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EFFECT OF α-METHYLSTYRENE OF THE CURING BEHAVIOUR OF VINYL ESTER RESINS

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The curing behaviour of bismethacryloxy derivative of diglycidyl ether of bisphenol A (vinyl ester resin) containing styrene as the reactive diluent (40% w/w) was studied using gel point determination method and DSC. Seven samples of styrene/α-methylstyrene in the ratio 40:0, 35:5, 30:10, 25:15, 20:20, 15:25 and 0:40 were studied. Delayed curing was observed in samples containing increasing proportions of α-methylstyrene. The energy of activation decreased from 869 kJ mol^{-1} to 333 kJ mol^{-1} as the concentration of α-methylstyrene increased in the formulations. However, no difference in thermal stability was observed by replacement of styrene by α-methylstyrene. It was concluded that in vinyl ester resin samples 10–15% α-methylstyrene and 30–25% styrene can be used as reactive diluent.

Bis(methacryloxy) derivatives of diglycidyl ether of bisphenol A resins (vinyl ester resins) can be converted to a cross-linked network by free radical polymerization of vinylic double bonds. These resins can be used in pure form or may contain a vinyl type reactive diluent such as styrene [1–3]. In our earlier papers we have reported the effect of styrene on the properties of vinyl ester resins [4, 5]. Partial replacement of styrene by α-methylstyrene may be helpful in the vinyl ester resin formulation because α-methylstyrene (α-MS) is an effective exotherm depressant. Studies on styrenated polyester resins have indicated that α-MS does not adversely affect the physical properties of the cured products but prolongs the time required to reach the exotherm peak temperature. The exotherm peak temperature is also reduced [6]. There is also a significant difference in the cost of the two monomers. Therefore it was considered of interest to study the curing behaviour of vinyl ester resin containing styrene/α-methylstyrene.

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Experimental

Materials

Epoxy resin (Araldite LY 556, Ciba-Geigy) having an epoxy equivalent 185 g/equiv (obtained by titration), methacrylic acid (Fluka), styrene (Fluka), α-methylstyrene (Ferak), imidazole (Loba-Chemie Indo Austranal Co.) and hydroquinone (Loba-Chemie Indo Austranal Co.) were used without further purification.

Synthesis of vinyl ester resin

In a 2 l reaction vessel equipped with a mechanical stirrer 900 g of diglycidyl ether of bisphenol A, 413 mL of methacrylic acid, 4.03 g of hydroquinone and 3.21 g of imidazole were placed. The reaction was carried out for 14 h till the acid number was found to be less than 10. The amber coloured solution of the vinyl ester resin thus prepared was stored at low temperature.

Characterization of resin

The viscosity of the resin containing different amounts of styrene and α-methylstyrene was determined by a Brookfield Synchro-Lectric Viscometer at room temperature (~30 °C) using spindle LV 2.

Gel point determination of the resins was done using 70 g of resin, 2.8 g of benzoyl peroxide and 1.5 ml of N,N-dimethylaniline at 25°. The increase in temperature of samples as a function of time was measured and the gel point was determined by noting down the peak position (by extrapolation).

Neat resin castings were prepared by using a mild stainless steel mould having a teflon spacer. The vinyl ester resin containing styrene/α-MS and 2% benzoyl peroxide was carefully poured into the mould and precaution was taken to remove all trapped air bubbles from the solution. This assembly was placed in an air oven. The temperature was gradually increased to 90° and this temperature was maintained for $1^1/_2$ h. After cooling the mould, sheets of vinyl ester resin were removed.

Thermal studies were carried out by using a DuPont 1090 Thermal Analyzer having a 910 DSC and a 951 TG module. DSC studies were conducted in the dynamic mode in the temperature range 40–210° at a heating rate of 5 deg/min in static air. Isothermal curing studies were done at 100°.

The thermal stability of cured VE resin sheets was investigated using dynamic thermogravimetry at a heating rate of 10 deg/min in nitrogen atmosphere.

