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RESEARCH ARTICLE

CURING AND DEGRADATION BEHAVIOR OF VINYL ESTERS OF CYCLOALIPHATIC EPOXY RESINS

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Abstract

Curing and degradation behavior of two unsaturated esters based on cycloaliphatic epoxy resin containing glycidyl epoxy group (C_1E) and epoxy cyclohexane group (C_2E)were studied using DSC and TGA Techniques. DSC thermograms of ester C_1E and C_2E mixed with reactive styrene (40% w/w) and initiator benzoyl peroxide (2%) shows that the curing of ester C_2E takes place at higher temperature range in comparison to C_1E due to their dense rigid structure. The degradation behavior of cured esters are studied using thermal analyst 2000 equipped with 2950 thermal gravimetric analysis at heating rate 10^0C min^{-1}. The TG and DTG thermogram of both esters show single step degradation. The temperature of 1-10% weight loss for both ester was studied from TGA. Thethermal stability of the ester C_2E was found to be higher than that of C_1E.

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Introduction:-

[1,2]Cycloaliphatic epoxy resins, have attracted considerable attention in recent past due to their excellent handing characteristics and full required by antitracking potential, required by electrical industry.[3]The esterification of epoxy resins with unsaturated monocarboxylic acid viz. acrylic and methacrylic acid is an important way to improve their workability and curing properties. The esterification reaction give a product having ester group and carbon to carbon double bond linkage at the end of polymer chain. [4] These unsaturated esters undergo rapid free radical polymerisation in presence of free radical initiators such as benzoyl peroxide, dicumylperoxide, test butyl perbenzoate. The unsaturation also provides a reactive site to copolymers with vinyl monomer like [5]styrene, acrylates and [6] methacrylates, which intern increases flexibility, controls crosslink density and reduces cost.

[7,8] The chemical structure of epoxy esters, vinyl monomers and initiators was found to effect on rate of curing reaction, crosslinking density and finally on the properties of cured product. An investigation of cure is needed to establish relationship between processing and properties of these resins. [9,10]The curing behavior of unsaturated esters of bisphenol-A and novolac based epoxy resins and [11,12] their thermal stability have been studied by several investigators. The present work deals with the curing and degradation behavior of methacrylate terminated ester of cycloaliphatic epoxy resins.

Experimental:

Cycloaliphatic epoxy resins CY 184 and CY 179 from Ciba Speciality Chemicals, Mumbai, methacrylic acid and triphenylphosphine from Fluka A.G., Switzerland, were used for the synthesis of esters. Benzoyl peoxide as curing agent and styrene as reactive diluent from S.D. Fine Chemicals, Mumbai; were taken in the present study.

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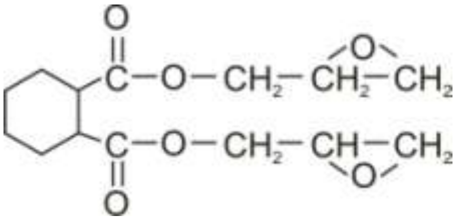
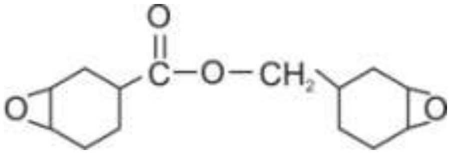
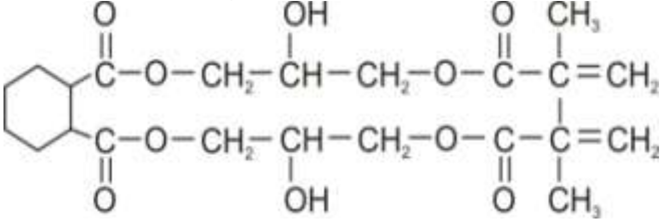


