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Curing kinetics of an epoxy-acid copolymer systems. Effect of mineral filler (CaCO_3)

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ABSTRACT

The effect of introducing a mineral filler (CaCO_3) on a commercial epoxy resin (DGEBA) cured with high molecular weight acid copolymers, on the kinetics properties has been studied by using differential scanning calorimetry (DSC). The kinetics properties were determined at different content of CaCO_3 in the systems. The enthalpy of the reaction (ΔH), the gel temperature (T_g), the temperature at the maximum peak (T_{max}) and the temperature at the final conversion (T_f) were obtained from DSC curves which were also used for kinetic calculations. The activation energy of cross linking reactions was calculated by the Freeman – Carrol relation. Only modest effects has been observed on T_g and T_{max} parameters to 80-90% by weight of CaCO_3 , whereas, an important decrease of T_f is observed from 10 % of CaCO_3 content. The effect of the calcium carbonate on curing parameters is very low to 50 % of CaCO_3 content, above this amount, the heat of curing (ΔH) decreased whereas, the activation energy (E) and the reaction order (n) increased. © 2011 Trade Science Inc. - INDIA

KEYWORDS

Poly(acrylic acid-co-styrene);
Poly(maleic anhydride-alt-styrene);
DGEBA;
Calcium carbonate;
DSC;
Kinetics.

INTRODUCTION

Mineral fillers have always played an important role in the field of the plastics industry. They are generally added to plastics in order to reduce their production costs while upgrading their properties. Mineral fillers are defined as fillers with low aspect ratios (approximately equal to one^[1]). Amongst mineral fillers, calcium carbonate CaCO_3 is particularly popular additives because of its excellent combination of low cost, high brightness, and the ability to be used at high loadings^[2] for many applications^[3-7]. It is clean, white

filler and thus leads itself well to pigmentation in any direction. Calcium carbonate CaCO_3 is available globally in a variety of particle sizes and purities and may be used with or without organic coating. It is supplied in five forms: water-ground, dry-ground, precipitated and surface-treated. For this reason, calcium carbonate has a marked influence on the mechanical and rheological properties of composites^[8-12].

In previous studies^[13-17], the cure kinetics of an epoxy resin DGEBA cured by acid copolymers: poly (acrylic acid-co-styrene) (PAAS) at different content of styrene and poly(maleic anhydride-alt-styrene) used

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as adhesives or composites have been studied. The carboxylic acid groups in acid copolymers are able to react with the oxirane groups of the epoxy resin. The oxirane ring opening, of the epoxy resin by the hydrogen of carboxylic groups, leads to reactions which create cross linked network between the macromolecular chains, insoluble in the usual solvents. The released hydroxyl groups during the cross linking reaction confer adhesive properties to the formed products. Polymers and copolymers with high molecular weight were used as hardeners in order to create an elevated numbers of links. Several acid motives were linked with the epoxy functions leading to a cross linked spatial structure with relevant properties.

In these studies, the state of cure was assessed as the residual heat of reaction and was varied by controlling both the time and temperature of the cure. The degree of cross linking increases while the residual heat of reaction decreases with the time and temperature. Additionally, the activation energy and order of the reaction increases with extend of cure. The variation of the heat of curing with the percent of acid content was demonstrated. The systems show an elevated heat of curing, leading to good reactivity, which is indicated by the decreasing of the activation energy.

The objective of this study is to analyse the effect on the kinetics properties by the introducing mineral filler (CaCO_3) on these systems.

Theory

For thermosets which follow nth order kinetics, the rate of conversion $d\alpha/dt$, is proportional to the fraction of unreacted reactive. This can be expressed in the classical expression as:

$$d\alpha/dt = k(1-\alpha)^n \quad (1)$$

where α is the fractional conversion of reactants consumed after time t , n is the reaction order and k is the specific rate constant.

Cure reaction that are auto catalyzed can be described by a relation such as:

$$d\alpha/dt = k\alpha^m(1-\alpha)^n \quad (2)$$

where m is a partial reaction order.

The auto catalyzed systems are characterized by the formation of some intermediate species, which markedly accelerates the cross linking reaction. Different methods are established resulting to DSC studies which

permit the evaluation of kinetic parameters.

