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DETERMINATION OF ACTIVATION ENERGY OF CYANET ESTER AND EPOXY RESINS USING DYNAMIC MECHANICAL ANALYSIS

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Abstract - The activation energy associated with the glass transition relaxation of thermosets has been determined by using the three-point bending clamp provided. In the present study, the dynamic mechanical analyzer NETZSCH Instruments DMA 242E was used to characterize two different types of thermoset resin. Each sample was given a linear heating speed of 5°C/min at four discrete frequencies in the temperature range RT °C to +250 °C.The activation energy for both transitions was determined by an Arrhenius plot from dynamic properties measured at different frequencies. The experimental results showed that the evaluation of activation energy is affected by the test frequency as well as the criterion by which the glass transition temperature (T_g) is established. It has been found that the activation energy based on the loss tangent (tan δ) peak is more reliable than on the loss modulus (E”) peak.

Keywords - Activation Energy, Dynamic Mechanical Analysis (DMA), Polymer Composites, Glass Transition

I. INTRODUCTION

Thermoset resins are a class of polymers that are widely used in composite materials due to their excellent mechanical properties, heat resistance, and structural stability. For each type of thermoset resin, the final mechanical properties of the cured resin, which affect bond strength with reinforcement in composite, are very sensitive to the curing time and temperature. It is, therefore, often necessary to conduct simple, short-term laboratory tests to evaluate the large number of resins available commercially in order to select the most appropriate resin for composite. The glass transition temperature, T_g , which delimits the range of service temperature is considered a reliable indicator of completeness of cure and thus is used as a quality control in composites [1-4].

A Dynamic Mechanical Analyzer (DMA) is an advanced instrument used to measure the mechanical properties of materials as a function of time, temperature, and frequency. It provides detailed information on a material's response to mechanical stresses or strains under controlled conditions, allowing researchers and engineers to study its viscoelastic properties. The activation energy (Ea) of a material or reaction is the energy required to initiate a process, such as a chemical reaction or a phase transition, like curing in polymers or composites. To determine the activation energy, we generally use the Arrhenius equation or Kissinger's method [5-11]. The activation energy of the glass transition can be obtained by applying the Arrhenius law [1-7]. In dynamic mechanical experiments, can be estimated by using the time-temperature superposition principle to superimpose the $\tan\delta$ peaks determined at different test frequencies [11–25]. Accordingly, individual $\tan\delta$ peaks can be shifted for superposition along the logarithmic time axis by the shift factor, $\log a_T$. The temperature dependence of the test frequency may then be expressed as [7]:

$$f = f_0 \exp\left(-\frac{\Delta H}{RT}\right) \qquad (1)$$

where f and fo are analogous to the rate constant and pre-exponential factor of theArrhenius equation and R is the gas constant. The shift of the glass transition temperatures, T_{g1}andT_{g2}, due to change in the test frequencies $f_1$and $f_2$allows the determination of the activation energy of T_g[7]:

$$\frac{f_1}{f_2} = \frac{\exp\left(-\frac{\Delta H}{RT_{g1}}\right)}{\exp\left(-\frac{\Delta H}{RT_{g2}}\right)} \qquad (2)$$

$$\log\left(\frac{f_1}{f_2}\right) = \log a_T = \frac{\Delta H}{R}\left(\frac{1}{T_{g2}} - \frac{1}{T_{g1}}\right)\log e \qquad (3)$$

$$Ea(\Delta H) = -R\left[\frac{d(\ln f)}{d(1/T_g)}\right] \qquad (4)$$

Equation (1-4) describes thetemperature-dependence of polymer relaxations,where ΔHis the activation enthalpy of the glass transition relaxation. In [3] this approach was applied for determining ΔH, although the authors plotted the $\log f$ ratherthan lnf and only used a single heating rate of 5°C $\min^{-1}$.

II. EXPERIMENTAL PART – MATERIALS AND METHODS

The two different thermoset resin systems were studied in this work. The cyanate ester resin system: Cyanate ester resin AroCy® XU 366 and Co-naphthenate 100:0.3, from Huntsman and the epoxy resin system: Syna-21 Liquid Resin and Lindride 66K Liquid Curing Agent (50:60) from Synasia. Curing cycles for the cyan ester resin system is 2h at 130°C and for the epoxy system are 10 min at 70°C + 10 min at 140°C.

