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Differential Scanning Calorimetric Studies (DSC) of oxazolidone modified epoxy resin using Pyromellitic Dianhydride (PMDA)

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ABSTRACT

High temperature resistant modified epoxy resins – oxazolidones, were synthesized, Diglycidal ether of Bisphenol-A (DGEBA) and Tolylene Diisocyanate (TDI). Development of modified epoxy resins stable at high temperatures is in demand, because they are versatile polymers widely used in technical applications like coatings, encapsulations, structural composites, castings and adhesives. Structural characteristics of oxazolidones were studied using FTIR spectroscopy. The curing behavior of oxazolidone modified Diglycidal Ether of Bisphenol-A (DGEBA) was investigated by Differential Scanning Calorimetry (DSC) by preparing blends with stoichometric amounts of Pyromellitic Dianhydride (PMDA). The compatibility of the system was established by one single sharp peak without any byproducts being formed.

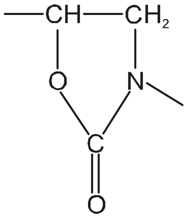
Keywords: Oxazolidone modified epoxy resin, Diglycidal ether of bisphenol-A, Higher thermal stability, pyromellitic dianhydride, Differential scanning calorimetry.

INTRODUCTION

Oxazolidones are an important class of thermosetting resins in which crosslinking occurs through reaction of the epoxide or oxirane group and have many attractive properties such as high thermal resistance, low shrinkage, ease of cure and processing, excellent moisture, solvent and chemical resistance, good mechanical and electrical properties and adhesive strength, ease of modification to optimize the properties of polymeric substrates. [1-4] Recent developments in epoxy resins include the synthesis of modified epoxy resins with better thermal properties. The present paper reports the modification of epoxy resin (DGEBA) with diisocyanates and subsequent cure with pyromellitic dianhydride (PMDA). The presence of the heterocyclic oxazolidone segment in the linear DGEBA chain, reduces the solubility and increases the melting point and melt viscosity of the resin. Oxazolidones are stiff and bulky groups along the polymer backbone which inhibit free rotation of the linear chain segments thus increasing thermal resistance. The absence of chemical bonds between the polymeric chains, correspond to their thermoplastic behavior.

MATERIALS AND METHODS

The reaction of diisocyanates with Diglycidal ether of Bisphenol A (DGEBA) in the presence of various catalysts served as a model reaction for the preparation of poly(oxazolidones)[5-6]. The type of catalyst used determines the mechanism of the oxazolidone synthesis. The role of the catalyst in this reaction is to facilitate the opening of the epoxide ring in order that the isocyanate group attached across it and hence form the hetrocyclic ring on the epoxide molecule. The catalyst is normally a Lewis base, which contains an unshared pair of electrons in the outermost orbital and seek reaction in areas of low electron density.



Structure of oxazolidone

Fig I

The general scheme for the synthesis of oxazolidones is as follows:

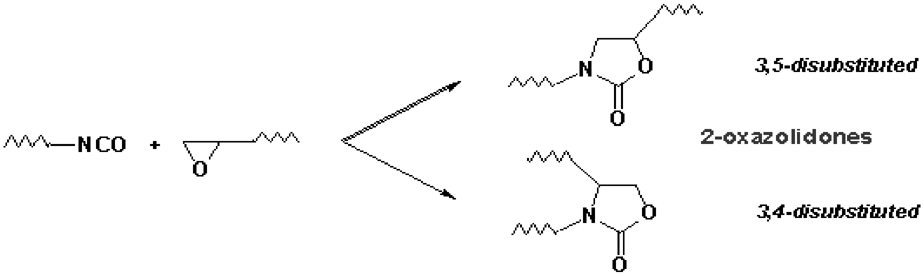


Fig II

Diglycidal ether of bisphenol-A (DGEBA), grade LY 556 was procured from Aldrich Chemicals was a viscous liquid with a MW of 382. The epoxide value of the oxazolidone modified resin determined experimentally by epoxide estimation method was 2.2, and the Epoxide equivalent determined by pyridinium chloride method was 191.