Results and discussion

Viscosity measurements

The Brookfield viscosity of VE resin samples containing styrene and α-MS is given in Table 1. An increase in the concentration of α-methylstyrene from 15 to 40% (w/w) resulted in a slight increase in viscosity. This may be attributed to the presence of methyl group which increases the size of this monomer compared to styrene, thereby increasing the resistance to flow. However, the overall increase in viscosity is only slight and will not affect the processing characteristics of the vinyl ester resin containing α-methylstyrene in place of styrene.

Curing studies

The curing of VE resin is expected to vary with the concentration and nature of the reactive diluent present. Results of gel point determination at 25° on samples containing different amounts of styrene and α-MS in VE resin are summarized in Table 1. The variation of temperature with time is shown in Fig. 1. It is obvious that addition of α-MS increases the gel time and results in a decrease in peak temperature, thereby indicating a decrease in the rate of polymerization.

Table 1 Brookfield viscosity and gel point of vinyl ester resin containing 40% (w/w) of styrene/α-MS

Sample designation	Styrene/α-MS ratio	Brookfield* viscosity, cps	Gel** time, min	Peak temperature, °C
A	40:0	37.5	49	77.1
B	35:5	32.5	57	45.1
C	30:10	35.0	63	30.7
D	25:15	37.5	82	26.3
E	20:20	40.0	73	26.4
F	15:25	42.5	—	—
G	0:40	47.5	—	—

* Determined at 30 °C using spindle LV2.

** Determined using benzoyl peroxide and N,N-dimethyl aniline as initiators at 25 °C.

Isothermal curing of samples B and C was done at 100° using DSC (Fig. 2). It was observed that the exothermic peak was reduced and curing was completed over a longer period of time as the concentration of α-MS increased in the samples.

Dynamic DSC was done on VE-styrene/α-MS resin samples and thermal scans were recorded from 40 to 220°. DSC traces of compositions A, C, E and G are shown in Fig. 3. From these DSC traces the onset temperature of curing (T_0), the

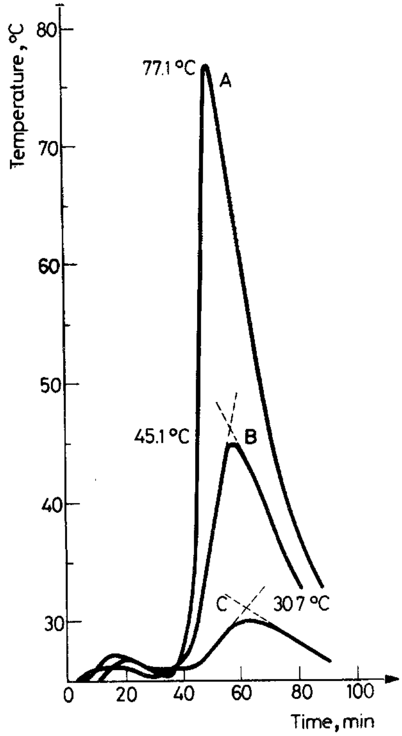


Fig. 1 Gel point determination of VE resins containing (A) 40% styrene (B) 35 : 5 styrene: α-MS (C) 30 : 10 styrene: α-MS

Table 2 Curing behaviour of vinyl ester resin containing styrene/α-MS

Curing characteristics	Sample designation					
	A	B	C	E	F	G
T_0, °C	115.8	118.0	120.1	121.1	117.2	115.3
T_{exo}, °C	122.0	124.1	128.5	131.6	128.8	132.6
T_2, °C	145.0	179.0	167.0	200.0	193.0	208.0
ΔH, J g^{-1}	138.0	165.0	147.0	150.0	160.0	162.0
E, kJ mol^{-1}	869.0	569.0	554.0	403.0	391.0	333.0

T_0: Temperature of onset of the exotherm.
T_{exo}: Temperature of peak.
T_2: Temperature of completion of the exotherm.
ΔH: Heat of reaction.
E: Activation energy.