DMA was used to characterize the temperature-dependent viscoelastic properties of the materials. The tests were performed using a dynamic mechanical analyzer DMA 242 E from NETZSCH and was used a three-point bending mode for all samples. The purpose was to calculate activation energy using Dynamic Mechanical Analysis (DMA) because it provides valuable insights into the thermal and mechanical properties of materials, particularly their viscoelastic behavior. The preparation of the samples for analysis was done according to the standards ASTM D 4065, ASTM D 4440, and ASTM D 5279 [8, 9, 10]. The samples with dimensions of 10 x 40 mm with a thickness of 3-4 mm were cut from the cast epoxy block and were tested using the 20 mm span three-point bend clamp. The T_g range was determined during scanning from room temperature (RT) to 250 °C. Each test was repeated using new samples cut from the same cast block. Figure 1 shows the appearance of the samples (prepared from both of thermosetting matrices) and the 3pbt test holder of the DMA instrument used for these tests.

Figure1:Samples prepared from both of thermoset matrices and the sample holder used in the DMA instrument for 3pbt

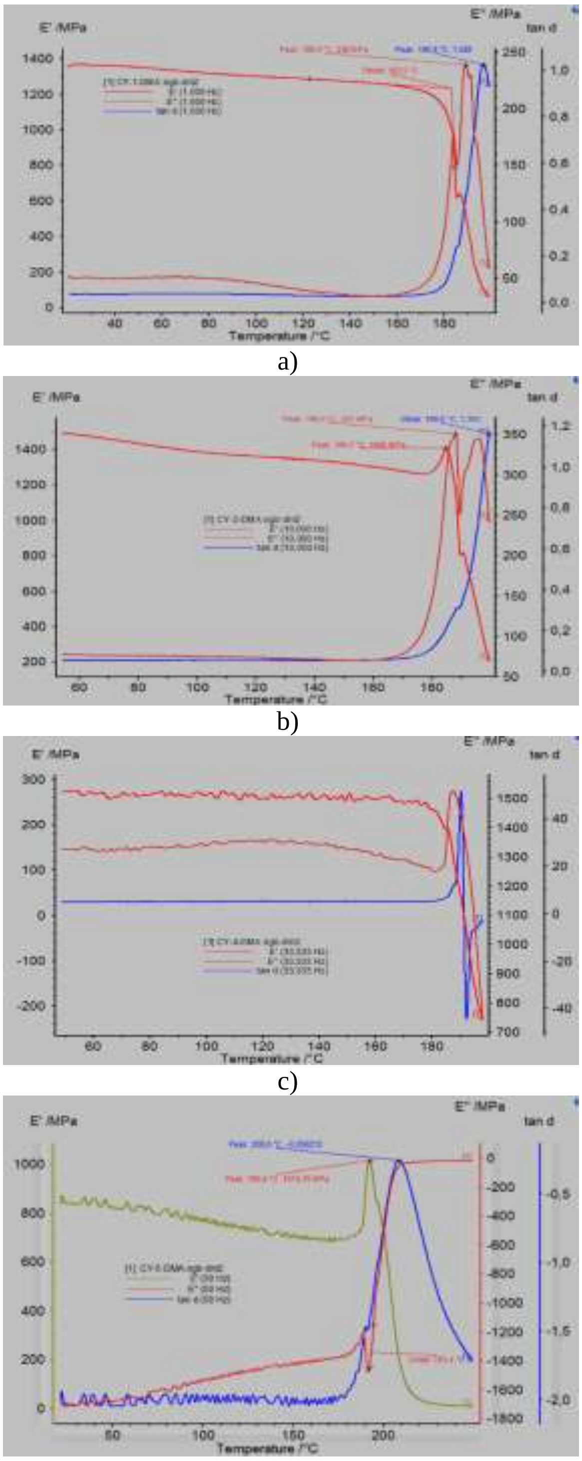
Two approaches were utilized to find the activation energy for the resin systems: Method A used four samples (one for each frequency) for testing, and Method B used a single sample for testing all four frequencies.