Diglycidyl ester of hexahydrophthalate – CY 184

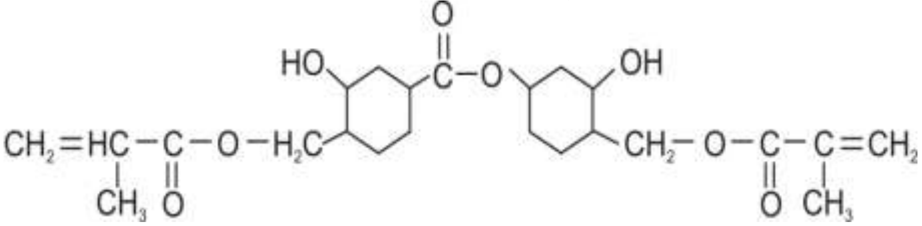


3, 4 – epoxy cyclohexyl methyl -
3', 4' – epoxy cyclohexane carboxylate – CY 179

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. [13] The experimental methods for the synthesis of esters, kinetics of esterification reaction and their characterization were given in our earlier communications. 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



Vinyl ester of C_1E



Vinyl ester of C_2E

The prepared esters were characterized for their structure by epoxy equivalent weight and FTIR spectroscopy.

The sample for studying the curing behavior of esters were prepared by mixing the resin with styrene (40% by weight of resin) and benzoyl peroxide (2% by weight of resins) followed by stirring with glass rod at 35° ± 1°C. A thermal analyst 2000 equipped with 2910 Differential Scanning Calorimeter were used to study the curing behavior of resins. DSC scans were obtained under dynamic condition with programme rate 10^0C min^{-1} from 50^0C to the temperature at which the exothermic reaction were completed. From thedynamic DSC scan a temperature was selected at which an appreciable rate of curing could be observed. The curing temperature 80'C and 90'C was used to cure the ester C_1E and C_2E, respectively in an air circulating oven for 1 hour. After cooling, the cured sample were scanned from 50"-200°C and no exotherm was observed. 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 at heating rate 100C min^{-1}. The relative stability of resinsample was quantitatively esteemed by comparing the temperature for particular degree of weight loss.

Result And Discussion:-

The typical DSC scans for the esters C_1E and C_2E mixed with benzoyl peroxide (2%) and styrene (40%) at heating rate 10^0C/min are given in Figure 1 and their findings are summarized in Table 1.

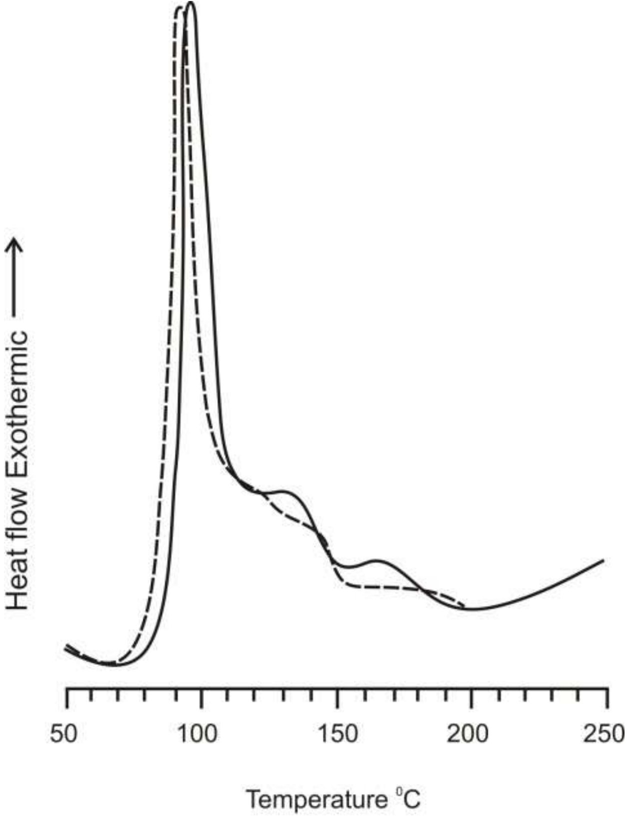
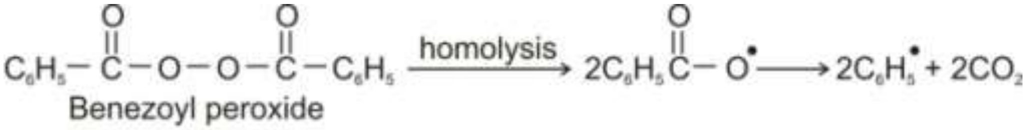


