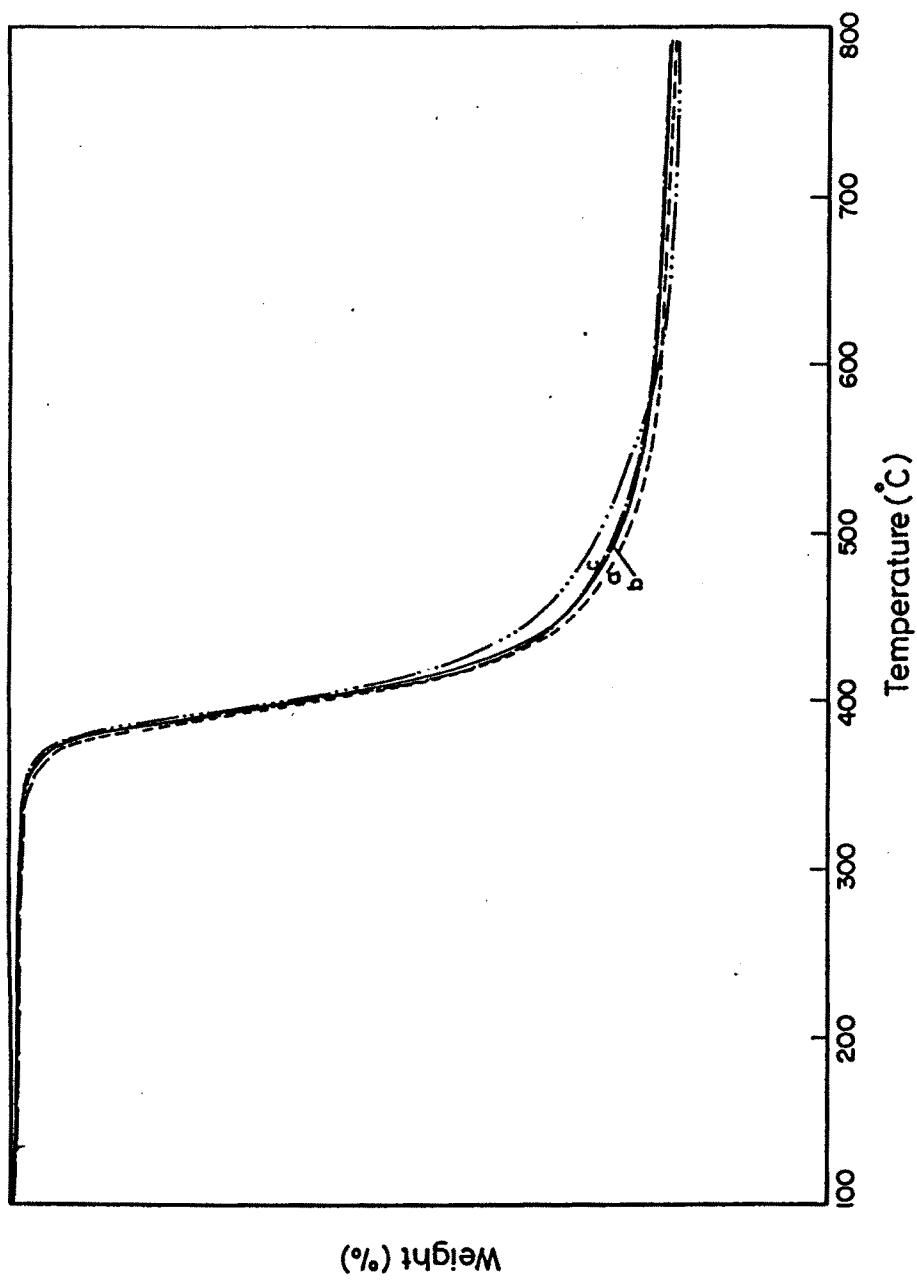


Figure 6.33 TGA curves of BMI-3 modified epoxy systems
(a) 5%, (b) 10% and (c) 15% BMI-3 modified epoxy systems

