CHAPTER-V

SUMMARY
CURING AND THERMAL BEHAVIOUR OF DGEBA IN THE PRESENCE OF DIORGANOTIN DICHLORIDES

To analyse the structure effect of diorganotindichlorides, various structure diorganotindichlorides were being used by keeping molar ratio staticdiorganotindichlorides : DGEBA i.e. 1:1. Presence of large transition is found in scans of DSCCharacteristic temperatures were noted and curing exotherm was observed as discussed earlier. Exothermic reaction was also calculated area below the exothermic transition. All samples possess single exotherm.

Founded trend in peakexotherm temperatures:

DBMTC> DDMTC> DPETC> DPMTC.

Curing characteristics are found proportional upon the electrophilicity of tin and induction of the alkyl or aryl group. The alkyl groups have + ve induction (+ I) where as aryl groups (benzene) have the – ve induction (- I). Highest curing temperatures with BMTC is found on electrophilicity and induction grounds.

DGEBA being cured isothermally among different dichlorides by heating in an air oven (100 °C 20°C for two hours) for finding the glass transition temperature. As there is no exothermic transition in cured samples so complete cross-linking reaction exists. Glass transition temperature favors the rigidity of polymer backbone. Greater value of $T_g$ was found for cured resin DPETC.

Dynamic DSC scans of isothermal experiments gives kinetic parameters. Activation energy for reaction found using Ozawa’s method.

Ea of curing found minimum in case of (DPMTC) and maximum in (DBMTC). Thus the activation energy of curing trend in the presence of different diorganotindichlorides.
DPMTC<DPETC< DDMTC< DBMTC

If we are comparing (I.D.T), (T_{max}), (F.D.T) & % C.R. at 800^{0}C. Stability of samples found up to 235^{0}C. All the samples show single step degradation. Char yield min. with DMTC and max. with PETC. C.R shows the sequence shown below:

DDMTC< DBMTC< DPMTC< DPETC

L.O.I. is bein estimated of the resins and we useVanKrevelen and Hoft.Eqn.

\text{LOI} = 17.5 + 0.4 \text{CR}

Where CR = Char yield

It has been observed that LOI value dependent on C.Y. is above 28. Combination of tin and chlorine as flame retarding elements can be used for finding of flame resistant DGEBA
The curing reaction is related to the stoichiometry and on behavior of curing agent. There is nil exothermic transition between 50-300°C. Rest of the various sample, the curing was observed at 105-281°C. Curing temp.is dependent on ratio and str. Sequence observed follows the following pattern:

\[
DDB_5 > DDB_4 > DDB_3 > DDB_1 > DDB_2
\]

Epoxies are cured by hardener such as DDS. Many mol. give their contribution to givecured network which might changes its property and decomposition was observed at 300°C though they have tendency to do so at 200°C. Both thermal stability and behaviour of curing has been disturbed due to the presence of DDS along with biuret. To provide a soln. to the curing of DGEBA we have to use both biuret & DDS. Due to the nature of amines act as together as one unit resultin production of only one Exotherm in given samples.

The reason for decrease in Ti is mixture of biuret + DDS. As we all know this fact that if any how we decreases thee- density on N atom so there will be amine grp. which will be helping in Dislocalising e- and ultimately the reactivity will suffer. Network cure is formed by possible reaction of DDS and biuret that also result in decrease of Ti. These days we concentrate on the study of DSC scans which were being studied at various rate of heat by making use of dynamic process.

Usually when we obtain high peaks it is due to rise in temp. Ea estimated by Ozawa’s process which brings the following points:
1. Constant conversion is ultimately shown by the temp. (Tp)
2. First order kinetics reaction
3. Arrhenius eq. and the relation between rate cont.

Equation shown below indicates the measurement of Dynamic D.S.C.

\[ E_a = \frac{R\Delta \log k}{0.4567\Delta \left\{ \frac{1}{T_p} \right\}} \]

K is considered as rate of heat,

\( E_a \) – Energy required bringing activate,

\( R \) – Universal constant for gas.
CURING AND THERMAL BEHAVIOUR OF DGBT IN THE PRESENCE OF AROMATIC IMIDE-AMINES

Oxirane group of DGBT (N,N’-diglycidylbenzophenonetetracarboxydiimide) while undergoing nucleophilic addition with amine will result in the generation of compact polymer structure. Amino group will open the epoxide ring and there will be generation of secondary amino group as well as –OH group during curing of epoxy resin by amines. Higher concentration of amine will result into etherification & this will add network defects inform of extra crosslinks.