In this study, the reaction is supposed to be following nth order kinetics. The Freeman-Carroll relation^[18] is applicable to many epoxy cure reactions and offers a rapid and simple calculation method. The activation energy and reaction order were calculated from this relation:

$$\frac{\Delta \text{Ln} dH/dt}{\Delta \text{Ln}(\Delta H - H)} = n \frac{E/R \cdot \Delta 1/T}{\Delta \text{Ln}(\Delta H - H)} \quad (3)$$

Where, dH/dt = heat flow, generated in the curing reaction; ΔH = is the total heat of curing; n = reaction order; E = the activation energy; R = constant ($8.314 \text{ J} \cdot \text{mole}^{-1} \cdot \text{K}^{-1}$); T = absolute temperature

On assuming that the hardening reaction in this case proceeds in accordance with the Arrhenius law, the relationship (3) may be represented by a straight line described by the equation:

$$Y = mx - c$$

Where, $m = E/R$ and $c = n$. From the slope of the straight line, the activation energy was calculated, the intercept c give n the reaction order.

EXPERIMENTAL

Materials

The epoxy resin was a commercial DGEBA (Dow chemical company; DER332) with an equivalent epoxy of 174g. Hardeners are polymer poly(acrylic acid) PAA, copolymers poly(acrylic acid-co- styrene) (PAASx) at different contents of styrene and poly(maleic anhydride-alt-styrene) (PAMS).

Polymer and copolymers were synthesized by free radical polymerization in solution and characterized by UV Spectroscopy to determine the composition, i.e., the real percent of styrene and acrylic acid in the synthesis products, (TABLE 1), and by GPC to determine the molecular weights of the synthesized products (TABLE 2).

TABLE 1 : Acid motive content in PAASx copolymers

| Polymer references | % of acid |
|--------------------|-----------|
| PAAS1 | 8.9 |
| PAAS2 | 29.5 |
| PAAS3 | 63.2 |
| PAAS4 | 79.6 |

TABLE 2 : Mn, Mp, Ip of synthesized products

| Copolymers | Mn g/mol | Mp g/mol | Ip |
|------------|----------|----------|------|
| PAMS | 60 400 | 91 800 | 1.52 |
| PAAS1 | 122 600 | 260 000 | 2.12 |
| PAAS2 | 142 500 | 259 400 | 1.82 |
| PAAS3 | 146 700 | 292 500 | 1.99 |
| PAAS4 | 134 600 | 212 500 | 1.58 |
| PAA | 83 300 | 116 200 | 1.39 |

Preparation and sampling

Resin and copolymers were dissolved in 2 ml of an usual polar solvent, tetrahydrofuran (THF), mixed at equimolecular acid/epoxy proportion, in the presence of a tertiary amine. The appropriate content of CaCO₃ (10 to 100%) is added. The mixture was stirred at room temperature until a clear homogeneous solution was obtained. Samples were dried and enclosed in aluminium pans for DSC analysis and introduced in a ventilated dryer.

Apparatus

The UV measurements were performed in THF solution in the range of 200-300 nm wavelengths. Molecular weights, in equivalent of standard PS, were determined by GPC in THF solution using μstyrogel columns and a differential refractometer detection.

Calorimetric measurements were performed with a DSC 930 DUPONT instrument equipped with a differential scanning calorimeter model 912 with two cells connected to an IBM 2100 microprocessor. The calorimeter was previously calibrated with an indium standard. The sample weights were 10mg. The sample

was introduced in the DSC, equilibrated at 25°C and then scanned at a heating rate of 10°C/min from 25°C to 250°C. Heating rate has an effect on the curing parameters^[19]. For the studied systems a maximum of the heat of the reaction is obtained for a heating rate of 10°C/ mn. The cure of an epoxy resin is an exothermic process, and the heat evolved can be detected quantitatively by the DSC, thus giving a measurement of the heat amount of reaction.

RESULTS AND DISCUSSION

The total heat of curing (ΔH_c), the gel temperature T_g, the maximum temperature T_m and the final temperature T_f are obtained from DSC curves which are also used for kinetic calculations. We give as an example the figure 1 which represents the exotherms of PAAS3/DGEBA-CaCO₃, used to measure the two parameters, the partial heat of cure (H) and the heat flow at the time t, dH/dt measured by the displacement of the cure exotherm from the baseline at any time. A minimum of ten values of H and dH/dt were tabulated for each exotherm.