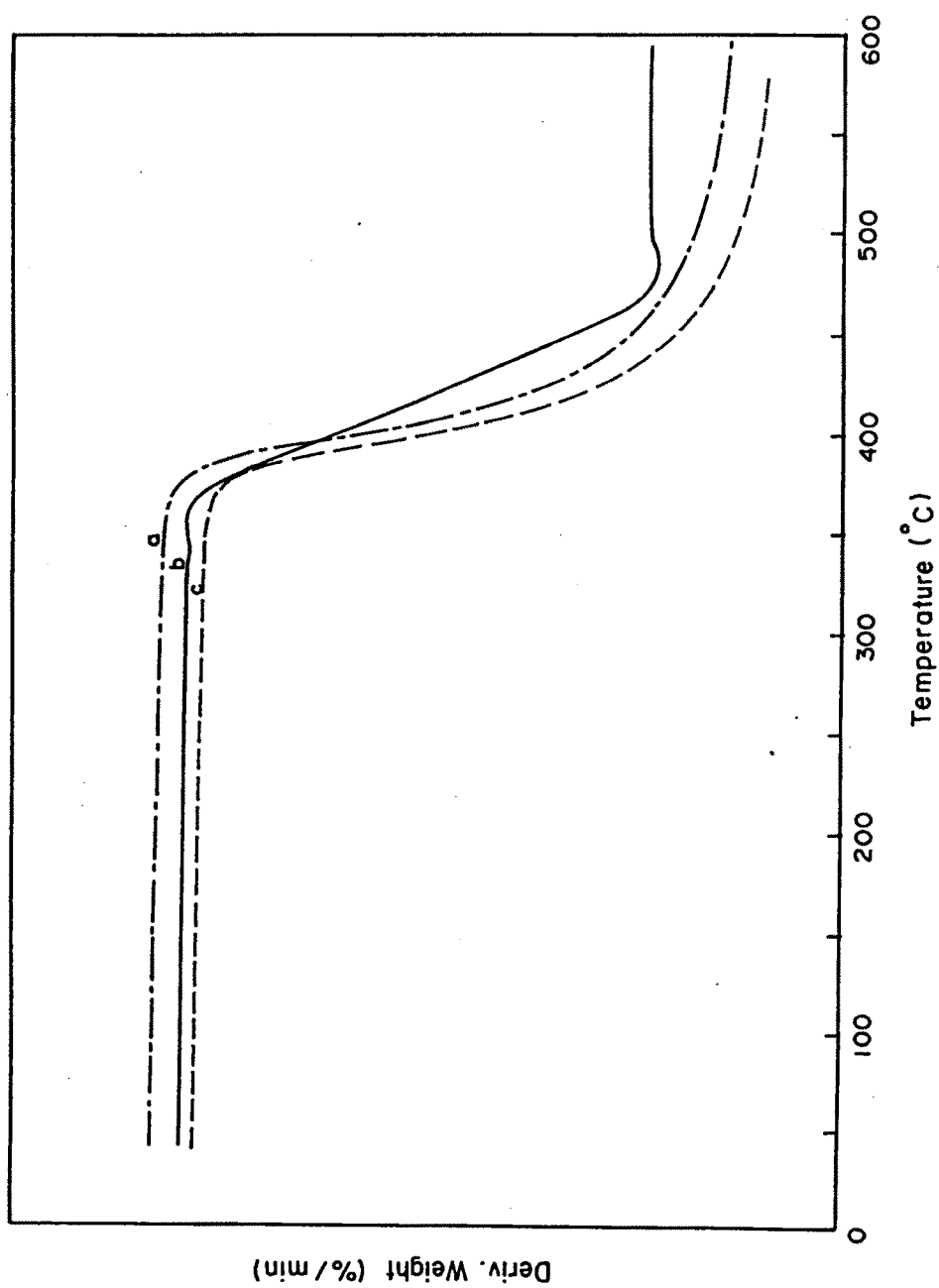


Figure 6.34 TGA curves of BMI-4 modified epoxy systems
(a) 5%, (b) 10% and (c) 15% BMI-4 modified epoxy systems