III. RESULTS AND DISCUSION FOR CYANATE ESTER RESIN

A first method

For four frequencies, Figure 2 shows a typical plot of the temperature dependence of E', E'' and tan δ. The results for the assessed $T_g$values according to the three criteria are shown in Table1. The results obtained for Tg from tan δare the highest, and the results obtained for $T_g$from E” and E’ are lower and like each other.

Because we were doing multi-sample testing (as A first method), the samples 1 through 4 were given different frequency (1, 10, 33 and 50 Hz)for heating rate 5 °C/min.Graphs are obtained separately for each trial, and $T_g$for E', E''and tan δ are read from them for each different frequency employed. The activation energy was derived using the calculated $T_g$values from E', E'' andtan δ. The direct effects of increased frequency on theglass transition temperatures are depicted in Figures 2 and 3. $T_g$rises with increased test frequencies, as we anticipated. The mean$T_g$was found to be between 189,3 and 193,4°C based on E''peaks and between 196,8 and 208,6°C based on tan δ peaks over the 1–50 Hz ranges. Table 2 provides values for the cyanate ester resin's activation energy derived from E', E'', and tanδ.



a)

b)

c)

d)

Figure. 2: Superposition of typical plots showing the variation of E’, E” andtan δ with increasing temperature. Sample: Cyanate ester resin, size:10x40x3 mmwith heating rate of 5°C/min and frequency a) 1 Hz; b) 10 Hz; c) 33,3 Hz and d) 50 Hz

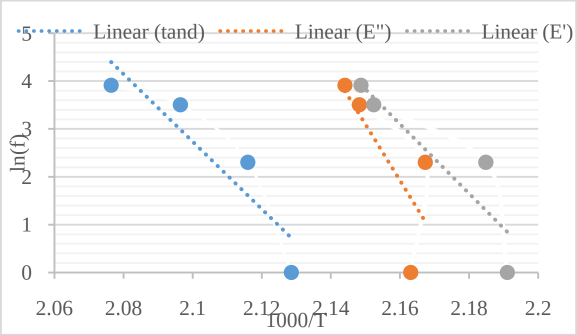


Figure3Linear dependence of ln(f) vs. 1000/T of cyanate ester resinwith first method (four- samples)

f (Hz)	E' Tg (°C)	E" Tg (°C)	tan δTg (°C)
1	183,4	189,3	196,8
10	184,7	188,4	199,6
33,3	191,6	192,5	204,0
50	192,4	193,4	208,6

Table 1
Tg from 3pb testwith DMA 242E of cyanate ester resin system

Value for the activation energy	(kJ/mol)
E’	585,94
E’’	976,98
tanδ	604,10

Table 2
Activation energy calculated through the quantities:E’, E’’ and tan δ of cyanate ester resin system

