

## Effect of Epoxidized Cottonseed Oil on Epoxy Resin and Its Thermal Behavior

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**Abstract:** In the present work the effect of loading of epoxidized cottonseed oil (ECO) on multifunctional epoxy and diglycidyl ether of bisphenol-A (DGEBA) were studied. First the epoxidized cottonseed oil was synthesized using peracetic acid. The modified network was obtained by blending ECO into epoxy resins having ECO content from 0 to 20 wt. %. The differential scanning calorimetry (DSC) determines the cross linking density of the neat and modified epoxy. The thermal degradation of both the epoxy materials was investigated using thermogravimetric analysis. The thermal stability decreased due to decrease in crosslinking density and increased due to high crosslinking. In multifunctional epoxy addition of epoxidized cottonseed oil enhances the chain mobility which decreases the thermal degradation temperature and cross-link density.

**Key words:** ECO, DGEBA, Multifunctional epoxy, DSC, TGA, Crosslink density, thermal stability.

### 1. Introduction:

Epoxy resin is the most versatile and highly consumed thermosetting resin. The production of epoxy resin started in 1940's in Europe and United States. Epoxide can be any compounds that have one or more 1,2-epoxy groups and can convert to thermosetting materials. By ring opening reaction, the active epoxide groups in the uncured epoxy reacts with many curing agents that can contain hydroxyl, carboxyl, amine, and amino groups [1]. Epoxy resins are widely used in structural adhesives, surface coatings, engineering composites, and electrical laminates. The high-performance applications like aerospace and critical defence applications require incorporation of multifunctional epoxies. Epoxy resins have excellent chemical resistance, excellent adhesion, good heat and electrical resistance, low shrinkage, and good mechanical properties, such as high strength and toughness. One of the drawback poses by epoxy is its high crosslink density which may cause brittleness and affect the toughness[2]. Among the vegetable oil-based polymers, EVOs can be used as reactive modifiers and diluents for epoxy composites. The EVO's has social and environmental advantages compared with traditional petroleum-based polymers [3]. The use of epoxidized oil up to certain extent in epoxy resin can help to reduce the cross-link density. Addition epoxidized oil into epoxy incorporates the second phase. Epoxy resin can also modified by rubbers to improve toughness but use of rubber can reduce final thermal properties of the epoxy resin. But the EVO can improve the toughness of the epoxy resins without remarkable variation in the thermal properties. [4].

Jin and Park worked on the thermomechanical behavior of epoxidized soybean oil and epoxidized castor oil on epoxy resin. They investigated that the thermal stability of the systems decreased as the EVO content increased, due to the lower crosslinking density of the DGEBA/EVO systems. The coefficient of thermal expansion of the systems was found to increase linearly with increasing EVO content. This could be attributed to the fact that the degrees of freedom available for motions of the segments of the macromolecules in the network structure were enhanced by the addition of EVO [3].

## 2. Experimental Details

### 2.1 Raw Material:

For synthesis of epoxidized cottonseed oil, refined cottonseed oil was procured from super market, glacial acetic acid (99-100 wt %), aqueous hydrogen peroxide (30 wt %), sulphuric acid (98 wt %) were obtained from Merck Specialities Pvt Ltd. For analytical purpose hydrogen bromide, sodium hydroxide, Wij's solution, sodium thiosulphate, potassium iodide was obtained from reputed company and were AR grade. The commercially available epoxy resin (aromatic and cyclic) was supplied by Atul Ltd., Walsad, India.

### 2.2 Method:

The epoxidized cottonseed oil (ECO) was synthesized in our lab. The epoxidation reaction is carried out in a 1 lit three neck flask equipped with mechanical glass stirrer. The whole assembly was immersed in a water bath. 200ml of cottonseed oil was taken in the reactor and with respect to this calculated amount of  $\text{CH}_3\text{COOH}$  and was added to the reactor and the mixture was stirred for about 30 minutes. Then the required amount of 30 % aqueous  $\text{H}_2\text{O}_2$  was added drop wise in such a way that the addition was completed in half an hour and the reaction was continued further for the required time duration. Samples were taken out intermittently, considering the completion of  $\text{H}_2\text{O}_2$  addition as zero time. The collected samples were filtered and then extracted with diethyl ether in a separating funnel, after that washed with cold and slightly hot water successively to remove free acid. The final product pH was checked to have a value 7.0 and then analyzed for iodine value, oxirane content.

