Chapter 9

Thermogravimetric and dielectric analysis of liquid rubber modified epoxy resin

Abstract

Thermal stabilities of HTLNR and ETLNR modified epoxy resin was studied using thermogravimetric analysis. The activation energy for decomposition of neat and modified epoxies has been estimated and compared. In this study, it was observed that incorporation of HTLNR or ETLNR in DGEBA network did not significantly affect the onset of degradation. It is evident that thermal stability as well as T\textsubscript{max} has increased marginally due to crosslinking reactions. Dielectric analysis was performed on epoxy/HTLNR and epoxy/ETLNR blends to understand the dielectric properties. Among the blends, epoxy/HTLNR blends showed enhancement in conductivity.

Part of the results of this chapter have been communicated to Polymer degradation and stability.
9.1 Introduction

Epoxy resins are important industrial polymers. As a result of their superior mechanical properties, low shrinkage during cure, thermal stability, and ease of processing, epoxy resins are finding increasing use in a wide range engineering applications, many of which involve high value added products [1]. For many end uses, it is necessary to add other components to the resin to improve its properties. The cured products have good physical strength, excellent moisture, solvent and chemical resistance but relatively poor thermal stability and flame resistance limits their applications in more demanding areas such as aerospace and electronic industry [2].

Thermal degradation is a kind of chemical aging. Because these reactions occur as a result of the presence of unreacted species, they will continue for a long time, continuously changing material properties [3]. The study of the degradation of a polymer is important because it can determine the upper temperature limit, the mechanism of a solid state process, and the lifetime for a thermoset [4]. Thermal data of the epoxy/liquid rubber systems are very important tool in understanding the molecular architecture and decomposition mechanisms [5]. The thermal degradation of blends does not follow a regular behaviour and is not much dependent on the compatibility of the blend system.

Several studies have been selected in order to explain thermal degradation mechanisms and weight loss [6-13], and also reduction of strength [14-16]. Mija et al. [17] showed epoxy bearing azomethine groups has a higher thermal stability than flexible diglycidyl ethers of bisphenol A epoxy. Su et al. [18] demonstrated improved thermal properties for sulfanilamide or methyl cyclohexane-cured epoxies bearing azomethine or biphenol rigid rod group. Lu et al. [19] have observed good high temperature resistance
of methylenedianiline or 4, 4′-amino-phenoxy hexane cured biphenol epoxy. The thermodegradative behaviour of blends of poly (ether ether ketone) and poly(aryl ether sulphone) was studied by Nandan et al. [20] in order to analyze their thermal stability. Kumar et al. [21] found that incorporation of siloxane into epoxy resin improves the thermal stability and enhances the degradation temperature according to its percentage concentration. Thermal properties of gamma-ray irradiated epoxy-clay nanocomposites toughened with carboxyl-terminated butadiene-acrylonitrile were studied by Lee et al [22]. Thomas et al. [23] studied the thermal stabilities of toughened epoxies based on diglycidyl ether of bisphenol A and varying content of hydroxyl terminated polybutadiene through thermogravimetric analysis. The activation energy for decomposition of neat and modified epoxies has been estimated. Thermal degradation behavior and the kinetic data of the epoxy/cycloaliphatic amine resin modified with ABS were calculated by Abad et al. [24] using isothermal and dynamic thermogravimetric methods.

TGA is widely used because of its relative simplicity. In TGA, the mass as a function of time and temperature is used to assess the thermal stability and degradation of polymers, which include the generation of kinetic data such as activation energies. It is employed to measure the weight loss and the derivative weight loss of the cured epoxy resin by heat. It is generally accepted that reliable degradation temperature and kinetic parameters, such as the initial decomposition temperature (IDT), the temperature of the maximum rate of weight loss (T\(_{\text{max}}\)), the integral procedural decomposition temperature (IPDT), and the activation energy for the decomposition (E), can be used to assess a material’s lifetime [25].