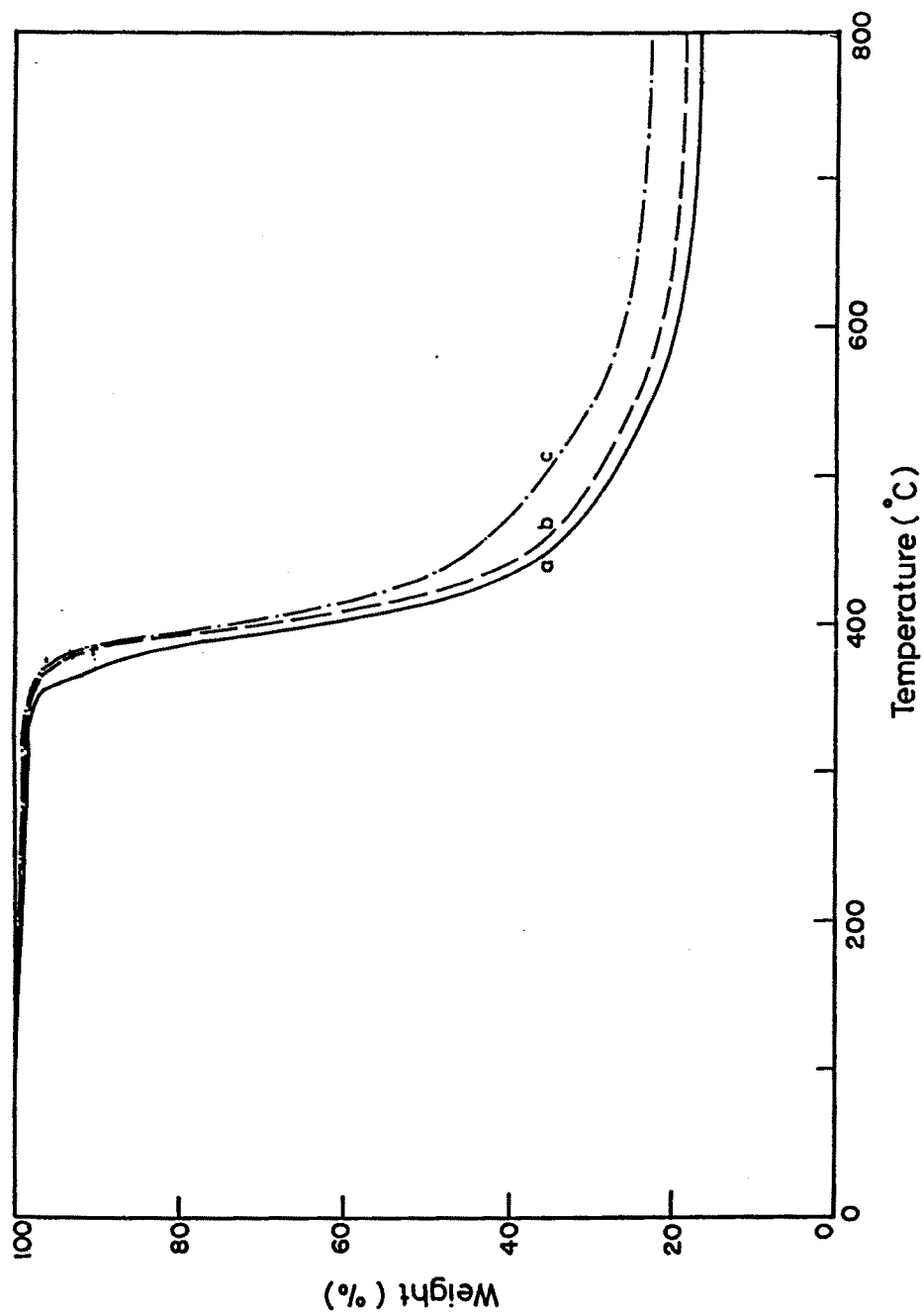


Figure 6.35 TGA curves of 10% siliconized epoxy / BMI-1 systems
 (a) 5%, (b) 10% and (c) 15% BMI-1 modified 10% siliconized epoxy systems

