Decomposition of Vinyl Esters of Cycloaliphatic Epoxy Resins: A Kinetic Study

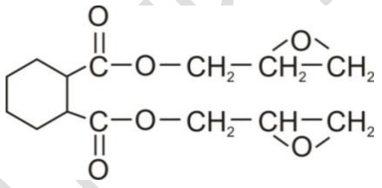
Abstract: Degradation behaviour of two methaacrylate terminated cycloaliphatic epoxy resins containing glycidyl epoxy group C_1E and epoxycyclohexane group C_2E were studied using thermogrametric analysis TGA techniques. The esters were cured by using styrene as diluent (40% w/w) and benzoyl peroxide as free radical indicator (2% w/w). The TG and DTG thermograms of both esters show single step degradation. The order of degradation reaction was found to be one for both esters. This was calculated using Coat and Redfern equation in accordance with best fit analysis and further confirm by linear regression analysis. From this value the activation energy and pre exponential factor was calculated. The study concluded that both vinyl esters have high thermal stability. Higher value of activation energy and frequency factor for ester C_2E shows that the ester is thermally more stable the ester C_1E, this is due to the presence of two cyclohexane ring in the resin C_1, increasing the number of cyclic rings within a cured epoxy resin structure generally leads to enhanced thermal stability.

Keywords: cycloaliphatic epoxy resins, vinyl esters, decomposition, benzoyl peroxide, styrene.

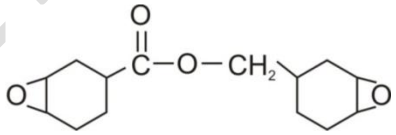
Introduction: Cycloaliphatic epoxy resins (CERs) are characterized by the presence of cycloaliphatic ring, mostly cyclohexane in which active epoxy group is either cyclohexene oxide or pendant glycidyl groups[1]. The epoxy groups are linked to each other by various type of bonds such as ether, ester, cyclic acetal, etc.[2]. The range of molecular weight of these reasons is usually lower than that of common epoxy resins, thereby they possess lower viscosity and can be cured to high degree of cross linking. The low viscosity improved their handling characteristic such as flow, wetting and ability to accept fillers at high loading and high degree of cross linking attributes to high mechanical strength and heat resistance. CERs have marked superiority over bisphenol A epoxy resins in arc resistance and arc- track resistance[3]. The common epoxy resins decomposes at high temperature arc and conductive carbon is produced which lead to early failure of insulator, while CER free of aromatic groups are resistance to carbonization under electrical arc. CERs are particularly important for casting high voltage insulators which are being considered as replacement for traditional porcelain and glass insulators due to their life weight, impact resistance and each to produce large complex parts[4]. However, these resins have poor commercial workability due to their high cost and brittleness. The above drawbacks associated with these resins can be reduced to the acceptable limit of desired properties and cost by adding proper plasticizers[5], flexibilizers, fillers[6] and by blending with the resins of other epoxy systems such as those based on bis phenol A, novolac etc.[7]. The properties of CERs can also be improved by modification in the chemical structure of conventional epoxy resins[8,9]. The esterification of epoxides with unsaturated monocarboxylic acids is an important route to improve their workability and curing properties[10]. The esterification of epoxies are usually carried out with unsaturated monocarboxylic acid like acrylic and methacrylic acid in presence of basic catalyst. The esterified resins has terminal unsaturation, a form referred to structo terminal, where they are reactive causing it to cure rapidly and enable to give a product which has other desirable properties along with superior corrosion resistance[11,12]. The viscosity of neat vinyl ester is high, there by to make them processible, the diluents are required. Such diluents may be non reactive or reactive[13]. The reactive vinyl type monomers reactive are preferred over non reactive because they not only reduce the cost and viscosity of the resins but also the vinyl group present in the reactive diluents reacts with the double bond present at the end of polymer chain and become part of cured resins. The cross linking reactions of vinyl esters are carried out by adding free radical initiators[14]. These reactions are exothermic and proceed by free radical polymerization. The chemical structure of epoxy esters, vinyl monomers and initiators was found to be affect on rate of curing reaction, crosslinking density and finally on the properties of cured product[15,16]. An investigation of curing and decomposition behaviour is needed to established relationship between processing and properties of these resins. The curing and decomposition behaviour of unsaturated esters has been studied by several investigators[17,18]. The present work deals with the kinetics of decomposition of methacrylate terminated ester of cycloaliphatic epoxy resins.