In this study, efforts have been taken to understand the thermal and dielectric behaviour of liquid natural rubbers modified epoxy resin. It was
observed that the degradation pattern remained the same for both epoxy/HTLNR and epoxy/ETLNR blends. In fact, the elucidation of thermal degradation of liquid natural rubber modified epoxy resin has been done for the first time. Dielectric behaviour of epoxy/HTLNR and epoxy/ETLNR blends also have not been analysed so far.

9.2 Results and discussion
9.2.1 Thermogravimetric analysis of epoxy-HTLNR/ETLNR blends

The thermal degradation of neat epoxy resin is depicted in Fig. 9.1. The initial decomposition temperature of the neat resin is 391°C while maximum decomposition ($T_{\text{max}}$) occurs at 429°C.

![TGA curve of neat epoxy](image)

**Figure 9.1** TGA curve of neat epoxy

Figure 9.2 represents the degradation pattern of HTLNR. The degradation of HTLNR occurs in three stages. The onset of weight loss in the first stage occurs in the temperature range 80 to 130°C. About 10% mass loss is observed. This could be due to moisture in the sample and any volatile impurities. The onset of weight loss in the second stage
occurs around 290°C. The second stage degradation occurs with a peak temperature of 414°C. The second stage corresponds to a weight loss of 60%. The third stage of decomposition is rather rapid—it begins around 460°C and is completed in the range 460-590°C. The peak temperature appears at 520°C and the total weight loss at the end of third stage is above 99%.

The TGA curve of ETLNR is given in Fig. 9.3. There are three stages of degradation, first degradation between 220 and 380°C, second degradation between 350 and 460°C and the third between 500 and 630°C. The weight loss at the end of the first stage is 20%, second step is 50% and that at the end of the third step is over 99%. The temperature of maximum degradation of the second stage occurs at 420°C and that for third stage is 578°C. This initial weight loss is possibly due to volatilization of impurity traces and moisture which continues for some period at a very slow rate. As the actual decomposition begins at elevated temperatures, the weight loss occurs at a
faster rate. The main degradation step identified for rubbers clearly corresponds to the breaking down of polymer chains into volatile fragments. For polyisoprene chain, the main fragments are isoprene and dipentene. The peak temperature of the main degradation step increases with epoxidation. The $T_{\text{max}}$ of HTLN is 414°C and that of ETLNR is 420°C. This indicates that the breakdown of rubber molecules is delayed by the presence of epoxy group. This effect could be due to the higher extent of interaction among the rubber molecules caused by the presence of polar groups.

![Figure 9.3 TGA curve of ETLNR](image)

The thermal stability of the epoxy and ETLNR/HTLN blends were analysed using TGA and the thermograms of modified epoxy resin are shown in Fig 9.4 and 9.5 respectively. It was observed that a single stage thermal decomposition occurred in the TGA analysis. The anhydride-cured epoxy samples exhibit maximum degradation around 390°C with an approximately 40% mass loss. The initial decomposition temperature, $T_{\text{max}}$ and activation energy for decomposition for DGEBA and HTLN/ETLNR
blends tabulated in Tables 9.1 and 9.2 remained close to that of unmodified epoxy resin. It shows that the thermal stability of the blends was not affected by the addition of HTLNR or ETLNR to epoxy resin. Epoxy/HTLNR system possesses comparatively less activation energy for degradation due to the presence of rubber having more unsaturation sites.

\[ T_{\text{max}} \] was taken as the maximum in the DTG curve. \( T_{\text{max}} \) is 391°C in neat epoxy and varies in the range 364-386°C in the case of the DGEBA/HTLNR blends. In the case of DGEBA/ETLNR blends, it was found that the blends were stable up to 400°C in nitrogen atmosphere. The initial decomposition temperature (IDT) and the temperature at which the rate of decomposition is maximum (\( T_{\text{max}} \)) for the blends remained the same as that of unmodified epoxy resin. Overall, the thermal stability was not affected by blending with HTLNR/ETLNR.

**Figure 9.4** TGA curves of neat epoxy and epoxy/ETLNR blends
The above behaviour can be explained from the fact that though the degradation starts in rubber at a lower temperature, the rate is much faster in epoxy. The degradation in liquid rubber starts around 420°C. As the chain scission starts, highly unstable free radicals are produced, which abstracts hydrogen not only from the rubber chain, but also from the epoxy chain in the blend and in the process initiate its degradation. Because of kinetic effects, once degradation of epoxy starts, it is very rapid.