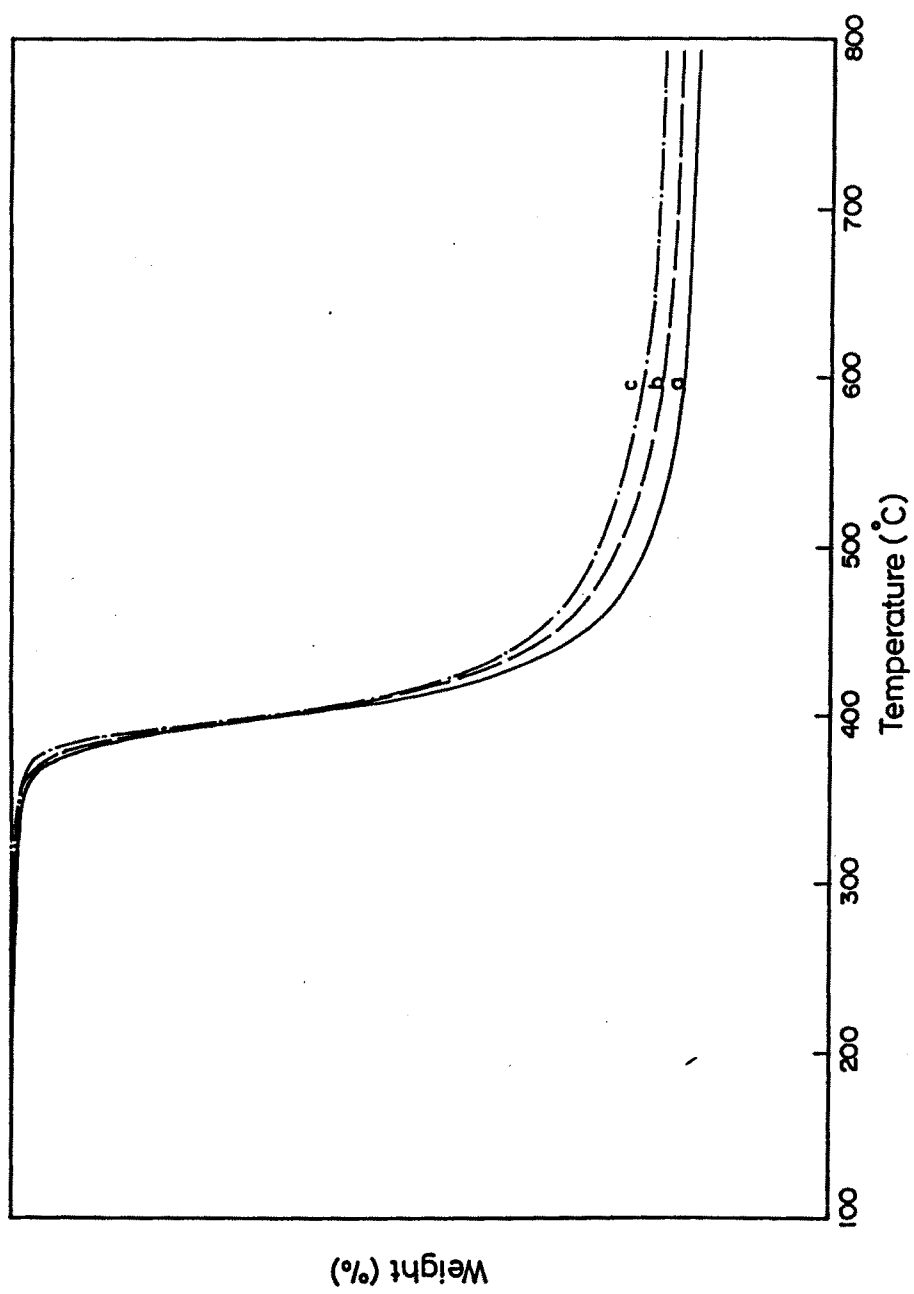


Figure 6.36 TGA curves of 10%-siliconized epoxy / BMI-2 systems (a) 5%, (b) 10% and (c) 15% BMI-2 modified 10% siliconized epoxy systems

