# THERMAL CHARACTERIZATION OF BISMALEIMIDE BLENDS

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4,4'-bismaleimidophenyl methane (BM) and 3,3'-bismaleimidophenyl sulfone (BS) were blended in solution using weight ratios 3:1 (MS31), 2:1 (MS21), 1:1 (MS11), 1:2 (MS12) and 1:3 (MS13). Chain extended bismaleimide resins were also prepared by treating BS/BM with 4,4'diaminodiphenyl ether in molar ratios of 1:0.3 (BM-E and BS-E resins). These resins were also blended with bismaleimides and the curing characteristics were evaluated by differential scanning calorimetry. Increase in BM content in BM : BS blends or increase in chain extended bismaleimide content in BM-E : BS or BS-E : BM blends resulted in a reduction of melting and curing temperatures. Indication about the extent of cross-linking was obtained from solubility measurements (in DMF) of isothermally cured resins (180 °C, lh and 220 °C, lh in an air oven). Thermogravimetric analysis of samples isothermally cured at 180 °C and 220 °C (lh each) was carried out in nitrogen atmosphere. Improvement in thermal stability of chain extended bismaleimides was observed on blending.

Bismaleimides are prime candidates as matrix resins for fibre reinforced composites and are finding increasing acceptance as engineering materials for high performance engineering applications. These resins are cured by thermally induced addition reaction giving highly crosslinked, void free network polymers having good physical properties, thermal stability, better fire resistance and lower water absorption than currently used epoxy resins. Chain extended bismaleimides, obtained by nucleophilic addition reaction with aromatic diamine have also been used as resins for advanced fibre reinforced composites.

In our earlier articles we have reported the synthesis and characterisation of bismaleimides and chain extended bismaleimides [1-7]. Effect of structure on thermal characteristics of bismaleimides was also studied. It was observed that the presence of electron donor groups in bismaleimides reduces the melting and curing temperatures of the resins. On the other hand, presence of electron withdrawing groups results in higher melting point and curing temperature [8-9].

Blending of bismaleimides containing electron withdrawing and electron donating substituents is expected to effect the melting and curing temperatures.

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## 1024 VARMA, TIWARI: CHARACTERIZATION OF BISMALEIMIDE

Eutectic mixture containing more than one bismaleimide/chain extended bismaleimides have been commercially available. Thus easily processible resin system "Kerimid 353", an eutectic mixture of three bismaleimides [10] was developed by Technochemie GmbH and marketed by Rhone–Poulenc. The various components of this eutectic mixture are di(4-maleimidophenyl) methane, 2,4-bismaleimido toluene and 1,6-bismaleimido-2,2,4-trimethyl hexane. The resin is melt processible and prepregs can be prepared by means of filament winding technique. Another commercially availale thermoset polyimide resin, Technochemie M751, is also an eutectic mixture of two components [11]. A literature survey has revealed that no systematic studies have been carried out to study the effect of blend composition on the thermal behaviour of these thermosetting resins.

It was, therefore, considered of interest to investigate the effect of blending bismaleimides/chain extended bismaleimides on their fusion and curing characteristics and thermal stability. In the present work 3,3'-bismaleimidophenyl sulfone (BS), containing electron withdrawing sulfone group, was blended with 4,4'bismaleimidophenyl methane (BM), which has electron donating methylene group in the backbone. The effect of blend composition on the thermal characteristics was evaluated by using DSC and TG.



Chain extended bismaleimides were also used in blend preparation and were obtained by treating BS/BM with 4,4'-diaminodiphenyl ether in the molar ratios of 1:0.3. The representative structure of the resin thus obtained is as follows:



# Experimental

#### Starting materials

3,3'-diaminodiphenyl sulfone was prepared by reduction of 3,3'-dinitrodiphenyl sulfone (Hindustan Organic Chemicals Ltd.) with sodium polysulfide in methanol [12], Acetone (Sarabhai Chemicals) was dried over  $K_2CO_3$ . Acetic anhydride (BDH) was distilled before use. Anhydrous sodium acetate (obtained by fusion), sodium sulfide (IDPL), sulfur powder (Glaxo), methanol (Sarabhai Chemicals), maleic anhydride, 4,4'-diaminodiphenyl methane (Fluka) and 4,4'-diaminodiphenyl ether (Fluka) were used as such.