From the TGA curves of epoxy/ETLNR and epoxy/HTLNR blends, variation of mass loss can be quantified with respect to the rubber content. The extent of thermal degradation at each temperature can be understood. In fact, it reflects the thermal stability of the blends. The percentage of mass loss is plotted against the rubber content in Figs. 9. 6 and 9. 7. The numerical values are represented in Tables 9.1 and 9.2.
Figure 9.6  Variation of mass loss with composition in epoxy/ETLNR blends

Figure 9.7  Variation of mass loss with composition in epoxy/HTLNR blends
Table 9.1  Percentage mass loss in neat and ETLNR modified epoxy resin

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°C</td>
</tr>
<tr>
<td>Neat epoxy resin</td>
<td>0.26</td>
</tr>
<tr>
<td>Epoxy + 5 wt% ETLNR</td>
<td>1.41</td>
</tr>
<tr>
<td>Epoxy + 10 wt% ETLNR</td>
<td>0.4</td>
</tr>
<tr>
<td>Epoxy + 15 wt% ETLNR</td>
<td>0.29</td>
</tr>
<tr>
<td>Epoxy + 20 wt% ETLNR</td>
<td>0.42</td>
</tr>
<tr>
<td>Neat ETLNR</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Table 9.2  Percentage mass loss in neat and HTLNR modified epoxy resin

<table>
<thead>
<tr>
<th>Sample</th>
<th>Mass Loss (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100°C</td>
</tr>
<tr>
<td>Neat epoxy resin</td>
<td>0.12</td>
</tr>
<tr>
<td>Epoxy + 5 wt% HTLNR</td>
<td>0.23</td>
</tr>
<tr>
<td>Epoxy + 10 wt% HTLNR</td>
<td>0.22</td>
</tr>
<tr>
<td>Epoxy + 15 wt% HTLNR</td>
<td>0.35</td>
</tr>
<tr>
<td>Epoxy + 20 wt% HTLNR</td>
<td>0.46</td>
</tr>
<tr>
<td>Neat HTLNR</td>
<td>2.81</td>
</tr>
</tbody>
</table>
Horowitz and Metzger [26] method was employed to calculate the activation energy for the thermal decomposition of the cured resin from TGA thermograms. Figs. 9.8 and 9.9 represent the plots of $\ln \left( \ln \left( \frac{1}{1 - \alpha} \right) \right)$ against $\theta$ for DGEBA/HTLNR and DGEBA/ETLNR blends. The activation energies of the systems are obtained from the slope of the kinetic plot. The activation energy of the blends is slightly lower than that of neat epoxy resin as given in Tables 9.3 and 9.4. The neat epoxy shows a value of 61 kJ/mol while 15 wt% HTLNR and ETLNR modified samples showed a value of 60 kJ/mol respectively. Higher value is observed for neat epoxy as it requires more activation energy due to higher cross-linking. With the addition of rubber the extent of cross linking is reduced resulting in decreased activation energies. Overall, thermal stability of the blends was comparable to that of neat epoxy resin.

**Table 9.3** Thermal properties of neat and HTLNR modified epoxies

<table>
<thead>
<tr>
<th>HTLNR content (wt %)</th>
<th>IDT (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>$E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>391</td>
<td>429</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>386</td>
<td>419</td>
<td>58</td>
</tr>
<tr>
<td>10</td>
<td>382</td>
<td>421</td>
<td>57</td>
</tr>
<tr>
<td>15</td>
<td>372</td>
<td>422</td>
<td>60</td>
</tr>
<tr>
<td>20</td>
<td>364</td>
<td>402</td>
<td>56</td>
</tr>
<tr>
<td>100</td>
<td>290</td>
<td>414</td>
<td>53</td>
</tr>
</tbody>
</table>
Table 9.4 Thermal properties of neat and ETLNR modified epoxies