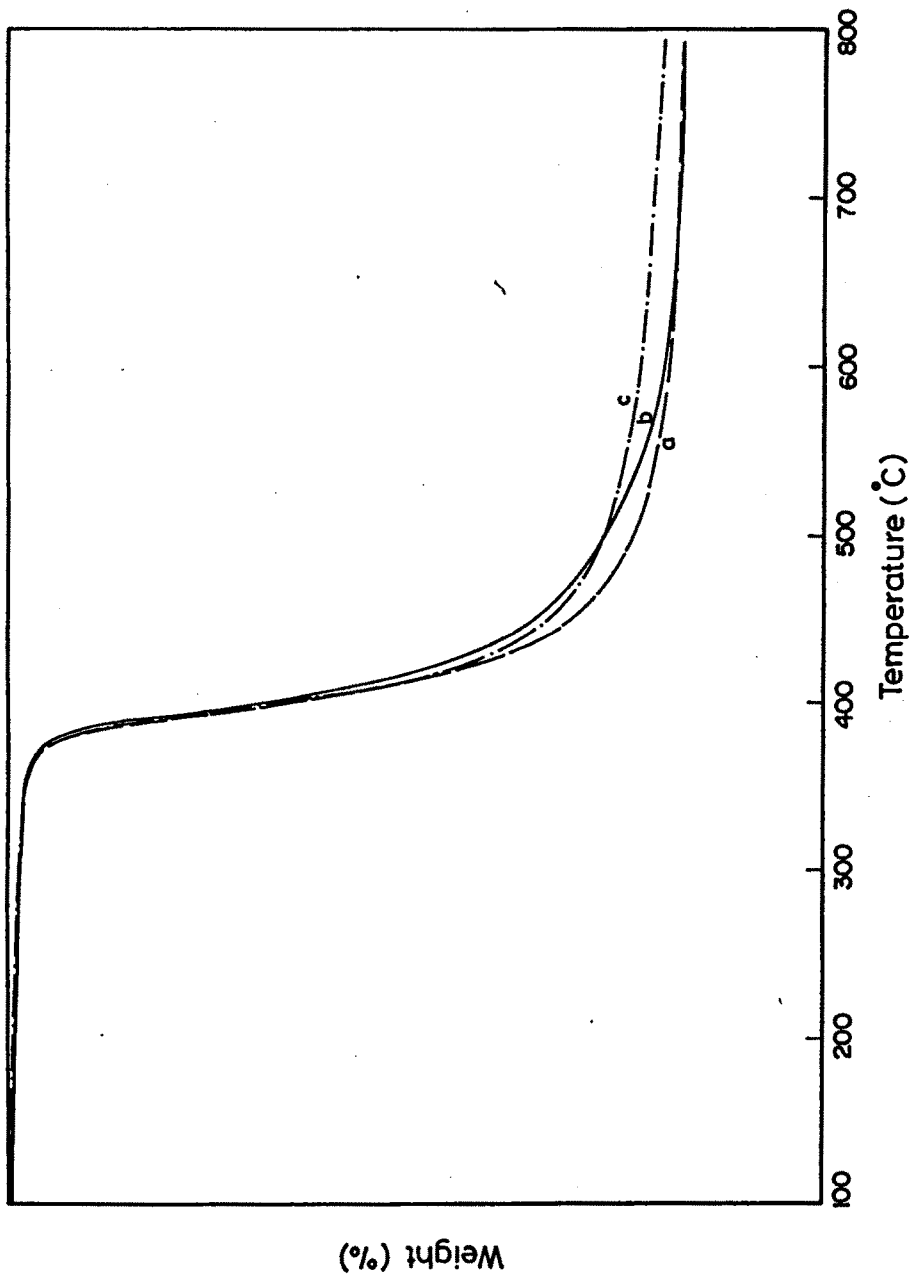


Figure 6.37 TGA curves of 10% siliconized epoxy / BMI-3 systems
(a) 5%, (b) 10% and (c) 15% BMI-3 modified 10% siliconized epoxy systems