Tolylene Diisocyanate (TDI) and Methylene Diphenylene Diisocyanate (MDI) were also obtained from Alderich Chemicals and used as received. Both were flushed with dry nitrogen prior to use. Since the reaction was conducted in solution, two different solvents were used – N Methyl Pyrrolidone (NMP) and Dimethyl formamide (DMF). Both were dried by keeping it over calcium hydride overnight, followed by distillation under reduced pressure.

Two schemes were used in this work.

Sr. No.	**Resin**	**Isocyanate**	**catalyst**	**Solvent**
1	DGEBA	Tolylene Diisocyanate	Tetrabutyl Ammonium Bromide	N Methyl Pyrrolidone
2	DGEBA	Methylene Diphenylene Diisocyanate	Tetrabutyl Ammonium Bromide	Dimethyl Formamide

Cycloaddition of diisocyanate to diepoxies results in the formation of linear oxazolidone modified epoxy resin(7-10).

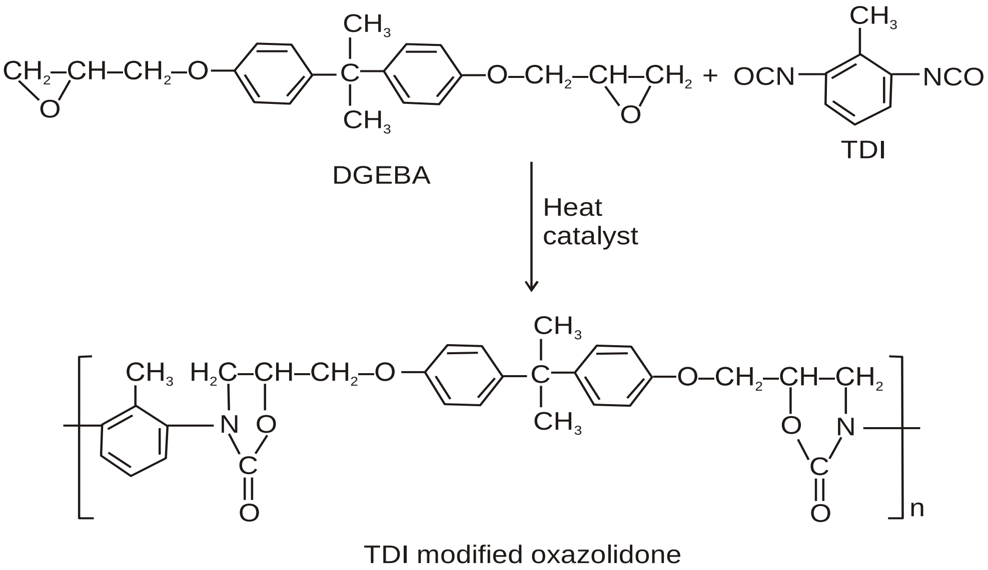
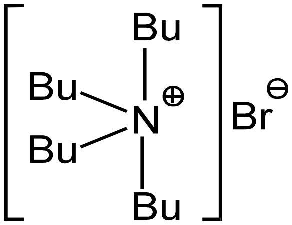