<table>
<thead>
<tr>
<th>ETLNR content (wt %)</th>
<th>IDT (°C)</th>
<th>$T_{\text{max}}$ (°C)</th>
<th>$E$ (kJ/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>391</td>
<td>429</td>
<td>61</td>
</tr>
<tr>
<td>5</td>
<td>365</td>
<td>427</td>
<td>59</td>
</tr>
<tr>
<td>10</td>
<td>362</td>
<td>421</td>
<td>57</td>
</tr>
<tr>
<td>15</td>
<td>365</td>
<td>424</td>
<td>60</td>
</tr>
<tr>
<td>20</td>
<td>360</td>
<td>426</td>
<td>60</td>
</tr>
<tr>
<td>100</td>
<td>350</td>
<td>420</td>
<td>54</td>
</tr>
</tbody>
</table>

The activation energy for thermal decomposition decreases from 61 kJ/mol to 53 kJ/mol as the HTLNR content is increased from 5 wt% to 100 wt%. A decrease in activation energy indicates a decrease in the thermal stability of the blends. Thermal stability, however, is a property determined by chemical structure and structural factors that vary with composition of the matrix.

Figure 9.8 Plots of $\ln\left[\ln\left(1 - \alpha\right)^{-1}\right]$ versus $\theta$ of neat and epoxy/HTLNR blends
This type of variation in activation energy for thermal degradation has been reported previously for other polymers [27, 28]. According to Lamas et al. [27] the quantification of kinetic parameters assuming an analytical form of the weight loss curve for heterogeneous systems has many limitations, especially since the effects of all factors that may affect the degradation rate have not been thoroughly investigated [29]. In fact, as pointed out by Mac Callum [30], activation energies in thermal degradation kinetics do not generally have any real significance other than that their use provides a convenient means for comparing the experimental data. Therefore, only the relative differences between the values measured in this work are taken into account.
9.2.2 Dielectric analysis of epoxy/HTLNR and epoxy/ETLNR

Dielectric analysis (DEA) is similar to dynamic mechanical analysis. While DMA resolves the complex behaviour of polymers through the use of an oscillating mechanical stress, dielectric analysis utilizes a periodical electrical field. It is useful in cases where the movement of dipoles or ionic species can be electrically stimulated to provide information about the ionic conductivity of a material. The response of the sample to the oscillating electrical field provides information on the capacitive and conductive properties of materials and quantifies them as a function of time, temperature and frequency [31].

DEA measures four key properties namely, permittivity, loss factor, ionic conductivity and dissipation factor. Permittivity, $\varepsilon'$, also known as dielectric constant, is proportional to the capacitance i.e., the ability of the material to store electric charge. It is a measure of the ease with which the dipoles in the polymer are aligned with the electric field. The loss factor, $\varepsilon''$, is proportional to the conductance [32, 33]. This is the energy required to align the dipoles and move ions. Since ionic movement in a polymer that is below $T_g$ is not significant, $\varepsilon''$ represents only the energy required to align the dipoles when a material is in the glassy state. Above $T_g$, $\varepsilon''$ is related to the ionic conductivity by the frequency. Ionic conductivity can be related to viscosity and is useful in tracking the curing process in thermoset materials. The dissipation factor is expressed as tan delta ($\varepsilon''/\varepsilon'$) and is analogous to the mechanical tan delta [34].

DEA appears to be an alternative technique for deriving the same type of structural information available by DMA, the scale of structural detail detectable by DEA is in the order of one nanometer. It is thus theoretically possible to detect grain structure in a blend with very small domains that may give the appearance of complete miscibility by DMA. It is also possible
to follow the reactions that occur in the later stages of cure in a thermoset system, observing changes that are not detectable by DMA. In DEA a single sample can be tracked over the wide range of viscosities typical of liquid – solid transitions, without encountering the mechanical limitations of a classical rheometer. Commercial DEA instruments will cover frequencies ranging over eight decades from $10^{-3}$ to $10^5$ Hz while DMAs will scan four decades in a range from $10^{-3}$ to $10^2$ Hz.