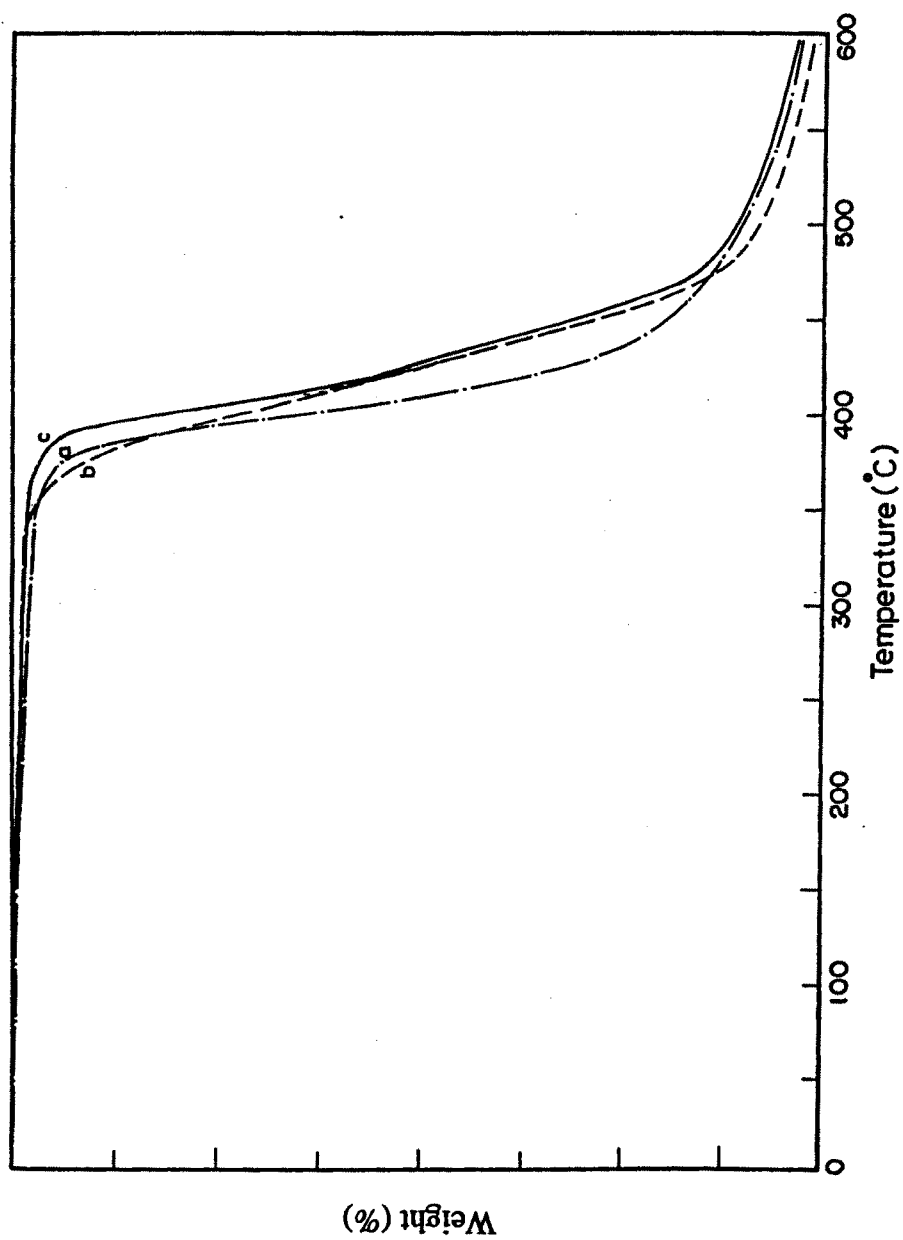


Figure 6.38 TGA curves of 10% siliconized epoxy / BMI-4 systems
(a) 5%, (b) 10% and (c) 15% BMI-4 modified 10% siliconized epoxy systems

bismaleimides modified systems exhibit higher improvement in HDT values when compared to that of aliphatic bismaleimides modified systems. In the case of aromatic bismaleimides modified epoxy and siliconized epoxy system, BMI-2 modified systems (Table 6.2) reveal higher improvement in HDT values compared to that of BMI-1 modified systems (Table 6.1) and the reason is same as explained in the case T_g and thermal degradation temperature. In the case of aliphatic bismaleimides modified epoxy and siliconized epoxy systems, BMI-3 modified systems (Table 6.3) show better improvement in the HDT values, whereas BMI-4 modified systems show decreasing trend (Table 6.4) and the trend is similar as observed in the case of T_g and thermal degradation temperature.

Table 6.1 Heat distortion temperature and glass transition temperature of epoxy, siliconized epoxy, BMI-1 modified epoxy and BMI-1 modified siliconized epoxy systems

Matrix System	Epoxy/HTPDMS/BMI-1 composition	Heat distortion temperature (°C)	Glass transition temperature (°C)
A	100/00/00	153	164
B	100/05/00	150	163
C	100/10/00	145	162
D	100/15/00	139	160
H1	100/10/05	146	166
I1	100/10/10	148	168
J1	100/10/15	151	172
N1	100/00/05	155	167
O1	100/00/10	156	173
P1	100/00/15	159	182