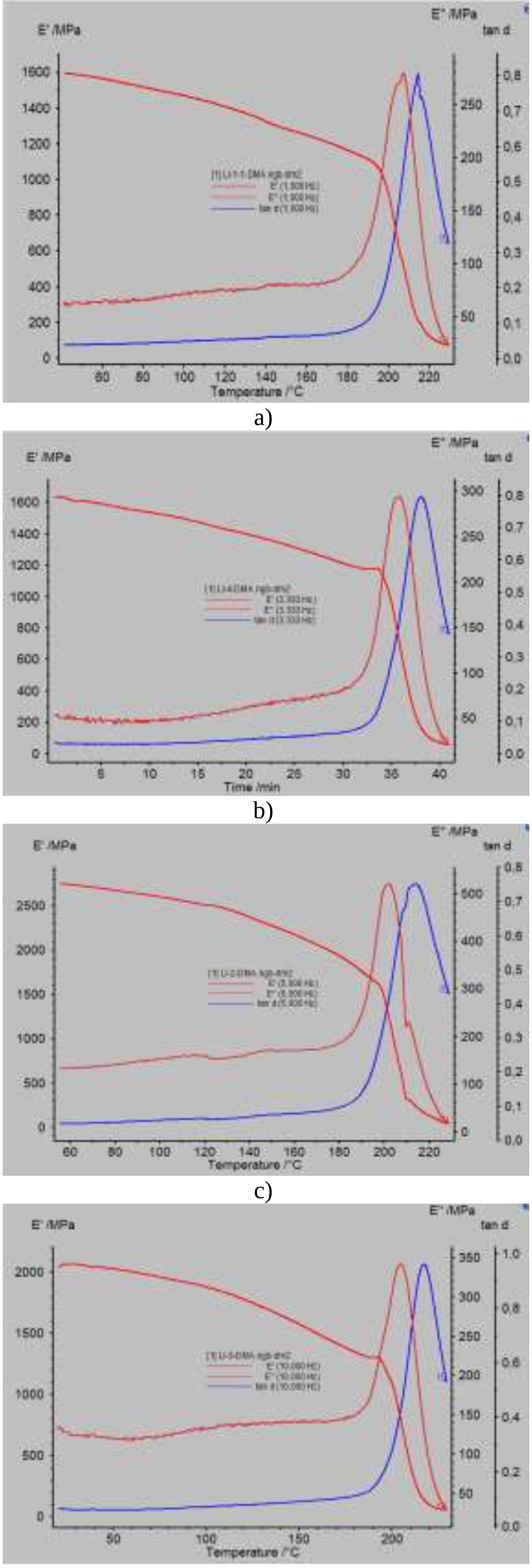
IV. RESULTS AND DISCUSION FOR EPOXY RESIN

The activation energy for this resin system was calculated using both approaches (method A and method B) to check for any deviations in the value.

A. First method

For four frequencies(1, 3,33,5 and 10 Hz) for heating rate 5 °C/min, Figure 4 shows a typical plot of the temperature dependence of E', E" and tan δ for multi-sample testing epoxy resin system. The results for the assessed T_g values according to the three criteria are shown in Table 3. Also for epoxy resin system, the results obtained for T_g from tan δ are the highest, and the results obtained for T_g from E” and E’ are lower and similar to each other.The activation energy was derived using the calculated T_g values from E', E" and tan δ. The direct effects of increased frequency on the glass transition temperatures are depicted in Figures 4 and 5.

As in the example above for cyanate ester resin and here for epoxy resin system, $T_g$rises with increased test frequencies, as we anticipated. The mean $T_g$was found to be between 200,4 and 204,9°C based on E" peaks and between 211 and 217,1°C based on peaks over the 1–10 Hz ranges. Table 4 provides values for the epoxy resin's activation energy derived from E', E", and tan δ.



a)
b)
c)
d)

Figure. 4: Superposition of typical plots showing the variation of E’, E” and tan δ with increasing temperature. Sample: Epoxy resin, size:10x40x3 mmwith heating rate of 5°C/min and frequency a) 1 Hz; b) 3.33 Hz; c) 5 Hz and d) 10 Hz

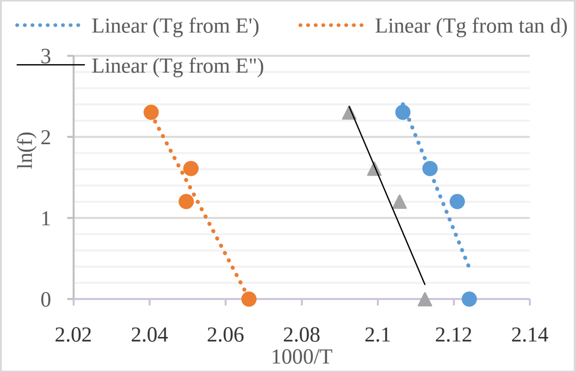


Figure5:Linear dependence of ln(f) and 1000/T of epoxy resin with first method (four- samples)

f (Hz)	E' Tg (°C)	E" Tg (°C)	tan δTg (°C)
1	197,8	200,4	211
3,3	198,5	201,9	214,9
5	200,1	203,4	214,6
10	201,7	204,9	217,1