Experimental:

Cycloaliphatic epoxy resins CY 184 and CY 179 from Ciba Specialty Chemicals, Mumbai, methacrylic acid and triphenylphosphine from Rituraj Enterprises, Kanpur, were used for the synthesis of esters. Benzoyl peoxide as curing agent and styrene as reactive diluent also from Rituraj Enterprises, Kanpur, were taken in the present study.

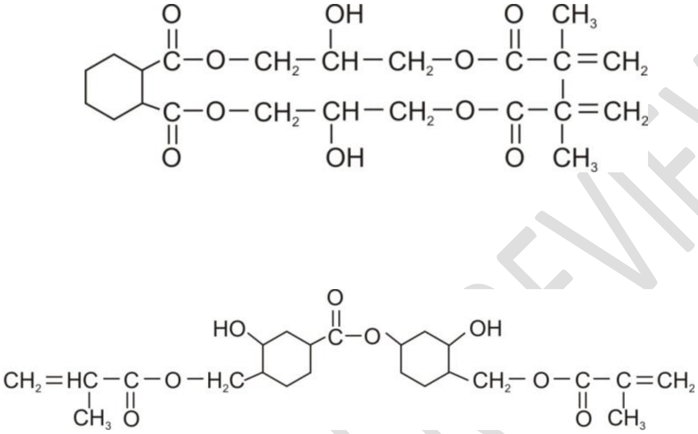


Diglycidyl ester of hexahydrophthalate – CY 184 (C_1)



3, 4 – epoxy cyclohexyl methyl -
3', 4' – epoxy cyclohexane carboxylate – CY 179 (C_2)

The esterification of cycloaliphatic epoxy resins were carried out using 1:0.9 stoichiometric ratio of resin and methacrylic acid in presence of triphenylphosphine as catalyst (1 phr by weight of resin). The reaction were carried out at 90°C ± 2°C till the ester of desired extent of reaction (92% conversion) were obtained. The experimental methods for the synthesis of esters, kinetics of esterification reaction and their characterization were given in our earlier communications[3,10]. The prepared esters of cycloaliphatic epoxy resins CY 184 and CY 179 were designated as C_1E and C_2E respectively and their structure are given below:



Structure of Prepared Vinyl esters C_1E and C_2E

The prepared esters were cured by mixing the resin with styrene (40% by weight of resin) and benzoyl peroxide (2% by weight of resins) at the temperature 90^0C for 1 hour in an air circulating oven[15]. The decomposition behavior of cured esters are studied using thermal Analyst 2000 (TA instruments) equipped with 2950 thermal gravimetric analysis. TG analysis were performed under nitrogen atmosphere from 50^0C- 700^0C at heating rate 10^0C min^{-1}. The relative stability of resin sample was quantitatively esteemed by comparing the temperature for particular degree of weight loss. The values of activation energy (E) and pre-exponential factor (Z) were determined by Coats and Redfern equation as given below:[19]

$$\log_{10}\left\{\frac{g(\propto)}{T^2}\right\} = \log 10\left\{\frac{ZR}{\beta E}\left[1-\frac{2RT}{E}\right]\right\} - \frac{E}{2.3RT} \quad \ldots\ldots\ldots\ldots(1)$$

Where

$$g(\alpha) = \left[\frac{1-(1-\propto)^{1-n}}{1-n}\right] \qquad \text{for } n \neq 1$$

$$g(\alpha) = -\log_{10}\{-\log_{10}(1-\alpha)\} \qquad \text{for } n = 1$$

$$\alpha = \frac{W_T - W_f}{W_O - W_f}$$

Where,

α = Fractional weight loss

W_T= Weight at temperature T

W_f = Final weight

W_o= Initial weight

R = Gas constant

Equation 1 can be reduce to,

$$y = c + mx$$

Where,

$$y = log_{\propto}\left[\frac{g(\propto)}{T^2}\right]$$

$$x = 1/T$$

$$m = \frac{-E}{2.3\,R}$$

$$c = log_{10}\left\{\frac{ZR}{\beta E}\left(1-\frac{2RT}{E}\right)\right\}$$

Best fit techniques was used to calculate the value of order of reaction which is further confirmed by regression analysis. The validity of the data was checked by t-test analysis if the calculated value of t ≥ table value of t the data significant.