Table 6.2 Heat distortion temperature and glass transition temperature of epoxy, siliconized epoxy, BMI-2 modified epoxy and BMI-2 modified siliconized epoxy systems

Matrix System	Epoxy/ HTPDMS/ BMI-2 composition	Heat distortion temperature (°C)	Glass transition temperature (°C)
A	100/00/00	153	164
B	100/05/00	150	163
C	100/10/00	145	162
D	100/15/00	139	160
H2	100/10/05	161	172
I2	100/10/10	170	184
J2	100/10/15	175	189
N2	100/00/05	168	178
O2	100/00/10	176	188
P2	100/00/15	182	191

Table 6.3 Heat distortion temperature and glass transition temperature of epoxy, siliconized epoxy, BMI-3 modified epoxy and BMI-3 modified siliconized epoxy systems

Matrix System	Epoxy/ HTPDMS/ BMI-3 composition	Heat distortion temperature (°C)	Glass transition temperature (°C)
A	100/00/00	153	164
B	100/05/00	150	163
C	100/10/00	145	162
D	100/15/00	139	160
H3	100/10/05	142	165
I3	100/10/10	145	167
J3	100/10/15	149	170
N3	100/00/05	154	166
O3	100/00/10	155	170
P3	100/00/15	158	180

Table 6.4 Heat distortion temperature and glass transition temperature of epoxy, siliconized epoxy, BMI-4 modified epoxy and BMI-4 modified siliconized epoxy systems

Matrix System	Epoxy/HTPDMS/BMI-4 composition	Heat distortion temperature (°C)	Glass transition temperature (°C)
A	100/00/00	153	164
B	100/05/00	150	163
C	100/10/00	145	162
D	100/15/00	139	160
H4	100/10/05	139	160
I4	100/10/10	135	158
J4	100/10/15	133	157
N4	100/00/05	149	163
O4	100/00/10	147	162
P4	100/00/15	145	160