The modified structure was obtained by blending epoxy resin and ECO in varying weight ratio ranging from 100:0 to 80:20. Two different types of epoxies are selected one is bisphenol-A based while another one is multifunctional. ARL-135 is the Bisphenol-A based epoxy having 190 gm/equivalent and the hardner used is AH-135. While L-552 is the multifunctional epoxy having 150 gm/eq. and the hardner used is K-552.

The commercial epoxy resin and ECO were blended at room temperature using mechanical stirrer. While blending care was taken to obtain homogeneous mixing and air bubble free blends. The stoichiometric amount of curing agent was added to the resin. After this the prepared blends were atmosphere cured.

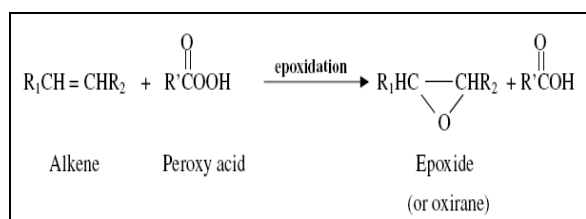
### 2.3 Analysis of raw material and product:

The % oxirane oxygen was determined by the method of AOCS Cd9-57(1997) under which the oxygen is titrated directly with hydrogen bromide solution in acetic acid. Iodine value was determined according to Wij's method [5]. The conversion of double bonds to oxirane rings were observed under FTIR spectra of cottonseed oil and ECO.

The ECO modified epoxy resin was characterize for Differential Scanning Calorimetry (DSC) using SHIMADZU DSC-50 under nitrogen flow of 50 ml/min at heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ . The heat evaluation was then monitored from 20 to  $300\text{ }^\circ\text{C}$ . DSC was used to study the cure behavior and heat flow during curing. Thermogravimetric analyses (TGA) were performed with a SHIMADZU TGA-50 analyzer to investigate the thermal degradation of the cured Epoxy/ECO blends from 30 to  $600\text{ }^\circ\text{C}$  under nitrogen flow of 50 ml/min at heating rate of  $10\text{ }^\circ\text{C}/\text{min}$ .

## 3. Result and Discussion

### 3.1 Synthesis of ECO



**Fig 1 Epoxidation Reaction**

The epoxidized cottonseed oil (ECO) was synthesized by reaction of cottonseed oil with glacial acetic acid and 30 % aqueous hydrogen peroxide using sulfuric acid as a catalyst. The optimum conditions obtained from the present study include reaction time of 4 hours and temperature of 60<sup>0</sup>C, hydrogen peroxide to ethylenic unsaturation ratio of 2:1, acetic acid to ethylenic unsaturation ratio of 0.5:1 and the sulphuric acid loading was 2% by weight of the total weight of hydrogen peroxide and acetic acid at stirring speed of 850 rpm. The simplified epoxidation reaction is summarized as follows.

Table 1, shows the comparative physical and chemical properties of the cottonseed oil and ECO.

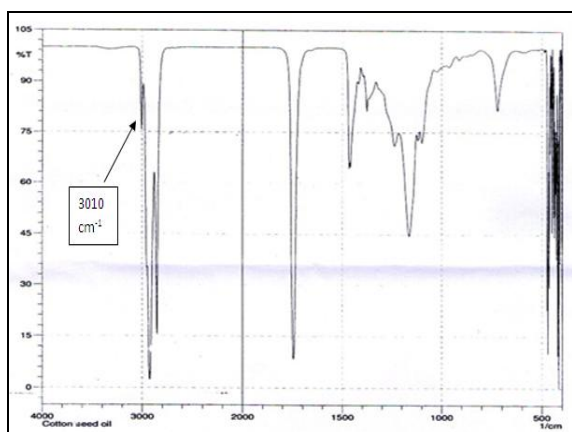
**Table 1, Comparative Physical Properties of Cottonseed Oil and Its Epoxidized Oil**