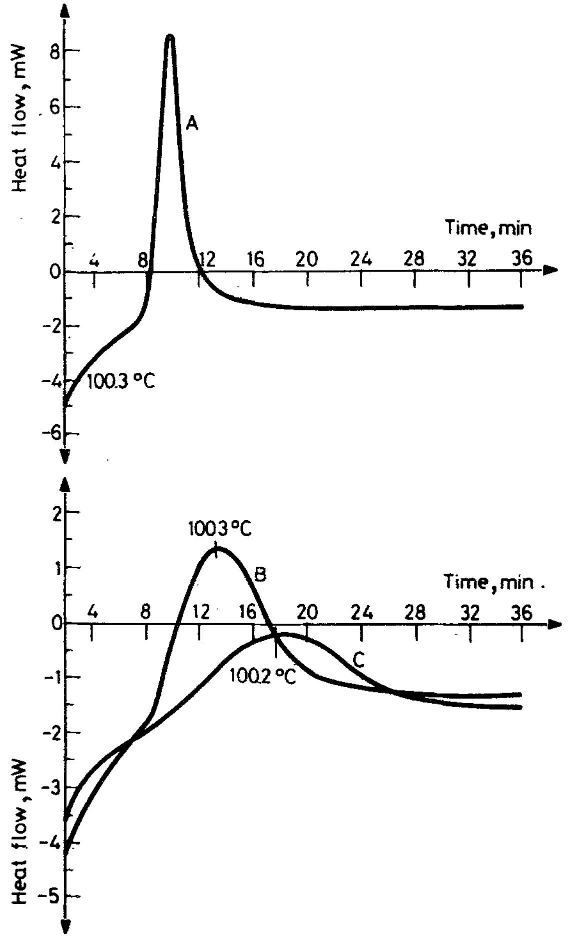
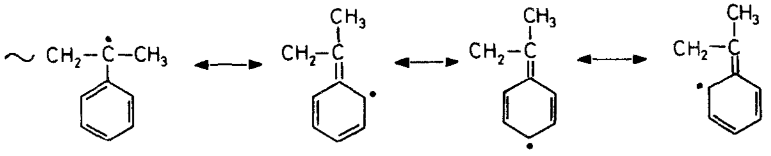


Fig. 2 DSC scans of isothermal curing of vinyl ester resin samples A, B and C

exothermic peak position (T_{exo}) and final temperature of curing (T_2) were noted down, the results of which are summarized in Table 2. It was observed that T_1 remained almost the same for samples containing increasing concentrations of α-MS. Delayed curing in samples containing α-MS was indicated by an increase in T_{exo} and T_2.

These results indicate that α-MS reduces the reactivity of free radical polymerization in styrenated VE resin samples. The lower reactivity of α-MS may be explained on the basis of an increased stabilization of the tertiary radical species due to resonance and hence reduced tendency for propagation.