Since the DEA process measures changes in polymer conductivity and dipole moment, it provides a more global and representative measurement, easily discerning changes, provided that the appropriate frequency of excitation is chosen. In the present study, dielectric studies have been performed on the blends of diglycidyl ether of bisphenol A with two liquid natural rubbers, HTLNR and ETLNR. The effect of liquid rubber content on the dielectric properties of epoxy resin has been elucidated.

According to the common classification of the electrical conducting materials, the materials with electrical conductivity lower than $10^{-6}$ S/cm are treated as insulators, with electrical conductivity between $10^{-6}$ S/cm and $10^{-2}$ S/cm as semiconductors, and consequently with greater than $10^{-2}$ S/cm as metals. A dynamic electric analyser was used to measure both the dielectric permittivity $\varepsilon'$ and the dielectric loss factor $\varepsilon''$ of the epoxy samples isothermally cured at different frequencies.

### 9.2.2.1 Dielectric constant of epoxy/HTLNR and epoxy/ETLNR blends

The variation of dielectric constant of epoxy/HTLNR and epoxy/ETLNR blends as a function of HTLNR content and ETLNR content is represented in Fig. 9.10. It was observed that dielectric constant increased slightly with the increase in HTLNR content at a particular frequency and then leveled off. But in the case of ETLNR blends a slight
increase was followed by a decrease and leveling off. In HTLNR dielectric constant values are comparatively higher than those of ETLNR. The variation of dielectric constant of epoxy/HTLNR and epoxy/ETLNR blends as a function of frequency is represented in Figs. 9.11 and 9.12 respectively.

![Graph showing dielectric constant as function of HTLNR and ETLNR content](image)

**Figure 9.10** Dielectric constant as function of HTLNR and ETLNR content
Figure 9.11 Variation of the dielectric constant with frequency in epoxy/HTLNR blends

Figure 9.12 Variation of the dielectric constant with frequency in epoxy/ETLNR blends
From Fig. 9.11 it is evident that at very low frequencies neat epoxy resin possessed low dielectric constant while the blends with HTLNR showed comparatively higher values. It could be due to the orientation polarisability generated by the presence of hydroxy groups in HTLNR. This together with the electronic and atomic polarisability leads to higher dielectric constant for HTLNR based blends. Hence the dielectric constant showed enhancement in values with increase in rubber content at all frequencies. The contribution from orientation polarisability is negligible at high frequencies as the proper orientation of molecules is not possible. Only at low frequencies it is significant as sufficient time is available for complete orientation of molecules.

9.2.2.2 Volume resistivity of epoxy/HTLNR and epoxy/ETLNR blends

The variation of volume resistivity with HTLNR and ETLNR loading is represented in Fig 9.13 and 9.14 respectively. It shows the ability of an insulator to resist the leakage of electric current. Volume resistivity of epoxy/HTLNR blends was found to decrease with increase in frequency and HTLNR content. The presence of polar OH groups facilitates the flow of current and hence reduced ability to resist the leakage of electric current. This in turn shows that the conductivity of epoxy resin increases upon the addition of HTLNR.
Figure 9.13  Variation of volume resistivity with frequency as function of HTLNR loading.

Figure 9.14  Variation of volume resistivity with frequency as function of ETLNR loading.
9.2.2.3 Conductivity of epoxy/HTLNR and epoxy/ETLNR blends

On adding HTLNR, the amount of polar OH groups increases which results in the enhancement of the conductivity of the samples. In the case of blends with lower wt% of HTLNR, the OH groups are randomly oriented, flow of current is not facilitated and this causes the conductivity to decrease. Higher amounts of liquid rubber in the epoxy matrix lead to organized macromolecular chains which facilitate the flow of current resulting in the enhancement of conductivity. The addition of ETLNR does not exhibit noticeable increase in the conductivity values due to the presence of less polar epoxy groups. The conductivity values are lower for these blends. The change in conductivity of epoxy/HTLNR and epoxy/ETLNR blends as a function of frequency is illustrated in Figs. 9.15 and 9.16. Thus the difference in the conductivity values between the epoxy/HTLNR and epoxy/ETLNR blends can be attributed to the nature of functional groups involved.