Figure - 1

Table 1:-

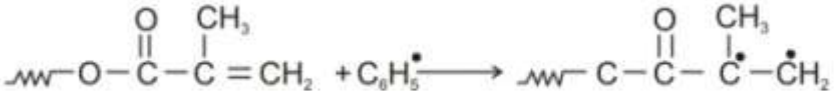
Sample Designation	**$T_0{}^0C$**	**$T_P{}^0C$**	**$T_C{}^0C$**
C_1E	85.5	99.7	195.3
C_2E	78.5	92.9	156.0

It is clear from the Figure that onsent temperature of curing (T_0), exothermic peak position (T_P) and final temperature of curing (T_f) for C_1E are higher than that obtained for C_2E which indicates that the resin C_2E cures at faster rate in comparison to C_1E.[14,15] The mechanism of curing of vinylester with benzoyl peroxide with styrene are given below.



$$C_6H_5-\overset{O}{\overset{\|}{C}}-O-O-\overset{O}{\overset{\|}{C}}-C_6H_5 \xrightarrow{\text{homolysis}} 2C_6H_5\overset{O}{\overset{\|}{C}}-O^{\bullet} \longrightarrow 2C_6H_5^{\bullet} + 2CO_2$$

Benezoyl peroxide



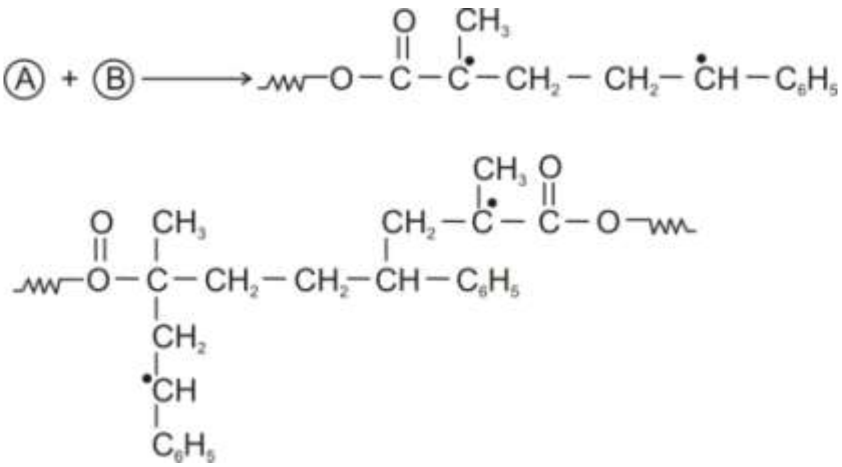
$$\sim O-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{C}}=CH_2 + C_6H_5^{\bullet} \longrightarrow \sim C-\overset{O}{\overset{\|}{C}}-\overset{CH_3}{\overset{|}{\dot{C}}}-\dot{C}H_2$$

Vinyl group of C_1E & C_2E (A)

$$CH_2=CH-C_6H_5 + C_6H_5^{\bullet} \longrightarrow \dot{C}H_2-\dot{C}H-C_6H_5$$

styrene

(B)



Crosslinked vinyl ester

The difference in the reactivity of two esters are due the position of reactive units attached to the cyclohexane. In C_1E unsaturation sites are attached to a cyclohexane ring through the dense linkages at ortho position. This results in limited mobility of reactive units while in C_2E the two unsaturation sites are located at two separate rings which allows the free movement of reactive units and therefore, it cures at faster rate in comparison to C_2E.

Thermal stability of ester of cycloaliphatic epoxy resins was asseessed after the sample were cured. Figure 2 and 3 shows the thermograms of cured ester C_1E and C_2E, respectively, at heating rate 10^0C/min form 50-700'C.