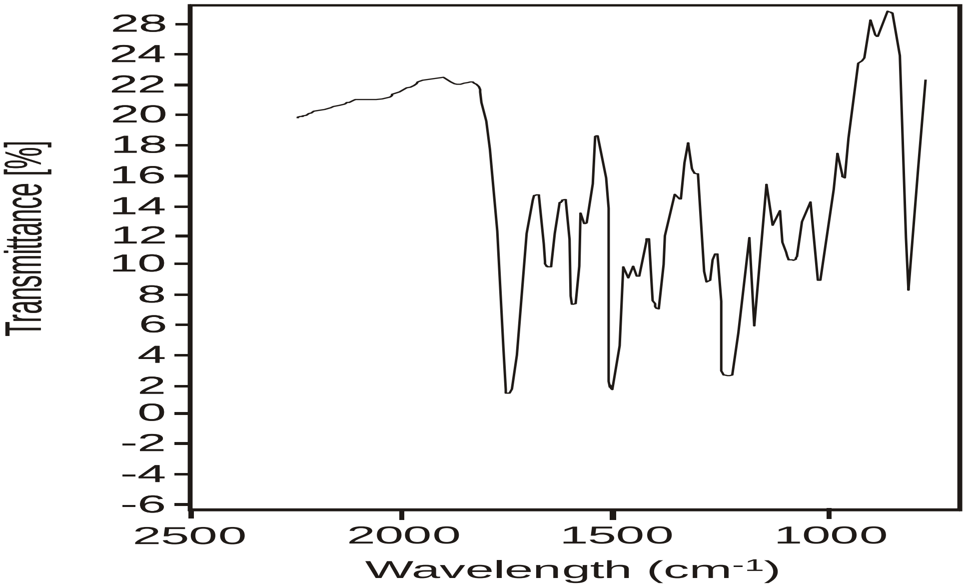
Fig.III

This reaction was between epoxy and diisocyanate was carried out in solvent phase using aprotic solvents i.e. Dimethyl Formamide (DMF) or N methyl Pyrolidone (NMP) in an atmosphere dry nitrogen. 5.73 gms (0.002 moles) of DGEBA and 0.1% of the catalyst – tetrabutyl ammonium bromide (by weight of the combined monomers) was also added, stirred and flushed with dry nitrogen gas for one hour and the temperature gradually raised to 185^{0}C, using an oil bath. 2.50 gms (0.002 moles) of the isocyanate mixed with 10 ml of the solvent was added drop wise with the help of a dropping over a period of one hour. The mixture was stirred continuously at this temperature while maintaining an inert atmosphere, for four hours and then cooled gradually.



Tetra Butyl Ammonium Bromide (catalyst)

The viscous product was precipitated in dry and distilled methanol, filtered and dried in a vacuum oven at 40^{0}C for six hours. This linear oxazolidone modified thermoplastic polymer was soluble in Dimethyl Formamide (DMF), Tetrahydrofuran (THF) and Dimethyl Sulphoxide (DMSO). The synthesized oxazolidone was characterized by Fourier Transform Infra red Spectroscopy (FTIR) carried out on NICOLET MAGNA- 750.



FTIR spectrum of oxazolidone modified DGEBA

Fig IV

FTIR of the synthesized linear polymer shows characteristic peak for oxazolidone at 1754cms^{-1} whereas the peak for DGEBA at 915 cms^{-1}is almost nonexistent, indicating that all the epoxy groups have been consumed. Peak for isocyanate at 2270cms^{-1} is also absent, indicating that all the isocyanate has reacted with epoxy to produce oxazolidones.