## Preparation of bismaleimides

Bismaleimides, BM and BS were prepared using the procedure reported earlier by reacting maleic anhydride with diamines in acetone [6, 13, 14]. The cyclization of amic acid intermediate was carried out by using sodium acetate and acetic anhydride. The crude product was purified by passing a chloroform solution through silica gel column. Excess of chloroform was removed under vacuum using a rotary evaporator.

The bismaleimide resins were characterized by using 5DX Nicolet FTIR spectrophotometer. The elemental composition of the resins was determined by using Perkin–Elmer 240C Elemental Analyser.

Chain extension of BM and BS with 4,4'-diaminodiphenyl ether was carried out in acetone. The molar ratio of bismaleimides and diamine was 1:0.3. The details of such chain extension reaction have been reported elsewhere [6, 15].

#### Blending of bismaleimides

Blending of bismaleimides, BM:BS, chain extended bismaleimides BM-E/BS-E:BM/BS and BM-E:BS-E was carried out in solution using the weight ratios (w/w) 3:1, 2:1, 1:1, 1:2 and 1:3. Known quantities of resin were dissolved in chloroform to form a homogeneous solution. Excess of chloroform was then removed under vacuum using rotary evaporator. The shining powder of resin blend was then collected. The resin blends thus obtained have been designated on the basis of constituents and blend composition. Thus, for example the blend of BM:BS resin containing 3:1 weight ratios has been designated as MS31, BM-E:BS resin of 1:1 weight ratio as MES11. The details of blend designation are given in Table 1.

	Composition,	Composition, Designation		Percentage of			
Kesin system	w/w besignation		N	С	Н		
1	2	3	4	5	6		
BM : BS	1:0	MS10	7.76	72.9	4.28		
			(7.8)	(70.39)	(3.9)		
	3:1	MS31	6.80	60.97	3.3		
			(7.56)	(67.2)	(3.6)		
	2:1	MS21	6.95	63.8	4.3		
			(7.5)	(66.19)	(3.55)		
	1:1	MS11	7.09	62.84	3.5		
			(7.3)	(64.2)	(3.4)		
	1:2	MS12	7.03	58.23	2.88		
			(7.16)	(62.3)	(3.2)		
	1:3	MS12	6.32	58.08	3.0		
			(7.08)	(61.44)	(3.16)		
	0:1	<b>MS</b> 01	6.88	59.9	3.02		
			(6.86)	(58.82)	(2.9)		
BM-E:BS	1:0	MES10	7.74	70.45	4.69		
			(8.7)	(70.0)	(4.0)		
	3:1	MES31	7.87	65.62	4.28		
			(8.25)	(67.72)	(3.97)		
	2:1	MES21	7.14	62.71	3.92		
			(8.10)	(66.75)	(3.86)		
	1:1	MES11	8.17	60.64	3.75		
			(7.79)	(64.79)	(3.63)		
	1:2	MES12	7.68	62.82	3.92		
			(7. <b>49</b> )	(62.8)	(3.4)		
	1:3	MES13	7.18	59.3	3.5		
			(6.11)	(61.8)	(3.28)		
RS_F · RM	1.0	SEM10	6.6	59.9	4.09		
00-L.DW	1.0	0,01110	(7.78)	(60.5)	(3.3)		
	3.1	SEM31	7.4	60.15	4.09		
	5.1	000000	(6.8)	(57.6)	(3.06)		
	2 · 1	SEM21	6.8	60.18	4.21		
	2.1	0011121	(7.14)	(59.9)	(3.2)		
	1 · 1	SEM11	7.0	62.81	4.06		
			(7.8)	(64.8)	(3.6)		
	1.2	SEM12	7.75	64.58	4.06		
	1.2	02	(7.8)	(66.49)	(3.7)		
	1:3	SEM13	7.98	64.58	4.17		
			(7.8)	(67.39)	(3.66)		

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# 1026

	Composition,		Percentage of			
Resin system	w/w	Designation	N	С	Н	
1	2	3	4	5	6	
BM-E: BS-E	3:1	MESE31	7.58	68.56	5.09	
			(8.45)	(67.87)	(4.06)	
	2:1	MESE21	7.04	66.25	4.90	
			(8.37)	(66.99)	(3.98)	
	1:1	MESE11	7.11	63.88	4.7	
			(8.7)	(65.25)	(3.65)	
	1:2	MESE12	8.02	63.11	4,57	
			(8.06)	(63.63)	(3.69)	
	1:3	MESE13	7.8	62.24	4.45	
			(7.99)	(62.83)	(3.62)	

Figures in parenthesis indicate calculated values.