Characteristics	Experimentally Obtained (Cottonseed Oil)	Experimentally Obtained (Epoxidized Cottonseed Oil)
Specific Gravity at 30 °C	0.917	0.973
Iodine value( g I2/100 g Oil)	96	21.40
Acid Value (mg KOH/g Oil)	0.55	-
Oxirane value	-	3.68
Viscosity(Ford Cup)	98 sec	182 sec

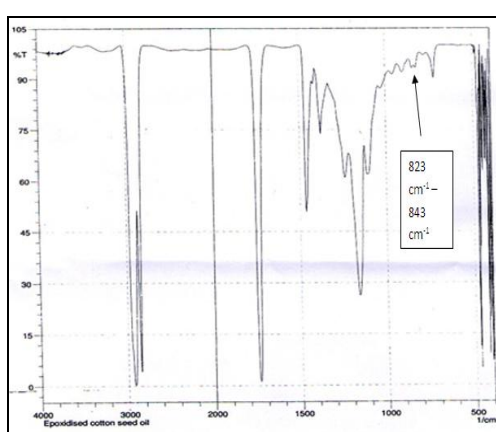
The synthesized ECO was quite viscous as compare to cottonseed oil with a oxirane value of 3.68. Due to side reactions lower value of oxirane content may occur.

### 3.2 FTIR Analysis

The FTIR spectra were recorded using 8400S SHIMADZU(1). The chemical structure of the synthesized ECO was characterized by FT-IR. From the fig.2 and fig. 3, it was clear that the peak related to carbon-carbon double bonds from cottonseed oil at 3010 cm<sup>-1</sup> disappeared on epoxidation and the epoxy groups were found in epoxidized cottonseed oil (doublet at 823 cm<sup>-1</sup> and 843 cm<sup>-1</sup>) indicating that all of the carbon-carbon double bonds were turn into epoxy groups. Vleck and Petrovic reported the presence of epoxy groups at 822–833 cm<sup>-1</sup>, which agrees well with this study [6].



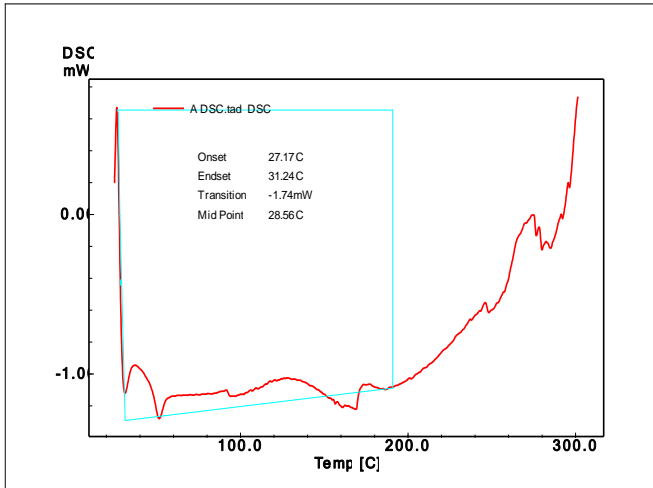
**Fig.2 FTIR Spectra of Cottonseed Oil**



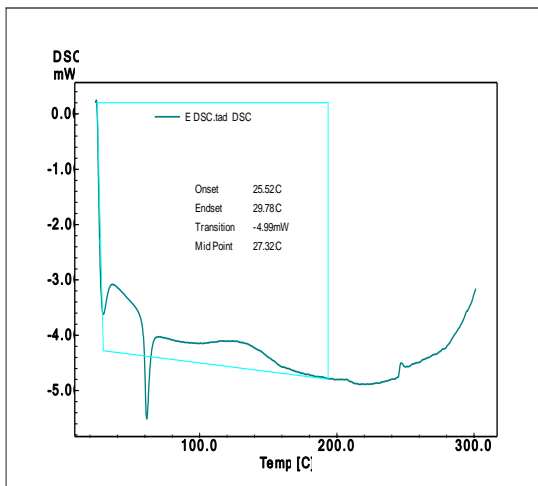
**Fig.4 FTIR spectra of epoxidized cottonseed oil**