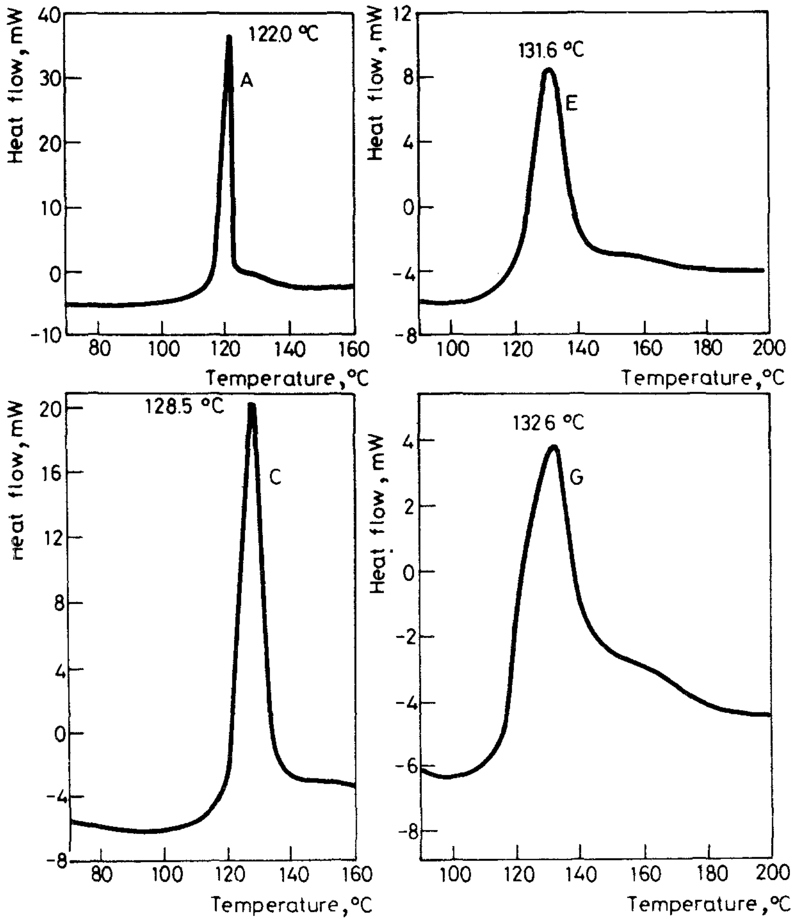


Fig. 3 DSC curves of various vinyl ester resin samples (heating rate 5 deg/min)

From the area under the exotherm the heat of curing (ΔH) was evaluated. It was observed that ΔH values increased as the concentration of α-MS increased. This may be attributed to the stability of the terpolymer. However, considerable loss of styrene/α-MS was observed during cure, which made the ΔH data less reliable.

The energy of activation (E) was determined using Borchardt/Daniels kinetics program. Figure 4 shows the Arrhenius plot (ln k *vs.* $1/T$) for samples A to G. The energy of activation decreased as the concentration of α-MS was increased in the samples. The lower energy of activation in samples containing α-MS showed that curing was less dependent on temperature in these systems. This could again be attributed to the stability of tertiary radicals as compared to secondary radicals when styrene was the monomer.

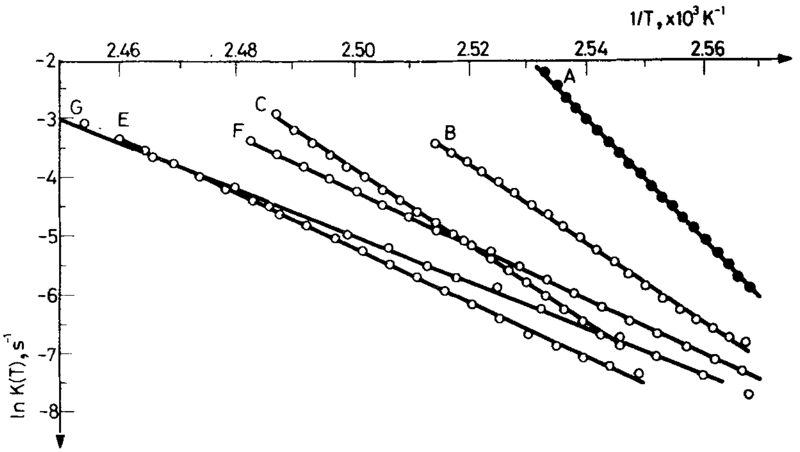


Fig. 4 Plots of ln k versus $1/T(K^{-1})$ for various vinyl ester resins samples

Thermogravimetric analysis

The thermogravimetric traces of cured samples showed two mass loss steps (Fig. 5). Resin samples containing styrene and α-MS were stable up to 300° and started losing weight above this temperature. Rapid decomposition was observed at 350–450° and almost total volatilisation of the sample occurred around 500°. However, in all the resin samples an initial mass loss of about 3 to 8% was observed above 90°. This may be due to residual styrene or α-MS in these samples. This is an indication that the cure was still not complete at 140°.

The relative thermal stability of the cured resin samples could be determined by comparing the temperature of onset of major decomposition T, temperature of completion of decomposition T_f. Since the decomposition proceeded in two steps, two sets of characteristic decomposition temperatures were obtained which have been designated by a suffix of 1 or 2. The results of these thermal studies are summarized in Table 3. Increase in the α-MS content resulted in a decrease in the initial decomposition temperature. No other significant difference in the thermal behaviour of various resin samples was observed.