## Curing of blends

Curing was done by heating the various resin samples in shallow aluminium dishes at  $180^{\circ}$  for lh and then at  $220^{\circ}$  for lh in an air oven. The extent of crosslinking was determined by solubility measurements. For this purpose cured resins were heated in DMF at  $150^{\circ}$  for 5 minutes. The insoluble residue was filtered, washed several times with acetone, dried and weighed. Percentage solubility of the resins was then calculated.

% solubility = 
$$\frac{W_0 - W_1}{W_0} \times 100$$

where  $W_0$  = initial weight of polymer;  $W_1$  = wt. of insoluble material.

#### Thermal characterization

A DuPont 1090 thermal analyser having a TG951 module and a DSC 910 module was used to evaluate the thermal behaviour of resins. The TG measurements were done in nitrogen atmosphere (flow rate 60 cm<sup>3</sup>/min) and a sample size of  $10 \pm 2$  mg was used. DSC studies were carried out in static air atmosphere.

#### Results

Blending of bismaleimides having different electronic requirements may lead to formation of loosely bound complexes. The existence of such a charge transfer complex may be substantiated by IR spectroscopy. Hence bismaleimide resin blends were analyzed for any change in the position of absorption bands. In the IR spectra, characteristic band associated with imide group was observed at 1720 cm<sup>-1</sup>. The other prominent absorptions arising due to phenyl group (at 1600 cm<sup>-1</sup> and 1490 cm<sup>-1</sup>), CN (at 1390 cm<sup>-1</sup>), SO<sub>2</sub> group (1155 cm<sup>-1</sup> and 1330 cm<sup>-1</sup>),  $-CH_2-(1445 \cdot 1485 \text{ cm}^{-1})$  were also observed. In blends containing chain extended bismaleimides, band at 1630 cm<sup>-1</sup> (due to N—H in plane bending) and at 3380–3480 cm<sup>-1</sup> (N—H stretch) were observed. No additional absorption bands indicative of loosely bound complex was observed.

Results of elemental analysis of resin blends are given in Table 1. The results agree in most cases with the calculated values. Resin blends having carbon content ranging from  $\sim 73\%$  to  $\sim 60\%$  were obtained.

Thermal behaviour of blends of bismaleimides, bismaleimides : chain extended bismaleimide and chain extended bismaleimides is discussed separately.

# Thermal behaviour of blends of BM : BS

In the DSC scans of neat BS and BM, endothermic transitions due to melting were observed at 213° and 157° respectively. The melting temperature reduced on blending and the reduction depended on blend compositions. When BM and BS were blended in equal ratios (MS11) two endothermic transitions appeared at 145° and 182° corresponding to melting of BM and BS respectively. However, as the content of BM is increased, the melting transition corresponding to BS was reduced significantly (Figs 1 and 2).

Exothermic transition peak arising due to curing was observed above the melting temperature. These exothermic transitions were characterized by determining (a) kick off temperature of polymerization  $(T_i)$  which was noted from the initial deviation in the position of base line. (b) Onset temperature for curing reaction  $(T_1)$  (c) exothermic peak temperature  $(T_{exo})$  (d) temperature  $(T_2)$  for completion of reaction and (e) heat of curing  $(\Delta H)$ .  $T_1$  and  $T_2$  were obtained by extrapolating the steep portions of front side and back side of exothermic transition to the base line.

On blending  $T_{exo}$  values also reduce considerably. On addition of small amount of BM (MS13), the  $T_{exo}$  value reduces from 297° to 282°. As BM content was increased, the  $T_{exo}$  values decreased and in MS31 where BM was maximum, the  $T_{exo}$ value (256°) was even lower than that of neat BM (264°) (Table 2).