The thermogram for the decomposition of cured esters C_1E and C_2E in presence of a styrene as reactive diluent at 10^0C per minute for 50^0- 700^0C are shown in figure 1 and 2, respectively.

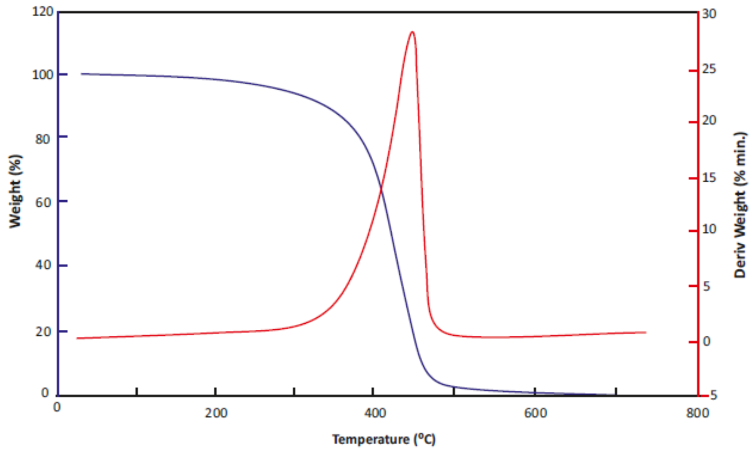


Figure. 1

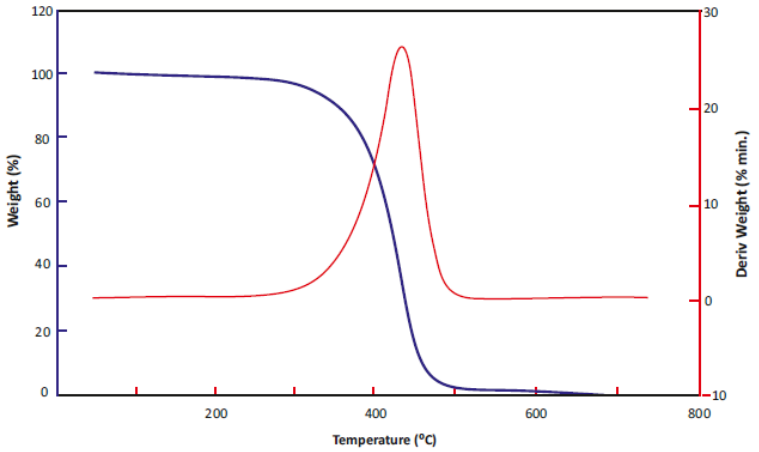


Figure. 2

It is apparent from TG thermogram of both the esters that the degradation consists of single step. Both the esters was stable up to 200^{o}C and started losing weight above this temperature. Rapid decomposition was observed between 280^o- 470^{o}C and almost 95% volatization of the samples occurred in this temperature range. DTG curves which shows the relationship between the reaction rate and temperature are also given in figure 2 and 3. These curves are showing only one sharp maximum at 432.05 and 440.97^{o}C for the cured C_1E and C_2E, respectively. The relative thermal stability of the cured samples could be determined by comparing the onset (T_i), peak (T_p) and completion temperature (T_f) of the decomposition and char yield at 700°C. The result of these thermal studies are summarised in table 1. This could be observed from the table that there is no significant difference in T_i, T_p and T_f values obtained for C_1E and C_2E, respectively. However, char yield was found to be significantly higher for C_2E in comparison to C_1E, indicating that the later is thermally more stable. The area under DTG curve which is proportionate to the total change in weight was found to be approximately same i.e., about 98.8% for both the esters.