Epoxies show that its cure reac. is dependent on following:

• Design of struct.
• Reactiveness of cure subs.

Hence on basis of observations about structural consequences of Imideamines at DGBT (N,N’-diglycidylbenzophenonetetracarboxydiimide). N,N’-diglycidylbenzophenonetetracarboxydiimide

Characterizing Imide amines

Medium of doing this is elementary analysis and amine eq. wt. It was also characterized using FourierTransform IR, 1H---NMR and 13C----NMR spectra.
Curing Behaviour

The curing behaviour of DGBT was verified:

- Small parts of DSC in a stable atmosphere of the air by using TA2100-910 DSC module.
- DSC scans are being heated at a rate of 10°C/minute.

Recent studies have shown that in order to estimate DGBT curing EA of different amines is preferably done with heat method.

Thermal Stability:

On seeing the stability on thermal basis of DGBT the heat is done in oven from 180 to 220°C and 145 to 185 degree centigrade up to three hours when there is PE/BE/PM/BM/PS/BS respectively.
Findings and Observation found:

- Imideamine found insoluble in acetone and M.E.K.
- Colour of Imideamine was white to orange
- Imideamine found soluble in DMF, DMAC, DMSO.

- In between 1730-1785 per centimeter signal observed of imide ring
  - Stretching because of presence of amine grp. was found in between 3285-3293 per cm.

- At a range between 810-838 per centimeter we could have obtained a large band. Carbon-nitrogen shows a band between 1400-1415 per centimeter.

- There is presence sulfonegrp. In molecule Showing a band at 1140-1320 per centimeter possess stretching too.

- Ar-O-Ar link of absorp band at 1015 per centimeter.

- FT-IR have all the bands showing accordingly in scheme

When there proceeds a nucleophile attack of amines on oxiranegrp. then DGBT is cured. Amines which will show the nucleophile character will determine the cure rxn. In todays world aromatic amines are found very helpful in order to study cure of DGBT.

Keeping in consideration the stoichiometric amt.of amides we can easily find out the cure behave of DGBT and its effect of the str. Samples were showing transition at a range of temp. in between 160-275 degree centigrade. We can make use of str. of diamine or dianhydride to find out the effect of temp. while making imide amines.

Here they are prepared by react. of pyromelliticdianhydride (PMDA)/ benzophenone 3,3′, 4,4′-tetracarboxylic dianhydride BTDA with diamines DDE,DDM and DDS. Lots of factor put their impact properties of Epoxy resins such as chemical str., hindrance based on steric factor.
For curing of the temp. the trend is:

DPS > DPE > DPM

Elevation in temp. is noted in case of imides because of presence of sulfone link and also possibly due to presence of sulphur dioxide.

IPS containing curing exotherm found sharp in the temperature range of 164.2 to 254.2°C. Amine took the responsibility for curing of DBE, DBS and DBM. Following trend is being observed in curing:

DBS > DBE > DBM

When we consider curing of DGBT then it is to be done with strong heating at high temp. of about 190 degree centigrade for an estimated time of 5 hrs. and also it includes the presence of PM/BM/PE/BE/PS/BS. Complete curing was found and there is not findings of any DSC exotherm despite there is presence of baseline shift that also points to G.T. (Tg) findings are shown in scheme 4.7. Tg is dependent on density and toughness of polymer.

Glass temp. is found to rely on the nature of anhydride & amine. Presence of sulfone group is responsible for high glass transition temp. among the samples and it is not dependent on dianhydrides.

Figure 4.4 and 4.5 show the DSC scans of DPM and DBM respectively.
Thermal Stability of Resins (Cured)

Thermal stability of cured DGBT network is dependent on the presence of hydroxyl groups (generated due to curing) and the structure of amines used for curing. In the present studies, amines used differ in their backbone structure and imide--amines had significantly higher molecular weight. This variation is expected to affect the –OH content in the cured resins, the flexible linkages of DGBT, and the aromatic character of the network.

- I.D.T = Temp. which initiates decomp.
- Tmax = Temp. wt. loss is maximum
- FDT = Final decomposition temperature
- Char yield = R weight