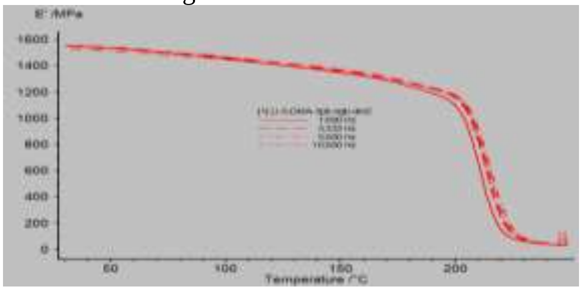
Table 3
Tg from 3pb testwith DMA 242E of epoxy resin system

Value for the activation energy	(kJ/mol)
E’	961.6
E’’	917.7
tanδ	735.2

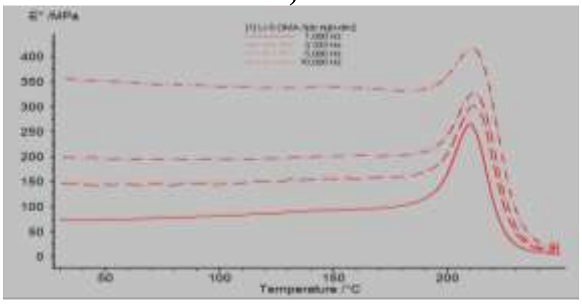
Table 4
Activation energy calculated through the quantities: E’, E’’ and tan δof epoxy resin system

B. Second method

The second method uses a single resin system sample that can be analyzed at many frequencies simultaneously to determine the activation energy automatically with the use of software. Figure 6 (a, b, and c) illustrates how all curves are generated simultaneously using this procedure. In this way, Ea is calculated using the loss factor tan δ.



a)



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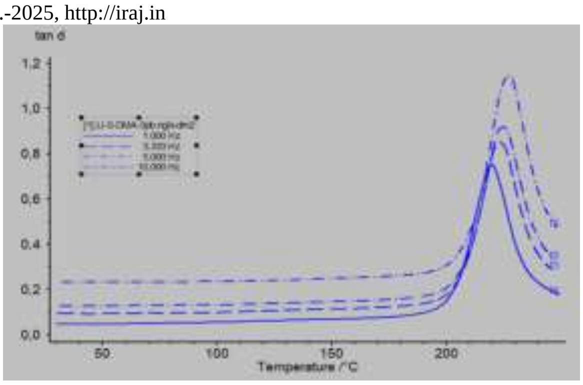

c)

Figure 6: Superposition of typical plots showing the variation of 1; 3,33; 5 and 10 Hz with increasing temperature. Only one sample: Epoxy resin 3pbt ssize:10x40x3 mm and the heating rate of 5°C/min a)E’; b) E”; c) tanδ1; 3,33; 5 and 10 Hz

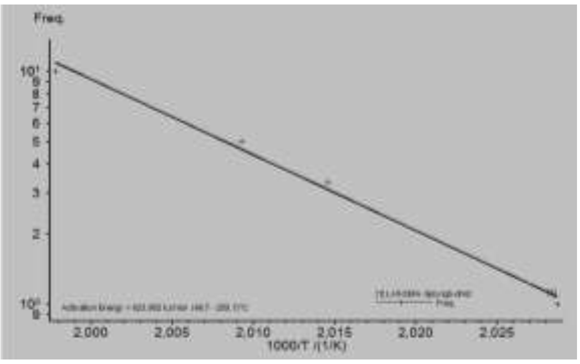

Figure 7.Obtained linear function for the activation energy of epoxy resin with second method (one samples)

This instrument's software can automatically calculate the T_g values derived from tan δ, as well as the linear function of the frequency logarithm with 1000/T and the material's activation energy (Figure 7).

According to research in the literature (19–25), a number of scientists believe that this activation energy is determined by calculating T_g from tan δ rather than T_g from E' and E". Thus, that is the basis for the DMA 242E Netzsch program, is designed to calculate activation energy (by T_g from tan δ) from theinstrument itself.

The activation energy determined from T_g from tan δ is 623.902 kJ/mol when using the second technique (B), and 735.2 kJ/mol when using the first way (A). Because it reduces the time and number of trials, the second technique of use is superior.