### 3.3 Differential Scanning Calorimetry:

The cure behavior, glass transition temperature and heat flow were investigated using DSC. Samples were prepared in the ratio ranging from 100:0 to 80:20 (weight basis) of epoxy resin: ECO with stoichiometric amount of suitable hardner. Following fig.4 and fig.5 shows the DSC Thermogram of Epoxy (ARL-135)/ECO blend with 80:20 ratio and DSC Thermogram of neat Epoxy (ARL-135) respectively. Table 2 gives the results obtained by DSC analysis of polymer samples.



**Fig.4 DSC Thermogram of Epoxy (ARL-135)/ECO blend with 80:20 ratio**



**Fig.5 DSC Thermogram of neat Epoxy (ARL-135)**

**Table 2, DSC Result of ARL-135/Epoxidized Cottonseed Oil-Hardner System**

Sample No.	ARL-135 : ECO	Onset Temperature (°C)	End Set Temperature (°C)	Heat Flow/Transition (mW)
A	80:20	27.17	31.24	-1.74
B	85:15	26.87	28.91	-1.93
C	90:10	20.09	30.73	-1.80
D	95:5	28.31	29.25	-2.41
E	100:0	25.52	29.78	-4.99

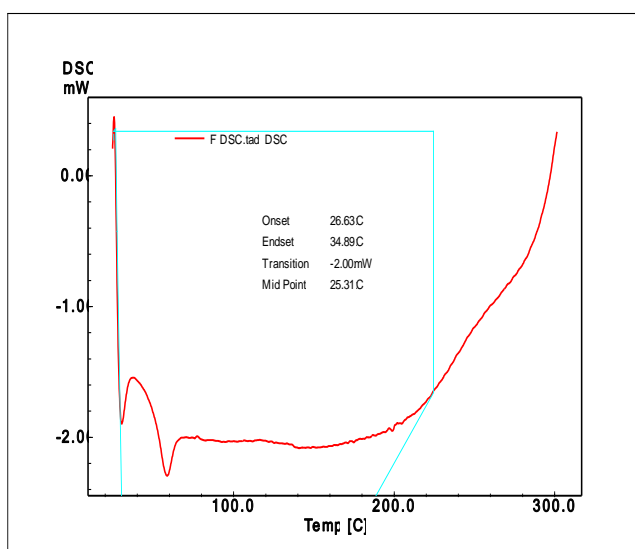
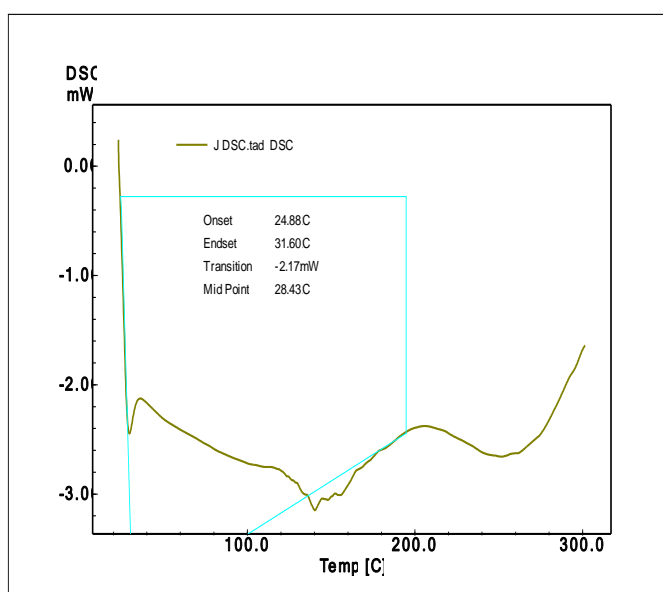
**(Where resin: hardner ratio is 100:32)**