The decrease in the magnitude of  $T_{exo}$  may be explained in terms of polar

J. Thermal Anal. 32, 1987

1028



Fig. 2 DSC trace of MS31 (in static air)

requirements of the two bismaleimide resins. The existence of  $SO_2$  group in BS increases the electron deficiency in the maleimide double bond due to inductive effects while in BM, the CH<sub>2</sub> group having a + I and + R effect helps in reducing the electron deficiency in the double bond. Therefore, when a blend of BM: BS in taken, then due to electrostatic interaction the polymerization is initiated at a lower temperature, thereby reducing  $T_{exo}$ . The copolymerization is thus facilitated by favourable polar effect. Similar results have earlier been reported for copolymerization of stilbene and maleic anhydride [16]. The heat of curing of bismaleimide was also influenced by blending (Table 2).

Blend designation	<i>T</i> <sub>m</sub> , °C	<i>T<sub>i</sub></i> , ℃	<i>Т</i> 1, °С	$T_{exo}, ^{\circ}C$	$T_2,$ °C	<i>∆H</i> , J/g
MS10	157	185	219	264	315	214
MS01	213	244	246	297	337	130
MS13	196	211	232	282	340	260
MS12	202	217	234	283	350	214
MS11	145	211	235	272	344	224
	182					
MS21	146	190	222	260	344	263
MS31	146	184	211	256	340	261

<b>Table 2</b> Thermal characteristics of B	M : BS	blends
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#### Table 3 Effect of thermal treatment (1 h) on solubility of BM : BS blends\*

Blend	Temperature	of treatment
designation	180 °C	220 °C
MS10	52.7	1.7
<b>MS</b> 01	99	37.4
<b>MS13</b>	95	3.5
MS12	94.6	4.3
MS11	86	2.8
MS21	67.1	1.0
MS31	59.6	0.9

\* Same samples were heated at 180 °C for 1 h and at 220 °C for 1 h.

The enhancement in cross-linking reaction on curing of blends was also confirmed from the solubility measurements (Table 3). Thus, when neat BS was heated to 220° for lh, the product had appreciably high solubility (37.4%) in DMF. However, by the addition of BM (MS13) the solubility was decreased to 3.5% under same conditions.

## Blends of bismaleimides and chain extended bismaleimides

Chain extension of bismaleimides (i.e. BM or BS) with 4,4'-diaminoc iphenyl ether resulted in disappearance of endothermic transition associated with melting. In BM-E: BS blends the melting temperature was lower than BS resin (Fig. 3). In case of BS-E: BM blends no endothermic transition associated with melting was observed.



Fig. 3 DSC trace of MES13 (in static air)

A single exothermic transition associated with curing reaction was observed in BM-E where as in BS-E this exotherm had a bimodal character. In BM-E: BS blends single exotherm was observed in all cases (Figs 3 and 4). In BS-E: BM blends a single exotherm was observed only in SEM 13 and SEM 12 (Fig. 5c). As BS-E content was increased, the bimodal character in these blends became more obvious (Figs 5a, 5b and 5d). A second exothermic transition around 250° increased on increasing BS-E content in resin blends (Fig. 5d). The results of DSC scans have been summarised in Table 4.



Fig. 4 DSC trace of MES31 (in static air)





Fig. 5a DSC trace of SEM11 (in static air)

Fig. 5b DSC trace of SEM21 (in static air)



Fig. 5c DSC trace of SEM13 (in static air)

Fig. 5d DSC trace of SEM31 (in static air)

Blend designation	<i>T</i> ,, °C	<i>Ti</i> , ℃	$T_1,$ °C	$T_{exo},$	<i>T</i> ₂, ℃	∆ <i>H</i> , J/g
MES10		86	89	233	293	158
MES13	194	202	215	254	332	181
MES12	184	197	205	243	314	150
MES11	172	187	187	239	311	152
MES21		142	160	230	311	165
MES31		144	151	215	295	117
SEM10		75	75	152	275	36
				245		15
SEM13	<del></del>	140	177	232	309	239
SEM12		133	169	226	320	202
SEM11		139	166	213	329	181
				250		
SEM21		134	163	207	336	178
				245		
SEM31		100	140	200	336	173
				251		

Table 4 Thermal characteristics of blends of chain extended bismaleimides and bismaleimide resins

The  $T_{exo}$  values reduced considerably on blending BS-E: BM and BM-E: BS. For example in MES13,  $T_{exo}$  value of BS reduced from 297° to 254° (Fig. 3). Similarly in SEM13,  $T_{exo}$  value reduced from 264° (BM) to 232° (Fig. 5c) (Table 4).