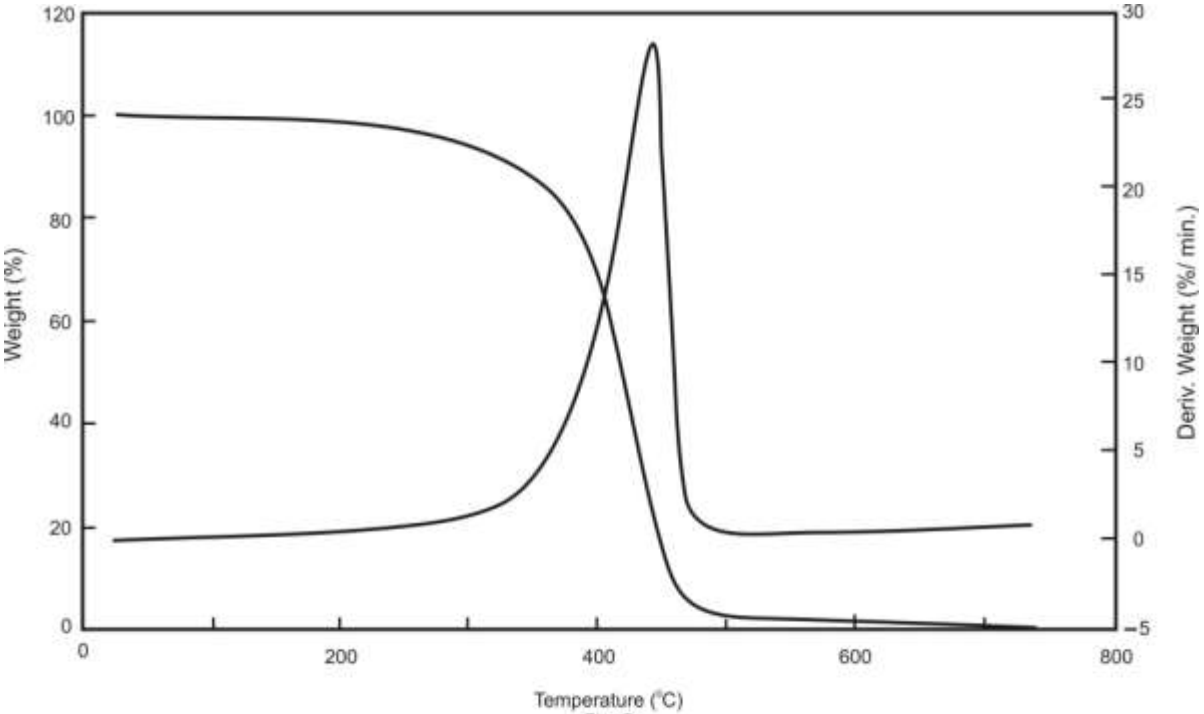


Fig. 2

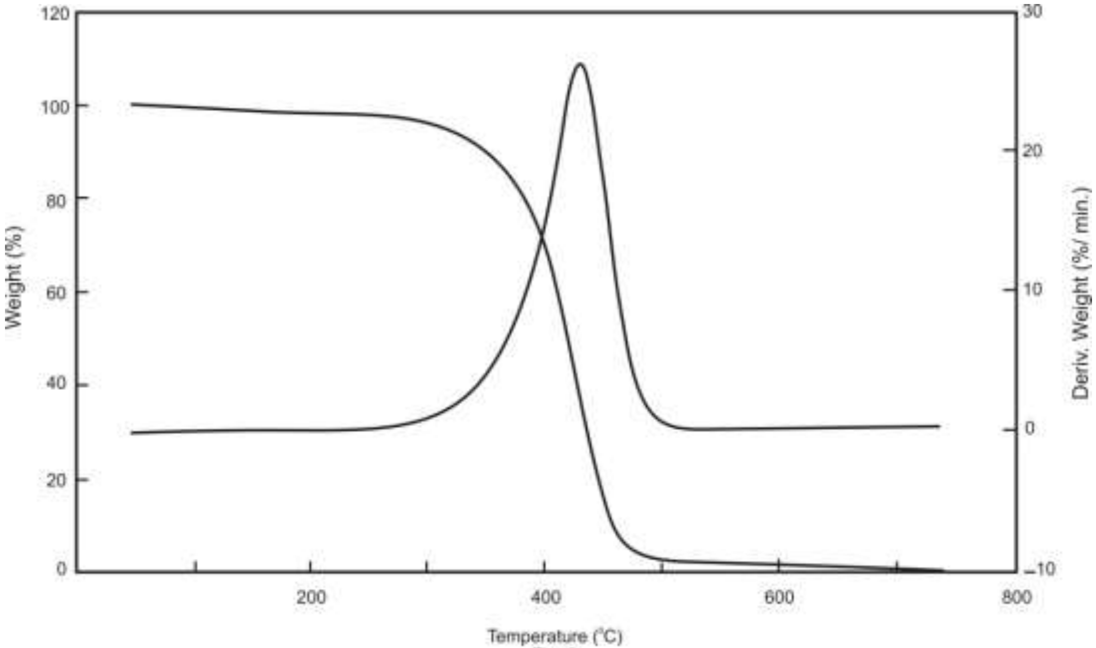


Fig. 3

[16] It is apparent from TG thermograms of both esters that the degradation consists of single step. Both esters were stable upto 200°C and started losing weight above this temperature. Rapid decomposition was observed between 280°-470°C and almost - 95% volatilization of the samples occurred in this temperature range. The relative thermal stability of esters C_1E and C_2E were also studied by comparing the temperature of 1 to 10% weight loss and the data are given in Table 2.

Weightloss %	Temperature K	
	C_1E	C_2E
1	456	494
2	475	538
3	492	574
4	530	588
5	567	603
6	586	615
7	595	619
8	605	626
9	611	632
10	618	636

The difference in the decomposition temperature upto 5% is significant. Thereafter, the difference descents and after 10% weight loss, the decomposition temperature of both esters become almost same. From the temperature for a particular degree of weight loss, it is apparent that the thermal stability of ester C_2E is higher in comparison to C_1E.

Conclusions:-

The study concluded that

1) The curing of ester based on cycloaliphatic epoxy resin having epoxy cyclohexane group starts earlier in comparison to the ester based on CER having glycidyl epoxy group.
2) The thermal stability of vinyl ester C_2E was also found to be higher than that of C_1E.