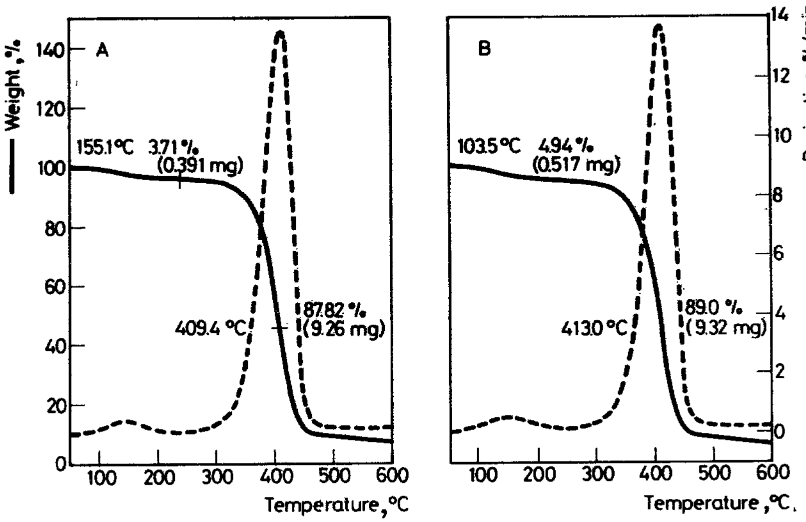


Fig. 5 Thermogravimetric curves of vinyl ester resin samples A and B

Table 3 Thermal behaviour of vinyl ester resin containing styrene/α-MS

Thermal characteristics	Sample designation				
	A	B	C	D	E
T_1, °C	85.0	103.5	75.0	70.0	75.0
$T_{\max_1}$, °C	155.1	153.4	141.61	115.0	160.8
T_{f_1}, °C	235.0	215.0	230.0	195.0	245.0
T_2, °C	373.0	377.2	361.1	360.8	363.7
$T_{\max_2}$, °C	409.4	413.0	412.9	403.6	405.5
T_{f_2}, °C	435.8	438.7	441.2	437.4	440.3

T: Initial decomposition temperature
$T_{\max}$: Temperature of maximum rate of mass loss.
T_f: Final decomposition temperature.
Suffix 1 and 2 refer to first and second decomposition steps.

The results of thermal characterization of vinyl ester resins containing different proportions of styrene/α-methylstyrene indicate that it is possible to replace up to 40% of styrene by α-methyl styrene. Further increase in α-methylstyrene delays the curing significantly.

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Zusammenfassung — Mittels DSC und Bestimmung der Gelierungstemperatur wurde das Aushärteverhalften des Bismethakryloxyderivaten des Diglycidyläthers von Bisphenol A (Vinylesterharz) mit 40 Gewichtsprozenten Styrol als reaktives Streckmittel untersucht. Es wurden sieben Proben mit einem Styrol/α-Methylstyrol Verhältnis von 40:0, 35:5, 30:10, 25:15, 20:20, 15:25 und 0:40 untersucht. Mit steigendem Anteil an α-Methylstyrol konnte eine Verzögerung der Aushärtung sowie ein Absinken der Aktivierungsenergie von 869 kJ·mol^{-1} auf 333 kJ·mol^{-1} beobachtet werden. Der Ersatz von Styrol durch α-Methylstyrol veränderte jedoch die thermische Stabilität in keiner Weise. Vinylesterharzproben mit 10–15% α-Methylstyrol und 30–25% Styrol können als reaktive Streckmittel in Vinylesterharzen verwendet werden.

Резюме — Методом ДСК и определением точки гелеобразования изучен характер отверждения бис-метакрилокси производного диглицидилового эфира бис-фенола А, содержащего 40 вес.% стирола в качестве реакционного разбавителя. Изучены семь образцов стирол/α-метилстирол, взятых в соотношении 40:0, 35:5, 30:10, 25:15, 20:20, 15:25 и 0:40. В образцах с увеличиваюримся содержанием α-метилстирола наблюдалось замедление отверждения. С увеличением концентрации α-метилстирола энергия активации уменьшалась от 869 до 333 кдж·моль$^{-1}$. Однако, не наблюдалось различий в термоустойчивости при замене стирола α-метилстиролом. Сделано заключение, что образцы винилэфирной смолы, содержащие 10–15% α-метилстирола и 30–25% стирола могут быть использованы в качестве реактивных разбавителей для винилэфирной смолы.