Solubility measurements of isothermally cured resin samples confirmed the polymerization. In neat BS, BS-E and BM-E cross linking was observed only after heating at 220° for several hours (Table 5).

Blend	Tempe	erature
designation	180 °C	220 °C
MES10	87	19.4
MES13	47	1.8
MES12	29.4	1.7
MES11	18	1.6
MES21	17	1.9
MES31	7	0.2
SEM10	32.2	25.5
SEM13	19	1.3
SEM12	19.4	2.0
SEM11	20.2	2.7
SEM21	16.4	2.5
SEM31	17.2	2.7

Table 5 Effect of thermal treatment (1 h) on solubility of blends of bismaleimides and chain extended bismaleimides\*

\* Same samples were heated at 180  $^{\circ}\mathrm{C}$  for 1 h and at 220  $^{\circ}\mathrm{C}$  for 1 h.

Table 6 Thermal characteristics of BM-E: BS-E blends

Blend designation	<i>T</i> ,, °C	<i>Т</i> <sub><i>i</i></sub> , °С	<i>T</i> <sub>1</sub> , °C	T <sub>exo</sub> , °C	<i>T</i> ₂, °C	<i>∆H</i> , J/g
MESE13	83	110	120	150 231	268	33
MESE12	85	100	116	143 232	270	57
MESE11	83	99	116	144 238	275	48
MESE21	89	110	122	150	253	30
MESE31	89	109	122	157	222	21

1034 VARMA, TIWARI: CHARACTERIZATION OF BISMALEIMIDE

In chain extended resins (i.e. BM–E and BS–E) a secondary amino group is present which is formed during the chain extension reaction. When these chain extended bismaleimides are blended with bismaleimides and these blends are heated, the secondary amino group may participate in nucleophilic addition reaction with maleimide double bond leading to a cross-linked product. This Michael reaction of secondary amino group with a double bond of bismaleimide is expected to occur at lower temperature. Hence a reduction in  $T_{exo}$  is expected.



#### BM-E: BS-E blends

An endothermic transition due to melting was observed in case of BM-E:BS-E blends. The transition appeared around 82–89°. The  $T_{exo}$  values were not influenced on blending. When BM-E content was higher (MESE31) only single exothermic transition was observed (Fig. 6b). With the increase in BS-E content a bimodal type of exotherm was observed and this bimodal character was very noticeable in MESE13 (Fig. 6a).

Isothermal curing of these chain extended bismaleimide blends was carried out at 180° for 1h and at 220° for 1h, 2h, 3h and at 230° for 1h. The cured resins were then tested for their solubility in DMF and were found highly soluble. The solubility decreased with increase in time and temperature of isothermal heating (Table 7).

#### Thermogravimetric analysis

Thermal stability of the bismaleimide blends (cured) was evaluated by thermogravimetric analysis. From the TG trace initial decomposition temperature (IDT), temperature of maximum rate of weight loss  $(T_{max})$ , final decomposition temperature  $(T_f)$  and residual weight at 800° (percentage char yield  $Y_c$ ) were



Fig. 6a DSC trace of MESE13 (in static air) b DSC trace of MESE31 (in static air)

Table 7 Effect of therma	l treatment on solubilit	ity of BM-E: BS-E blends*
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 Blend designation	180 °C 1 h	220 °C 1 h	220 °C 2 h	220 °C 3 h	230 °C 1 h
 MESE10	87	19.4	3.3	1.7	
MESE01	32	25.5	11.5	8.1	4
MESE13	37.6	19	15.4	9.4	6
MESE12	50	24	12.2	7	9
MESEII	47	27	17.5	12	10.3
MESE21	28.6	19	13.3	9	8
MESE31	41.6	27	18	11	8.6

\* Same samples were heated at 180 °C for 1 h at 220 °C for 1 h, 2 h, 3 h and at 230 °C for 1 h.

determined. IDT and  $T_{\rm f}$  was obtained by extrapolation. The cured resins were obtained by isothermal heating of resin blends at 180° for 1h and 220° for 1h.