3) The degradation reaction of both esters follows one step degradation.

References:-

1. MarkH.F.;BikalesN.M.;OverbergerC.G.;MengerG., Encyclopedia of PolymSciEngg. Wiley Interscience New York, Vol 6, p 322. 1986
2. BarabarnaA.T.; LoshinB.V.;PiloppovaO.E., Colloid and PolymerScience 3, 294, 2018
3. StevenJ.J.; Epoxy Resin Technology P F Bruin, Ed, Wiley Interscience New York, p 113, 1968
4. WenJ.W.C.S.,PolymEngg. Sci 34, 1297, 1994
5. GanemM.;MostaigneB., J. Marcromol.Sci. Pure and Appl. Chem.A 30, 829, 1993.
6. AgrawalS.; MishraA.;RaiJ.S.P., J. Appl.Polym. Sci. 87, 12, 2948, 2003
7. BatogA.E.;Pet'koI. P.;PenczekP., Adv. Polym. Sci. 144, 49, 1999
8. ThakkarJ.P.; PatelR. G.; PatelV.S., Br. Polym, J. 20, 49, 1988
9. Daniel R. Bortz; Erika G.Heras, Macromolecules 45, 1, 238, 2012
10. MalikM.;ChaudharyV.; VermaI.K., J. Appl. Polym. Sci. 82,416, 2001
11. Gaur B.; Rai J.S.P., J. Appl. Polym. Sci. 33, 4211, 1992
12. Ray D.; Sarkar B.K.; Basak R.K.; Rana A.K., J. Appl. Polym. Sci. 94, 123, 2014
13. Srivastava A.; RaiJ.S.P., J. Polym Res. 4, 3198, 2005
14. Dua S.; Mccullough R.L.; Palmese G.R., Polym. Composite 20, 379, 1999
15. Timothy F.S.; Wayne C.; John F., European Polym. J. 4, 38, 705, 2002
16. Geetanjali S.G.; Shivakumar S.; Saleh B., Adv. Mater. Sci. Engg. Article ID 6030096, 2021.