From the above result end set temperature of the blends (sample A, sample C) is shifted to little higher temperature with increasing the ECO content into the epoxy resins in comparison of neat epoxy. This phenomenon indicates that the addition of epoxidized oil into epoxy resin retard the curing reaction because of the feature of internal epoxy groups and the low reactivity of the epoxidized cottonseed oil lead to an increase of curing temperature [7]. The onset temperature of the blends (sample A, sample B, sample D) is shifted to little higher temperature as compared to the neat epoxy sample. This result can be attributed to the polymerization of epoxidized cottonseed oil at relatively high temperature compared with neat ARL-135. The values of transition (mW) for the system increased with increasing epoxidized oil content of the ARL-135/Epoxidized Cottonseed Oil System. The increase in transition (mW) is strongly believed to be related to a decrease in cross-link density.

**Table 3, DSC Result of L-552/Epoxidized Cottonseed Oil-Hardner System**

Sample Number	L-552 : Epoxidized cottonseed oil	Onset Temperature ( $^{\circ}\text{C}$ )	End Set Temperature ( $^{\circ}\text{C}$ )	Heat Flow/Transition (mW)
F	80:20	25.52	29.78	-4.99
G	85:15	26.63	34.89	-2.00
H	90:10	26.92	33.45	-3.88
I	95:5	28.33	30.88	-2.30
J	100:0	31.07	39.21	-0.68

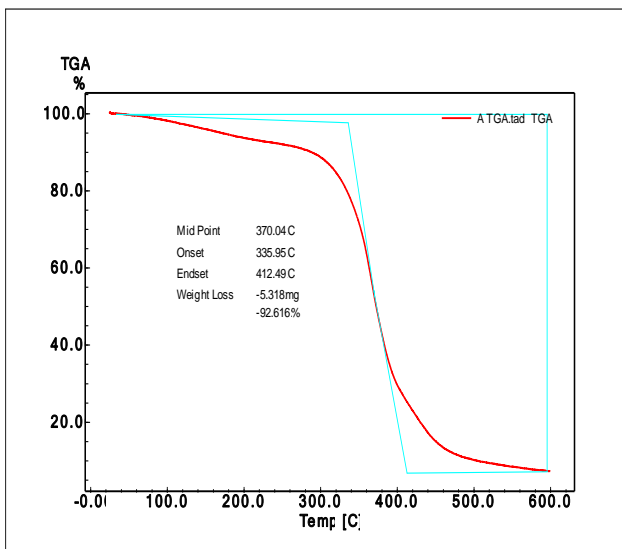
(Where resin: hardner ratio is 100:38).

**Fig.6 DSC Thermogram of Epoxy (L-552)/ECO blend with 80:20 ratio****Fig.7 DSC Thermogram of neat Epoxy (L-552)**

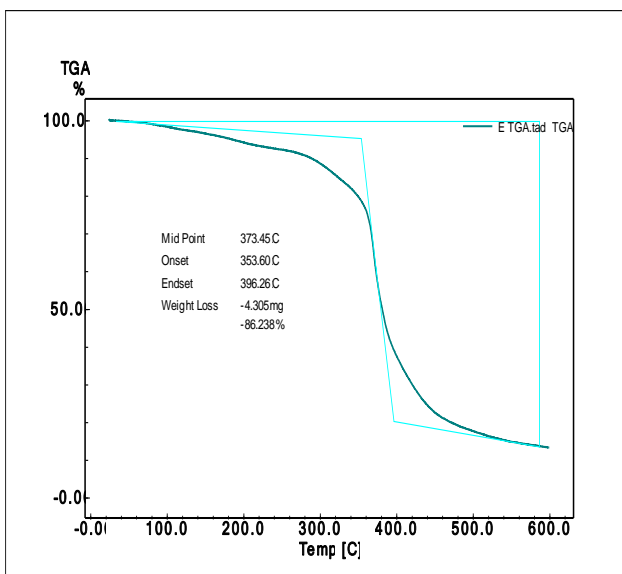
Similarly the **Table 3**, gives the DSC Result of L-552/Epoxidized Cottonseed Oil-Hardner System. **Fig. 6 and Fig. 7** gives the DSC Thermogram of Epoxy (L-552)/ECO blend with 80:20 ratio and DSC Thermogram of neat Epoxy (L-552) respectively. From the above results end set temperature of the blends is shifted to lower temperature with increasing the ECO content into the epoxy resins. This phenomenon indicates that the addition