![Figure 9.15](image-url)  
Figure 9.15 Variation of conductivity as a function of frequency of epoxy/HTLNR blends
Conductivity was found to increase with increase in rubber concentrations and frequency. This shows that the decrease in resistance with rubber concentration and frequency was rightly observed earlier in Figs. 9.13 and 9.14. The variation of conductivity with the rubber content in epoxy/ETLNR blends and epoxy/HTLNR blends is plotted in Fig. 9.17. It was observed that in the case of HTLNR blends, conductivity increases gradually while ETLNR blends showed a leveling off at higher rubber concentrations.
9.2.2.4 Dissipation factor of epoxy/HTLNR and epoxy/ETLNR blends

The variation of dissipation factor with frequency as a function of rubber content is depicted in Fig. 9.18 and 9.19. The electrical loss or the amount of energy dissipated by the insulating material when the voltage is applied to the circuit can be represented by means of dissipation factor. It is a measure of the electrical energy converted into heat in an insulator. The loss factor depends on the ionic conductance as well as dipole polarization.
**Figure 9.18** Variation of dissipation factor for epoxy/HTLN blends

**Figure 9.19** Variation of dissipation factor for epoxy/ETLN blends
On increasing frequency the dissipation factor decreased whereas with the increase in concentration of liquid rubber the polar OH groups increased which resulted in enhanced orientation polarization and in turn the dissipation factor in the case of epoxy/HTLNR blends. The enhancement was comparatively lesser for the epoxy/ETLNR blends.

### 9.3. Conclusion

Thermogravimetric analysis of epoxy/liquid rubber blends in nitrogen atmosphere was useful in the study of their thermal degradation behaviour. The results show that though epoxy is more stable than HTLNR and ETLNR, based on their $E_a$ values, the degradation rate was much faster in epoxy. Both the liquid rubbers decompose essentially in triple stage degradation while neat epoxy undergoes single stage degradation. The blends also showed single stage degradation. Further it was observed that the presence of one component influences the thermal degradation behaviour of the other component and the resultant blend has a comparable thermal stability. The destabilizing influence at low concentration of ETLNR/HTLNR in the blend is due to the chemical interactions of the degradation products of ETLNR/HTLNR, which starts degrading at lower temperature with epoxy and reduction in the viscosity of the medium. Perhaps complete mechanistic knowledge of the degradation process in the blend, using properly interfaced TGA, will give better understanding of the observed behaviour.

Incorporation of HTLNTR or ETLNR in DGEBA network did not significantly affect the onset of degradation. It is evident that thermal stability as well as $T_{\text{max}}$ has increased marginally due to crosslinking reactions. Thermal stability of the cured resin is more than modified ones. The systematic knowledge of blend stability and the kinetics of degradation of the blends may give rise to some idea of the extent of
chemical interactions occurring between components, their bond strength, activation energy, melting temperature, etc., as evident from changes in heat energy. Although thermogravimetric analysis is a powerful tool for polymer anlaysis, its scope is limited as no information is obtained about the qualitative aspects of the evolved gases during polymer degradation.

Dielectric measurements are advantageous as they can be made insitu continuously on a single sample throughout the entire cure process. Dielectric constants of epoxy/HTLNR and epoxy/ETLNR blends were higher than that of neat resin. At low frequencies noticeable enhancement in the values were observed in the case of epoxy/HTLNR blends due to the orientation polarisabilty of the rubber segments. Higher values of conductivity were noted for epoxy/HTLNR blends compared to epoxy/ETLNR blends as HTLNR involve more polar hydroxyl groups in it. This leads to a low volume resistivity for epoxy/HTLNR blends. Dissipation factor is comparatively higher for epoxy/HTLNR blends. The dielectric behaviour of commercial thermosetting blends with liquid rubber has been explored here. Ionic impurities present in such systems result in very high levels of electrode polarization which can completely obscure the phenomena of interest. It is one of the reasons why dielectric cure monitoring has not yet gained a wide acceptance in the commercial world.
References