The results of these analyses are given in Table 8. Typical thermogravimetric traces are given in Fig. 7. The characteristic decomposition temperatures and char yield depended on the nature of the resin and composition of resin blend. Char yield of 44% was observed in BS resin while in BM it was 51. Blending of these resins resulted (i.e. MS13 and MS31) in an improvement in char yield. This conclusion is based on the observed difference in theoretical values (obtained by calculating the  $Y_c$  taking into account the BM, BS composition and individual char yields of the resins) and experimental values. Similarly an improvement in IDT,  $T_{max}$  and  $T_f$  was observed.

Blend	IDT °C	$T_{\text{max}},$ °C	$T_{\rm f},$ °C	Y <sub>c</sub> , %
MS10		502	532	51
MSIU	400	503	507	J1 44
MSUI	439	4/0	514	48
MS13	472	487	514	40
	(466)	(483)	(513)	(46)
<b>MS</b> 31	495	508	535	51
	(479)	(498)	(526)	(49)
MES10	373	433	520	43
MES13	444	469	509	50
	(437)	(465)	(510)	(44)
MES31	417	445	510	51
	(394)	(444)	(517)	(43)
SEM10	381	418	500	44
SEM13	469	489	522	51
	(460)	(482)	(524)	(49)
SEM31	409	447	517	49
	(407)	(439)	(508)	(46)
MESE13	385	437	520	43
	(379)	(422)	(505)	(44)
MESE31	384	432	524	46
	(375)	(430)	(515)	(43)

Table 8 Results of thermogravimetric analysis of bismaleimide resin blends (cured) (in N2)

Figures in parenthesis indicate calculated values (obtained from the rule of mixtures).

Chain extension of bismaleimide with 4,4'-diaminodiphenyl ether resulted in a decrease in IDT,  $T_{max}$ ,  $T_f$  and  $Y_c$ . Thus IDT of BM-E resin (designated as MES10) was almost 100° lower than BM resin. Blending of these resins with bismaleimides significantly improved thermal stability as is evident from the data given in Table 8.

Blends of chain extended bismaleimides (MESE13 and MESE31) started degrading at a lower temperature.  $T_{max}$  and char yields of these resins were also lower.

#### Conclusions

The following conclusions can be drawn on the basis of above studies:

1. Blending of a bismaleimide containing electron donating substituent with a bismaleimide containing electron withdrawing substituent reduces melting and curing temperatures. Extent of cross-linking, as determined from solubility measurements, is also enhanced.

1036



Fig. 7a TGA trace of SEM31 (in nitrogen atmosphere) b TGA trace of SEM13 (in nitrogen atmosphere)

2. Chain extended bismaleimide when blended with bismaleimide further reduces the curing temperature due to the participation of secondary amino group in addition reaction with maleimide double bond and formation of a cross-linked product.

3. Thermal stability of cured resins is influenced by the structure of resins. Higher char yields were obtained when bismaleimides were blended. Chain extended bismaleimides also showed an improvement in thermal stability when blended with bismaleimides.

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## References

- I. K. Varma, G. M. Fohlen and J. A. Parker, U.S. Pat. 4, 276, 344 (1981).
- 2 I. K. Varma, G. M. Fohlen and J. A. Parker, U.S. Pat. 4, 395, 557 (1983).
- 3 I. K. Varma, G. M. Fohlen and J. A. Parker, J. Macromol. Sci. Chem. Ed., 19 (1983) 209.
- 4 I. K. Varma, G. M. Fohlen and J. A. Parker, J. Polym. Sci. Polym. Chem. Ed., 21 (1983) 2017.