of epoxidized oil into epoxy resin accelerate the curing reaction because of the feature of internal epoxy groups and the reactivity of the epoxidized cottonseed oil lead to an decrease of curing temperature. The onset temperature of the L-552 – epoxidized cottonseed oil system is shifted to lower temperature as compared to the neat epoxy sample. This result can be attributed to the polymerization of epoxidized cottonseed oil at relatively low temperature compared with neat L-552. The values of transition (mW) for the system decreased with increasing epoxidized oil content due to low epoxide equivalent weight (EEW) of the ARL-135/Epoxidized Cottonseed Oil System. The reduction in transition (mW) is strongly believed to be related to an increase in cross-link density.

**3.4 Thermogravimetric Analysis:** The thermal degradation behavior of the prepared blends was studied using TGA. Thermal stability factors including initial decomposed temperature and temperatures of maximum rate of degradation ( $T_{\text{endset}}$ ) of the blends can be determined from TGA thermogram. Following **Fig. 8 and Fig. 9** shows the TGA Thermogram of Epoxy (ARL-135)/ECO blend with 80:20 ratio and TGA Thermogram of neat Epoxy (ARL-13) respectively.



**Fig.8 TGA Thermogram of Epoxy (ARL-135)/ECO blend with 80:20 ratio**



**Fig.9 TGA Thermogram of neat Epoxy (ARL-13)**

**Table 4, TGA results of of ARL-135-Epoxidized cottonseed oil-Hardner System**

Sample No.	ARL-135 : Epoxidized cottonseed oil	Onset Temperature °C	End set Temperature °C	Weight Loss (mg)	% Weight Loss
A	80:20	335.95	412.49	-5.318	-92.616
B	85:15 (Degradation occurs at two places)	189.46	252.57	-0.268	-6.445
		322.38	423.68	-3.017	-72.559
C	90:10 (Degradation occurs at two places)	67.83	540.13	-0.203	-6.602
		369.75	377.35	-2.544	-82.732
D	95:5 (Degradation occurs at three places)	314.29	351.43	-1.262	-22.710
		364.86	400.84	-2.212	-39.806
		516.68	527.79	-4.770	-85.838
E	100:0	353.60	396.26	-4.305	-86.238

(Where resin: hardner ratio is 100:32)

**Tables 4**, gives the TGA results of ARL-135-Epoxidized cottonseed oil-Hardner System give the results obtained by TGA analysis of polymer samples.

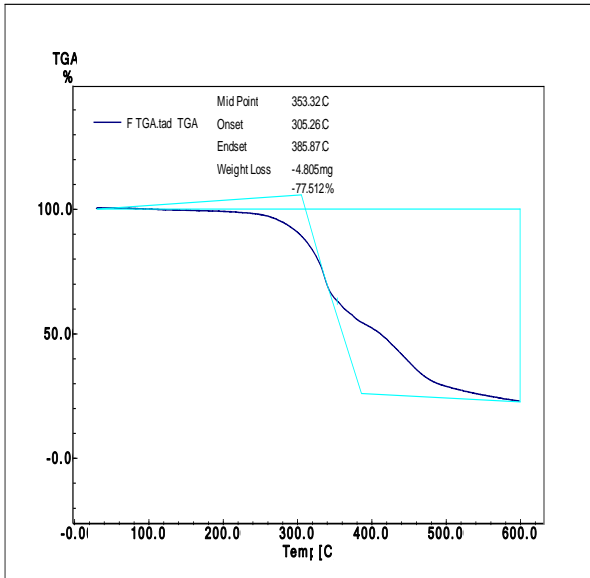
From the above table, it was found that the decomposition of the blends commences at lower temperature than that of neat epoxy and rapidly continues to higher temperature. The initial degradation temperature of the blends is decreased remarkable with respect to neat epoxy; this is attributed to the reduced cross-linking density of the epoxy network, due to the incompletely curing reaction [8].