V. COMPARE Ea FOR EPOXY AND CYANATE ESTER RESIN

A comparison of the activation energy values determined from DMA for the two resin systems (cyan ester and epoxy) using the three approaches (E’, E” and tan δ) is presented in Figure 8. The particular requirements of the composite part being produced determine which processing conditions are best for the resin. The ideal option will be cyanate ester resin, which has a lower activation energy, if the require is rapid curing at lower temperatures. Epoxy resin, which has a higher activation energy, is the superior choice when longer work durations and greater control over the curing process are needed.

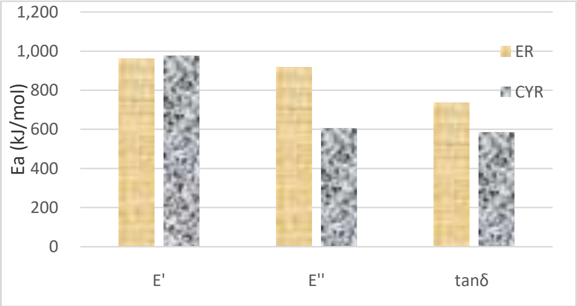

Figure 8: Comparison analysis of the calculated activation energy of both resin systems (epoxy ER and cyanate ester CYR), according to three categories (E', E" and tanδ)

The DMA method can be used to determine whether the polymerization process is finished. We conducted an experiment using this resin system for this reason. Figure 9 shows that the graphs of E', E", and tan δcan be used to make this comparison. There is a difference between the graphs for each of these values: in the sample where the polymerization is finished, the graph stabilizes after the change and obtains a constant value; in the sample where the polymerization is not finished, the graph does not obtain a constant value, and it is unknown if it will continue to change as the temperature rises.

According to the two samples' produced curves, which are displayed in Figure 9, the polymerization is complete for the green sample and not yet complete for the red sample. The graph of tanδ's temperature dependence best illustrates this difference; for the sample with complete polymerization, a well-defined peak is obtained, whereas for the sample with incomplete polymerization, the peak is still not readily apparent at the specified temperature (Figure 9 under в).

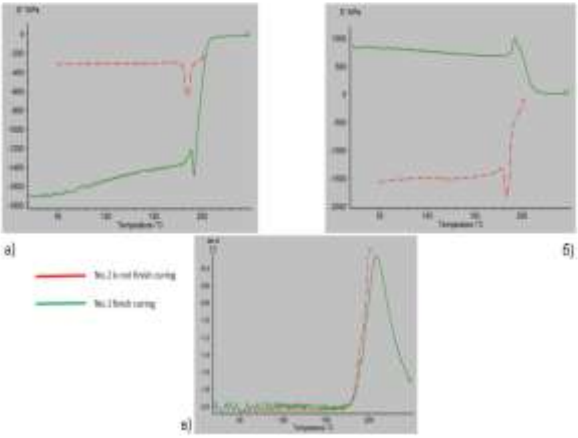

Figure 9: Representation for the curing process (a) E''vs.T, (b) E' vs.T, (c) tan δvs.T

VI. CONCLUSION

In summary, activation energy is a key factor in determining the efficiency, cost, and performance of thermosetting resins in composite manufacturing, affecting the temperature, time, and final properties of the cured product.
Through dynamic-mechanical analysis of multiple samples from the cyan ester and epoxy resin system analyzed at various frequencies on the same heating rate, their T_g values have been determined using of three methods (E', E" and tanδ).The obtained results have shown that the T_g values obtained from E' are always slightly lower than those obtained from E" and tanδ, which are similar to each other. The glass transition temperature of the cyan ester resin is about 200°C, and of the epoxy about 210°C based on tan δ. The activation energies derived from E', E", and tan δ are not the same.The activation energy derived from E' has the highest value, the activation energy derived from E" has a lower value, and the activation energy derived from tan δ has the lowest value. According to DMA calculations (method A), the epoxy resin's activation energy is greater than the cyan ester resin's. This is because epoxy resin has a greater glass transition temperature.

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