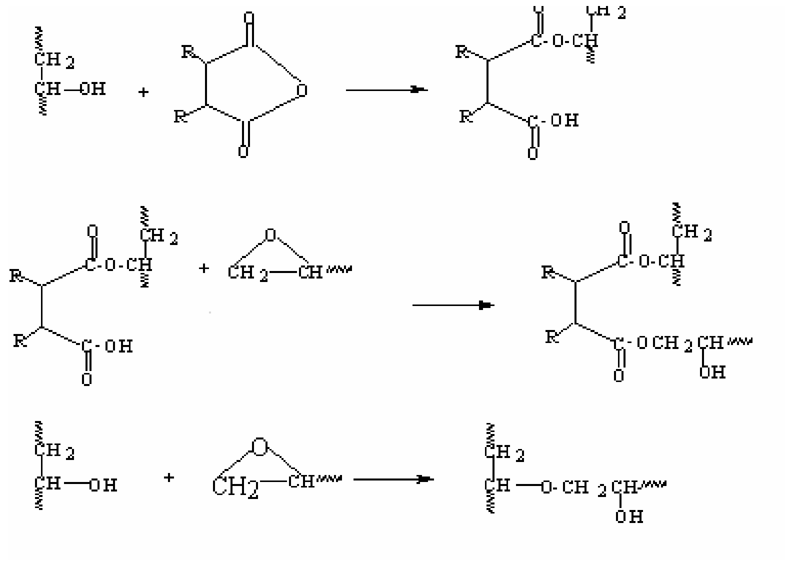
DSC STUDIES

The properties of the cured epoxy resin depend on their structure, [10-15] the extent of cure and time and temperature of cure. Hence, to obtain resins with high performance applications, it is necessary to understand the structure and the properties of the network of the cured resin[16,17]. A cross-linked thermoset polymer structure is obtained when equimolar quantities of resin and hardener are combined. However, in practical applications, epoxy formulations are optimized for *performance* rather than to complete stoichiometric cures. The curing process is a chemical reaction in which the epoxide group in epoxy resin reacts with a curing agent (hardener) to form a highly cross-linked three-dimensional network. The molecular mobility in system decreases as the cure proceeds due to crosslinking of several chains into a network of infinite molecular weight.

Curing agents which are polyfunctional are used in near stoichometric amounts and leads to formation of three dimensional network composed of resin molecules cross linked via curing agents. The cure reaction proceeds through a ring opening mechanism which governs the reaction between an epoxy and an anhydride.

The anhydride can only react through an epoxy group, hence the synthesized oxazolidone is dispersed in pure epoxy before the curing with anhydrides to provide reactive sites for anhydrides.

The curing of oxazolidone modified DGEBA, using stoichometric amounts of Pyromellitic Dianhydride (PMDA) on DuPont 2100 Thermal Analyser at 10^{0}C per minute was as follows:

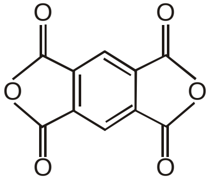


Curing of epoxies resins in presence of anhydrides

Anhydride hardeners show some outstanding properties, i.e. low exotherm and shrinkage during curing, as well as low water absorption and almost internal stress free systems after curing. During cure, the heat formed by the exothermic reaction can lead to a considerable rise in temperature , known as ‘exotherm’. The actual exotherm depends on

- Rate at which polymerization is occurring
- Rate at which the heat evolved is being dissipated

Carboxylic acid anhydrides are one of the most important high temperature curing agents used for the conversion of epoxy resins to highly crosslinked, glassy, three-dimensional networks. Optimum properties are obtained when stoichiometric equivalents of epoxy and anhydride are used with high temperature cures. The anhydride can only react through an epoxy group, hence the synthesized oxazolidone is dispersed in pure epoxy before the curing with anhydrides to provide reactive sites for anhydrides. In the present work, the curing behaviour of Oxazolidone modified DGEBA with stoichiometric amounts of pyromellitic dianhydride (PMDA) and Benzyl Dimethyl Amine (BDMA) as a catalyst was used. These blends were investigated by differential scanning calorimetric studies.



PMDA

Fig. V

Preparation of blends

This investigation reports the isothermal curing of oxazolidones, with PMDA using a tertiary amine – Benzyl dimethyl amine (BDMA) as a catalyst. Blends were prepared and characterized by DSC studies, which is a useful method for direct measurement of the rate of exothermic polymerization.

The synthesized oxazolidone was dissolved in epoxy resin to facilitate uniform mixing and the mixture was warmed to 50^0C and stirred till a uniform solution was obtained. Various stoichiometric amounts of Pyromellitic Dianhydride was added gradually, till it was evenly dispersed in the epoxy. 5 phr of tertiary amine (BDMA) was added in all cases and samples were drawn for DSC analysis. Pyromellitic dianhydride (m.p. 286^{0}C) is a solid which has been found to have high cross linked density and good thermal resistance. It is very reactive towards epoxide and can be used at room temperature, so that subsequent hot cure can promote the reaction.

The first series of blends were prepared by varying the amount of oxazolidone from 1%, 5%, and 10% and keeping the PMDA at 0.1 mole ratio.

Curing Behaviour

For curing studies, TA 2100 Thermal Analyzer having a 910 DSC module was used to record DSC scans at a heating rate of 10^{0}C/min in static air atmosphere. 2 mg of samples was used in each experiment. Freshly prepared samples obtained by mixing required amounts of anhydrides and DGEBA were used for recording DSC scans.