**Table 5, TGA Result of L-552/Epoxidized cottonseed oil-Hardner System**

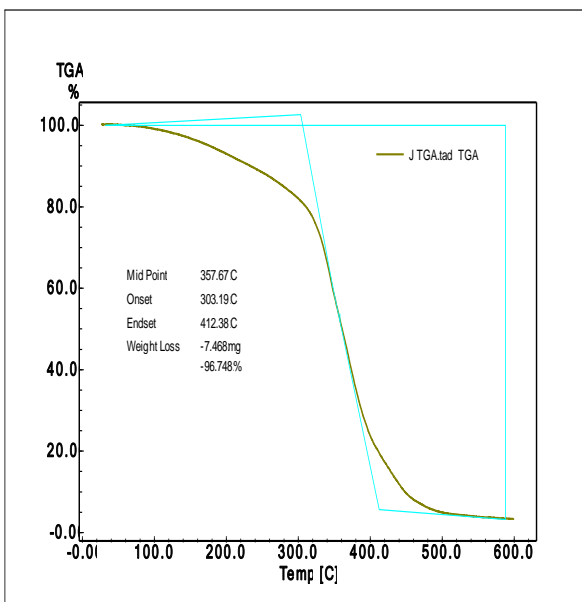
Sample No.	ARL-135: Epoxidized cottonseed oil	Onset Temperature °C	End set Temperature °C	Weight Loss (mg)	% Weight Loss
F	80:20	305.26	385.87	-4.805	-77.512
G	85:15 (Degradation occurs at two places)	317.27	351.91	-2.404	-44.240
		409.25	479.23	-2.228	-41.001
H	90:10 (Degradation occurs at two places)	318.70	356.24	-4.272	-60.699
		440.04	484.30	-2.107	-29.937
I	95:5 (Degradation occurs at two places)	310.91	365.11	-2.868	-61.086
		434.25	485.55	-1.236	-26.326
J	100:0	303.19	412.38	-7.468	-96.748

(Where resin: hardner ratio is 100:38)

Above **Table 5**, gives the TGA result of L-552/Epoxidized cottonseed oil-Hardner system in different composition. **Fig. 10** gives the TGA Thermogram of Epoxy (L-552)/ECO blend with 80:20 ratio whereas **Fig.11** gives TGA Thermogram of neat Epoxy (L-552).



**Fig. 10 TGA Thermogram of Epoxy (L-552)/ECO blend with 80:20 ratio**



**Fig.11 TGA Thermogram of neat Epoxy (L-552)**

From the above results, it was confirmed that the decomposition of the blends commences at higher temperature than that of neat epoxy and rapidly continues to higher temperature. From which it can be confirm that the blends have excellent thermal stability. The initial degradation temperature of the blends is increased remarkable with respect to neat epoxy; this is attributed to the increased cross-linking density of the epoxy network, due to the completely curing reaction.

#### 4. Conclusion:

In the present work the ECO was prepared with oxirane content 3.68 and is its effect on the thermal and crosslinking properties were studied. From the results obtained it can be concluded that with increase in percentage of epoxidized cottonseed oil content in ARL-135, the thermal stability of the blends was decreased and the transition was increased. This could be caused by the low reduced cross linking density of the epoxy network in low reactivity of Epoxidized Cottonseed Oil of the blends. The decrease of cross-link density of



ARL-135 may improve its flexibility property and can be used as an impact modifier for ARL-135 in both thermal and environmental respect.

Whereas, with increase in percentage of epoxidized cottonseed oil content in L-552, the thermal stability of the blends was increased and the transition was decreased. This could be caused by the increased cross-linking density of the epoxy network in reactivity of epoxidized cottonseed oil of the blends. The increase of cross-link density of L-552 may improve its strength and can be used as a strength modifier for L-552 in both thermal and environmental respect.

## 5. Acknowledgement:

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