## 1038 VARMA, TIWARI: CHARACTERIZATION OF BISMALEIMIDE

- 5 I. K. Varma, A. K. Gupta, Sangita and D. S. Varma, J. Appl. Polym. Sci., 28 (1983) 191.
- 6 I. K. Varma, Sangita and D. S. Varma, J. Polym. Sci. Polym. Chem. Ed., 22 (1984) 1419.
- 7 I. K. Varma, Sangita and D. S. Varma, J. Appl. Polym. Sci., 29 (1984) 2807.
- 8 I. K. Varma, G. M. Fohlen and J. A. Parker, ACS symposium series "Cyclopolymerisation and polymers with chain ring structures" Ed. G. Butler and J. E. Kresta, 195 (1982) 253.
- 9 I. K. Varma and S. Sharma, Polymer, 26 (1985) 1561.
- 10 H. Petrovicki, H. D. Stenzenberger and A. Von Harnier, Proc., 32nd SPE Tech. Conf., (1974) 88.

- 11 H. D. Stenzenberger, Brit. Pat., 1, 501, 606 (1976).
- 12 I. K. Varma and P. V. Satyabhama, J. Composite Material, 20 (1986) 410.
- 13 N. E. Searle, U.S. Pat., 2, 444, 536 (1948).
- 14 I. K. Varma, Manjeet S. Choudhary, B. S. Rao, Sangita and D. S. Varma, J. Macromol. Sci. Chem., A21 (1984) 793.
- 15 Sangita, Ph. D. thesis "Bismaleimides: Synthesis, Characterization and Applications", IIT Delhi, 1986.
- 16 R. W. Lenz, in "Organic Chemistry of Synthetic High Polymers", Interscience, New York 1968, p. 331.

Zusammenfassung — 4,4'-Bismalimidophenyl-methan (BM) und 3,3'-Bismalimidophenyl-sulfon (BS) wurden in Lösung in den Gewichtsverhältnissen 3:1 (MS31), 2:1 (MS21), 1:1 (MS11), 1:2 (MS12) und 1:3 (MS13) gemischt. Auch kettenpolymerisierten Bismalimid-Harze wurden durch Behandlung von BS/BM mit Diaminodiphenylether im Molverhältnis 1:0,3 dargestellt (BM-E- und BS-E-Harze). Die Kennwerte der Aushärtung von Mischungen dieser Harze mit den Bismalimiden wurden mittels DSC ermittelt. Eine Erhöhung des BM-Gehaltes in den BM: BS-Mischungen oder des Gehaltes der BM-E: BS oder BS-E-Mischungen an kettenpolymerisierten Bismalimiden führt zu einer Erniedrigung der Schmelz- und Aushärtetemperaturen. Hinweise über den Vernetzungsgrad wurden aus Löslichkeitsmessungen (in DMF) von Isotherm (je 1 Stunde bei 180 und 220 °C in Luft) gehärteten Harzen erhalten. Die thermogravimetrische Analyse der Isotherm bei 180 bzw. 220 °C 1 Stunde ausgehärteten Proben wurde in Stickstoffatmosphäre ausgeführt. Die thermische Stabilität der Bismalimide wird durch Verschneiden verbessert.

Резюме — 4,4-бис-малеинимидофенилметан (БМ) и 3,3-бис-малеинимидофенилсульфон (БС) были смешаны в растворе в весовых соотношениях 3:1 (МС 31), 2:1 (МС 21), 1:1 (МС 11), 1:2 (МС 12) и 1:3 (МС13). Были также получены смолы с удлиненным бис-малеинимидным звеном обработкой БС/БМ с 4,4-диаминдифениловым эфиром в молярном соотношении 1:0,3 (смолы БМ-Е и БС-Е). Эти смолы затем смешивались с бис-малеинимидами и методом ДСК параметры их отверждения. Увеличение содержания БМ в смесях БМ-БС или же увеличение содержания удлиненной бис-малеинимидной цепи в смесях БМ-БС или же увеличение содержания удлиненной бис-малеинимидной цепи в смесях БМ-БС или же увеличение содержания удлиненной бис-малеинимидной цепи в смесях БМ-БС или же увеличение содержания были получены измерением растворимости изотермически отвержденных смол (р течении 1 часа на воздухе при температуре 180 и 220°) в диметилформамиде. Термогравиметрический анализ изотермически отвержденных образцов был проведен в атмосфере азота. При смешении бис-малеинимидов с удлиненной цепью наб. юдалось улучшение их термоустойчивости.