RESULTS AND DISCUSSION

The curing of the oxazolidone modified epoxy resin depends on the nature of the curing agent as well as on the stoichometry. A broad curing exotherm was observed in all DSC scans. The exothermic transitions associated with the curing were characterized by the following parameters:

i. Onset temperature – where the curing starts
ii. Extrapolated temperature – temperature where the first detectable heat is released. It was obtained by the extrapolation of the steepest portion of the curve.
iii. T_{max} Temperature ^{0}C–temperature of the peak position of the exotherm
iv. T_{end} Temperature ^{0}C- temperature of the end of the curing of the exotherm
v. Heat of reaction (J/g) – calculated by measuring the area under the exotherm.

Following are the DSC results obtained by heating an uncured epoxy resin system at a rate of 10^{0}C/min. The plot shows the heat flow as a function of the sample temperature. A further increase in the sample temperature, the resin eventually undergoes curing and this is observed as a large exothermic peak. As the resin becomes more crosslinked, the heat of curing become increasingly smaller and, as the material becomes completely cured, the heat of cure becomes undetectable. The heat of cure may be used to determine the percent cure of a resin material. The results of these scans are summarized in **Table 1**

DSC scans of varying amounts of oxazolidones with 0.1 mole of PMDA

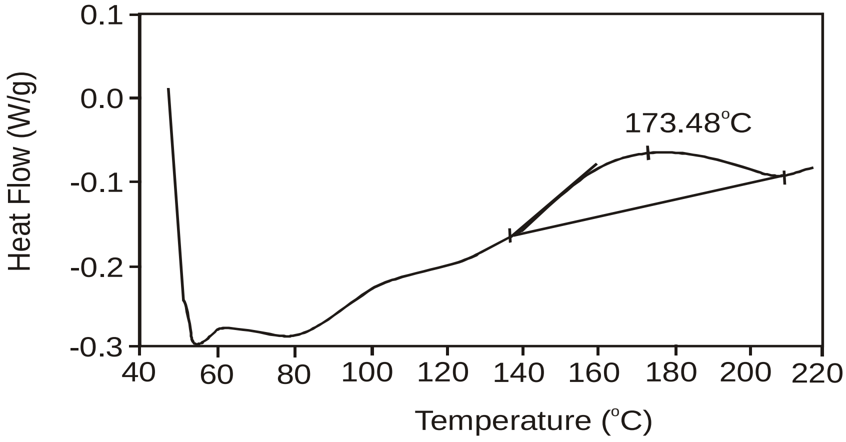


Fig. VI

DSC of pure oxazolidone

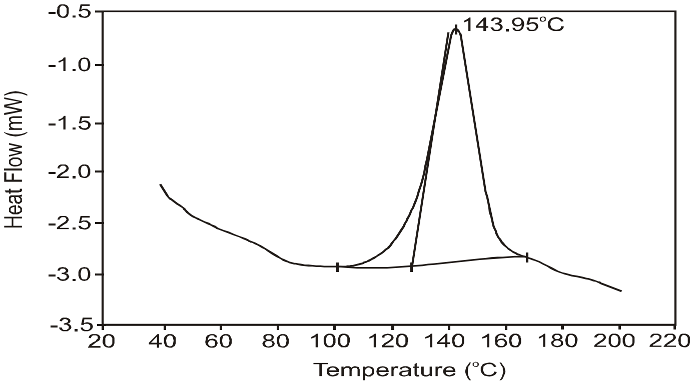


Fig. VII

1% of oxazolidone in the blend

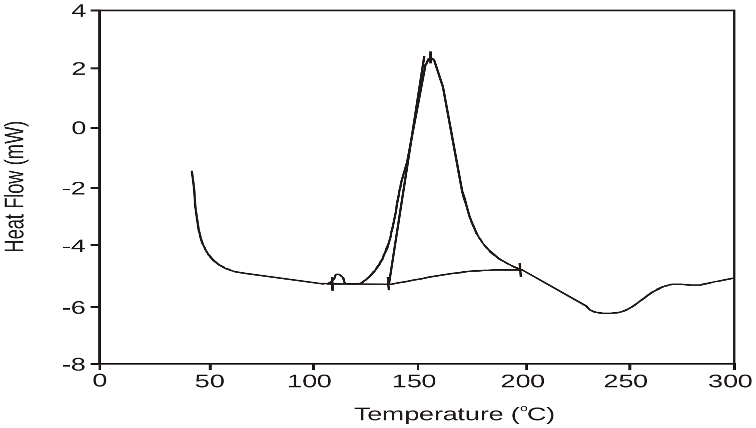


Fig. VIII

5% of oxazolidone + 0.1 PMDA

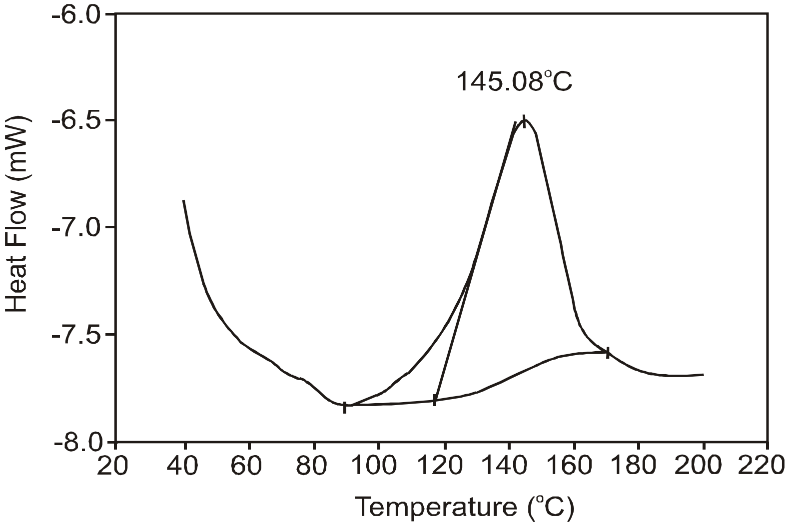


Fig. IX

10% of oxazolidone + 0.1 PMDA

Table I
OXAZOLIDONE MODIFIED EPOXY RESIN CURED WITH 0.1 PMDA

Sr. No.	Composition Epoxy/Anh	Onset Temp. (^{o}C)	Extrapolated Temp. (^{o}C)	T_{max} Temp. (^{o}C)	T_{end} Temp. (^{o}C)	Heat of Reaction (J/g)
1.	Neat Resin + 0.1 PMDA	89.29	118.47	145.08	178.93	59.13
2.	1% Oxz. + 0.1 PMDA	101.01	126.85	143.95	166.90	40.64
3.	5% Oxz. + 0.1 PMDA	101.95	135.55	156.42	198.51	49.10
4.	10% Oxz. + 0.1 PMDA	90.95	117.28	145.08	176.61	52.37

The onset temperature was observed to be in the range 101- 90^{0}C and it decreases with increasing oxazolidone in the blend. The extrapolated temperature is maximum when 5% oxazolidone is present in the blend. The heat of reaction increases as the amount of oxazolidone increases in the blend.

In the second series of blends, the amount of oxazolidone is kept constant at 10% and the amount of Pyromellitic Dianhydride was varied from 0.1, 0.2, 0.3,0.4 and 0.5 mole ratio.