Ester Name	**T_i (^{0}C)**	**T_p (^{0}C)**	**T_f (^{0}C)**	**Area %**	**Char Yield 700^{0}C(%)**	**Activation Energy Kcal mol^{-1}**	**Frequency Factor (min^{-1})**
C_1E \	386.03	432.05	456.16	98.62	3.2	18.15	45.52×10^{19}
C_2E	387.80	440.94	458.54	98.81	4.1	20.13	16.19×10^{20}

Table 1 Thermal behavior of esters C_1E and C_2E at 10^{0}C/min.

The Kinetic parameters order of reaction, energy of activation and frequency factor of degradation reaction were found using Coat and Redfern equation for different values of n (0, 1/2, 2/3, 1 and 2) graphs where plotted between x and y. The statistical data are given in table 2. The graph where plotted between $-\log10\{\log(1-\alpha)/T2\}$ and 1000/T, figure 4 for C_1E and Figure 5 for C_2E, the value of n = 1 gave the best fit and correlation coefficient was found 0.9798 and 0.9838 for C_1E and C_2E, respectively.

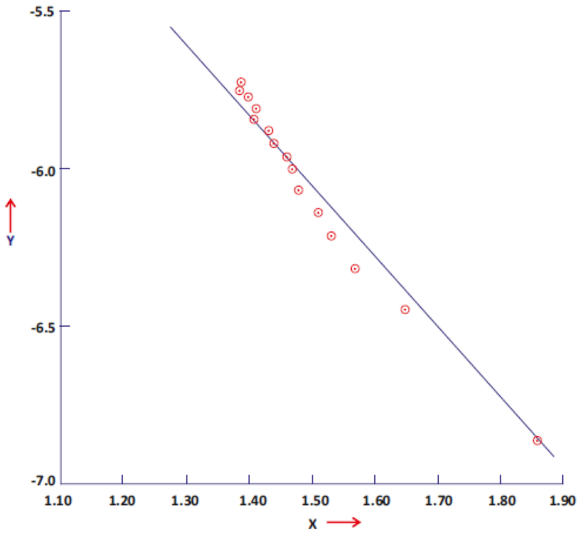


Figure. 3

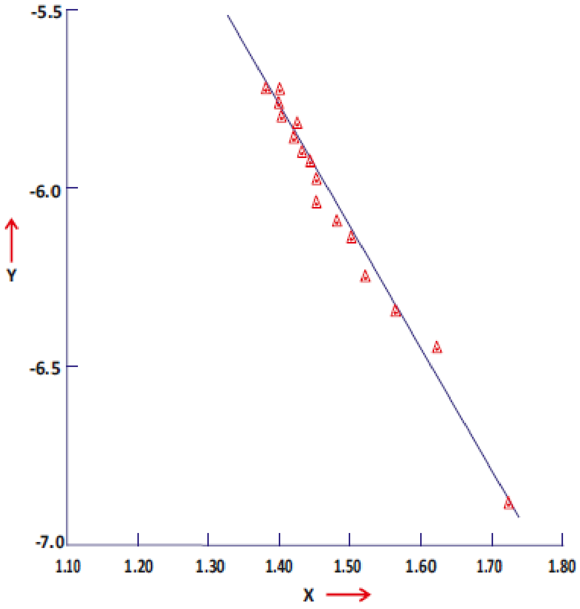


Figure. 4

The value of E (activation energy) and Z (frequency factor) were calculated from the slope and intercept of the plot and are given in table 1. It is apparent from the table that the activation energy is higher for C_2E indicating that is more stable. The validity of the data was checked by t test analysis the calculated value of t ≥ table value of t, its shows that the data are significant.