DSC scans of 10% oxazolidones with different moles of PMDA

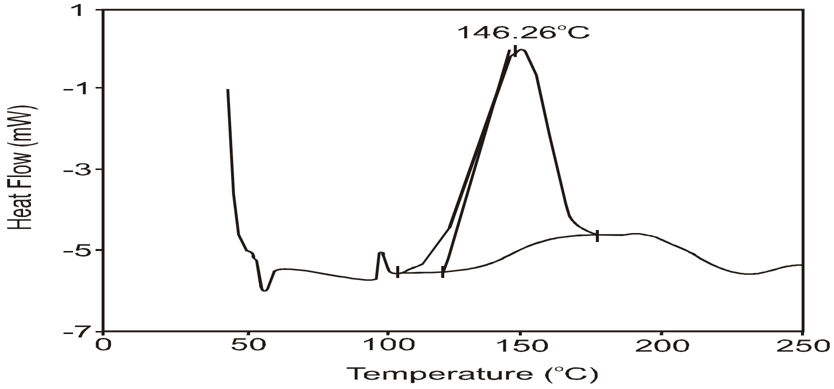


Fig. X

10% of oxazolidone + 0.1 PMDA

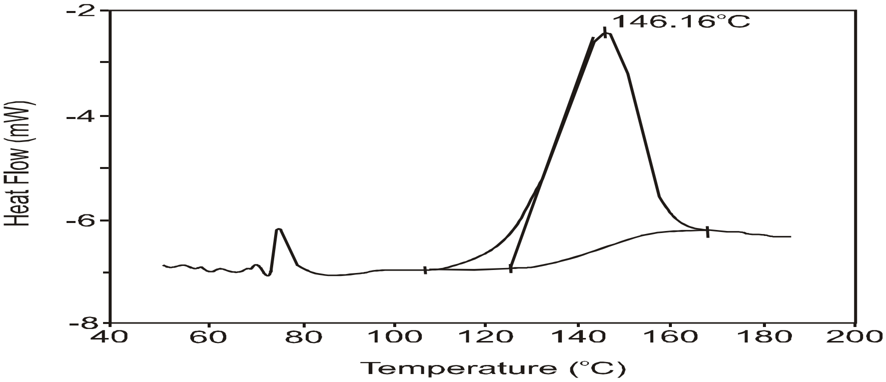


Fig. XI

10% of oxazolidone + 0.2 PMDA

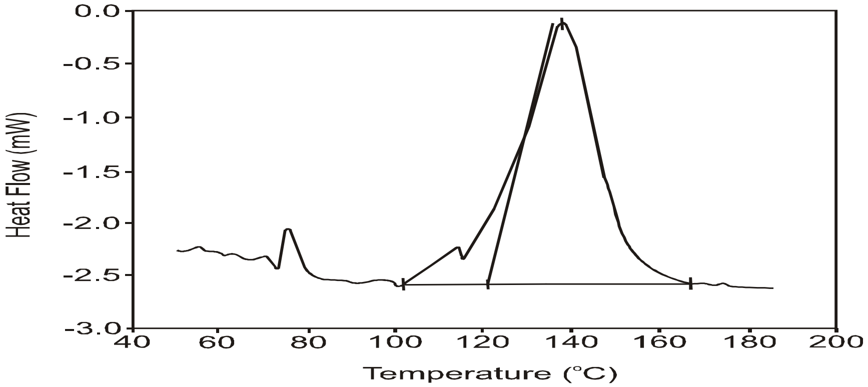


Fig. XII

10% of oxazolidone + 0.3 PMDA

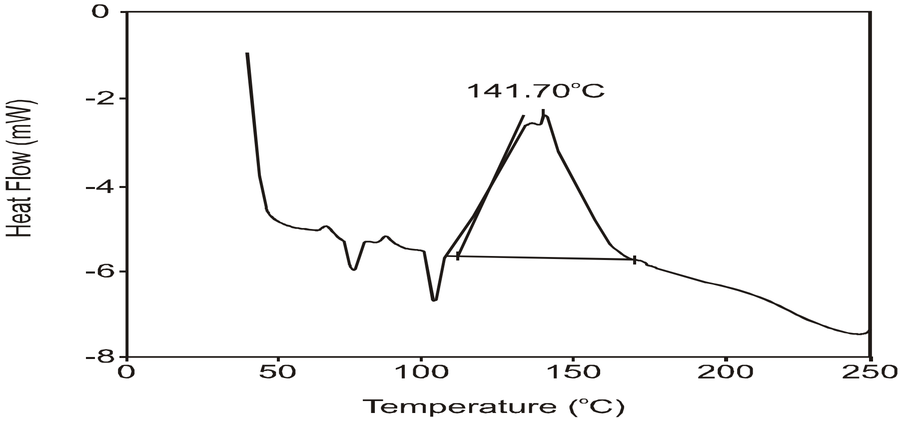


Fig. XIII

10% of oxazolidone + 0.4 PMDA

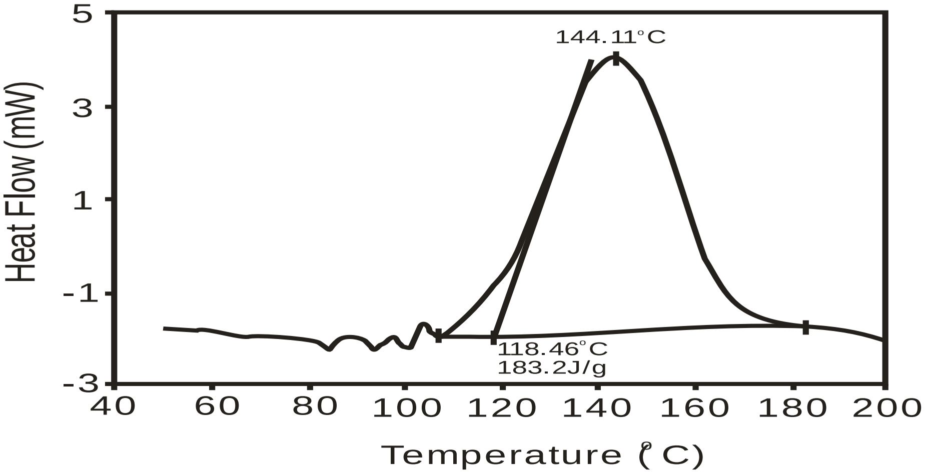


Fig. XIV

10% of oxazolidone + 0.5 PMDA

Table II

The results are summarized in **Table II -** curing of 10% oxazolidone blends with varying amounts of PMDA.

Sr. No.	Composition Epoxy/PMDA	Onset Temp. (°C)	Extrapolated Temp .(°C)	T_{max} Temp. (°C)	T^{end} Temp.(°C)	Heat of Reaction (J/g)
1.	Neat Resin + 0.5 PMDA	112.27	125.82	145.40	165.40	49.92
2.	10% Oxz. + 0.1 PMDA	102.25	120.42	137.52	160.70	37.03
3.	10% Oxz. + 0.2 PMDA	102.54	124.43	146.16	158.56	101.8
4.	10% Oxz. + 0.3 PMDA	103.55	120.04	146.26	160.71	133.1
5.	10% Oxz + 0.4 PMDA	107.49	112.65	141.70	171.87	69.98
6.	10% Oxz. + 0.5 PMDA	108.92	121.43	141.99	176.34	87.76

The cure kinetics of epoxy resin was evaluated with the help of DSC, which is a useful method for direct measurement of the rate of exothermic polymerization.

DSC provides a means of quickly determining whether curing reaction of a given thermoset is autocatalysed or follows nth order kinetics. A sample is maintained isothermally at an elevated temperature and the cure exotherm monitored as a function of time.

The DSC scans given above show that the heat of reaction increases with increasing amount of PMDA in the blend and is maximum when 0.3 mole of PMDA is present in the blend. The heat of reaction falls when PMDA is increased to 0.4 and 0.5 in the blend. From these DSC studies, we can conclude that 10% of the oxzolidone and 0.3 mole of PMDA in the blend gives best thermal stability.

From these DSC studies, we can conclude that 10% of the oxzolidone and 0.3 mole of PMDA in the blend gives best thermal stability. The heat of cure may be used to determine the percent cure of a resin material and the exothermic peak temperature reflects the maximum rate of curing of the resin.

CONCLUSIONS

From these studies, it can be concluded that the curing behavior of DGEBA was dependant on the amount of PMDA and the heat of curing was maximum when the molar ratio of oxazolidone was 10% and the amount of PMDA in the blend was 0.3 mole. The heat of cure may be used to determine the percent cure of a resin material and the exothermic peak temperature reflects the maximum rate of curing of the resin. The thermal stability of the oxazolidone modified epoxy resin depends on the structure of the cured network.

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