Name ester	Reaction Order (n)	Corel. Coeff. (r)	Degree of freedon	Standard error of estimate	Standard error	Regression Equation	T(cal.)	T(tab)
C_1E	0	0.9183	15	0.0515	0.1646	-2.4484x -2.3880	4.51	1.13
	1/2	0.8779	15	0.1190	0.3808	-2.3498x -2.2882	6.02	1.13
	2/3	0.8612	15	0.1354	0.4332	-2.5887x -2.0484	4.72	1.13
	1	0.9747	15	0.4494	1.4378	3.6533x -11.5786	8.05	1.13
	2	0.7013	15	0.3440	1.1008	-4.0465x +0.3440	0.39	1.13
C_2E	0	0.9612	15	0.0381	0.1656	-3.3521x -1.4293	8.63	1.13
	1/2	0.9510	15	0.0689	0.2995	-3.6182x - 0.6146	2.05	1.13
	2/3	0.8388	15	0.0817	0.3559	-3.8043x -0.3102	0.87	1.13
	1	0.9838	15	0.3596	1.5618	4.6531x -12.9572	8.29	1.12
	2	0.6012	15	0.2368	1.0278	-5.6848x -2.7493	2.67	1.13

Table 2. Statistical data for different value of order of reaction (n= 0, 1/2 , 2/3, 1, 2)

The relative thermal stability of ester C_1E and C_2E were also studied by comparing the temperature of 1 to 10% weight loss and the data are given in figure 5. The difference in the decomposition temperature up to 5% degradation is significant. Thereafter, the difference descends and after 10% weight loss the decomposition temperature of both the ester become almost same. From the temperature for a particular degree of weight loss, it is apparent that thermal stability of ester C_2E is higher in comparison to C_1E.

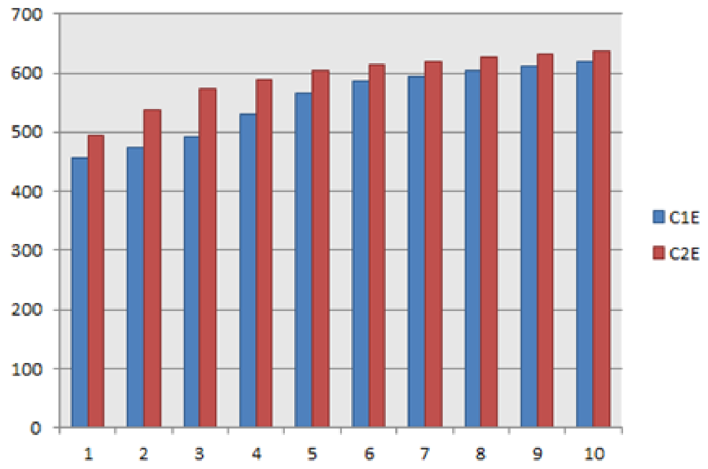


Figure. 5 Temperature of 1-10% weight loss for C_1E and C_2E

Higher thermal stability of ester C_1E is due to the presence of two cyclohexane ring in the resin C_1, this can be explained by the fact that increasing the number of cyclic rings within a cured epoxy resin structure generally leads to enhanced thermal stability[20]. Cyclic structures tend to be more rigid compared to linear chains, contributing to increased resistance to thermal deformation as well as the presence of cyclic rings can also help distribute heat more evenly throughout the polymer network, potentially delaying the onset of thermal degradation. The more cyclic rings present, the more tightly crosslinked the network becomes, which results in greater resistance to heat degradation and a higher glass transition temperature (Tg), thus improving the overall thermal stability of the epoxy material[21].

Conclusions: The decomposition behaviour of the vinyl esters of cycloaliphatic epoxy resins were studies using thermogrametric analysis TGA techniques. The kinetic parameters viz. order of reaction, energy of activation and frequency factor of degradation reaction where obtained using Coat and Redfern equation. For different values of n graph plotted between x and y and value of n= 1 gave the best fit with highly significant correlation coefficient. The value of E and Z where calculated from the slope and intercept of the plot. it is apparent from the table that the activation energy of ester C_2E is higher than C_2E. The result shows that the ester C_2E is thermally more stable the ester C_1E, this is due to the presence of two cyclohexane ring in the resin C_1, increasing the number of cyclic rings within a cured epoxy resin structure generally leads to enhanced thermal stability.

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