By plotting $\Delta \ln dH/dt / \Delta \ln (\Delta H - H)$ against $\Delta(1/T) / \ln (\Delta H - H)$, we obtained the value of E/R which is the slope of the straight line; the reaction order n is the intercept of this curve with Y axis.

TABLES 3 and 4 give the gel temperature T_g, the maximum temperature T_m, the final temperature T_f, the enthalpy of curing ?H, the activation energy Ea and the reaction order n of PAAS_x/DGEBA, PAMS/DGEBA and PAA/DGEBA systems at different content of CaCO₃.

TABLE 3 : T_g, T_{max}, T_f, ΔH of PAASx/ DGEBA- CaCO₃ and PAMS/ DGEBA- CaCO₃ systems.

| System | % CaCO ₃ | T _g (°C) | T max (°C) | T _f (°C) | ΔH (J/g) | System | % CaCO ₃ | T _g (°C) | T max (°C) | T _f (°C) | ΔH (J/g) |
|---------------------------------------|---------------------|---------------------|------------|---------------------|----------|---------------------------------------|---------------------|---------------------|------------|---------------------|----------|
| PAAS1/ DGEBA/ CaCO ₃ | 0 | 108.92 | 136.31 | 208 | 62.73 | PAAS4/ DGEBA/ CaCO ₃ | 0 | 112.85 | 136.17 | 230 | 193.63 |
| | 10 | 109.04 | 136.53 | 170 | 61.36 | | 10 | 112.88 | 136.26 | 175 | 190.24 |
| | 20 | 109.77 | 136.53 | 170 | 60.21 | | 20 | 113.45 | 136.33 | 175 | 188.47 |
| | 30 | 110.30 | 136.71 | 170 | 58.68 | | 30 | 113.77 | 136.46 | 175 | 182.47 |
| | 40 | 110.87 | 136.82 | 170 | 56.87 | | 40 | 113.92 | 136.55 | 175 | 178.63 |
| | 50 | 11.04 | 136.93 | 170 | 54.26 | | 50 | 114.58 | 136.73 | 175 | 169.50 |
| | 60 | 11.19 | 136.85 | 165 | 50.13 | | 60 | 114.78 | 137.03 | 165 | 159.35 |
| | 70 | 111.87 | 136.85 | 160 | 45.13 | | 70 | 115.30 | 137.88 | 165 | 140.68 |
| | 80 | 111.94 | 137.35 | 160 | 37.32 | | 80 | 116.36 | 138.55 | 165 | 120.14 |
| | 90 | 115.51 | 138.02 | 160 | 30.25 | | 90 | 118.36 | 139.38 | 165 | 99.80 |
| 100 | 115.86 | 138.84 | 160 | 22.06 | 100 | 119.11 | 140.39 | 165 | 69.90 | | |

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| System | % CaCO ₃ | Tg (°C) | T max (°C) | Tf (°C) | ΔH (J/g) | System | % CaCO ₃ | Tg (°C) | T max (°C) | Tf (°C) | ΔH (J/g) |
|---------------------------------------|---------------------|---------|------------|---------|----------|--------------------------------------|---------------------|---------|------------|---------|----------|
| PAAS2/ DGEBA/ CaCO ₃ | 0 | 95.19 | 121.81 | 222 | 127.77 | PAA/ DGEBA/ CaCO ₃ | 0 | 143.05 | 161.53 | 255 | 210.13 |
| | 10 | 95.20 | 122.09 | 175 | 126.80 | | 10 | 143.13 | 161.85 | 210 | 204.2 |
| | 20 | 95.26 | 122.49 | 160 | 124.50 | | 20 | 143.57 | 161.98 | 210 | 199.8 |
| | 30 | 95.40 | 122.84 | 160 | 122.50 | | 30 | 144.36 | 162.11 | 210 | 194.83 |
| | 40 | 95.52 | 123.39 | 160 | 119.68 | | 40 | 144.98 | 162.44 | 200 | 190.76 |
| | 50 | 95.88 | 124.26 | 150 | 113.39 | | 50 | 145.38 | 162.73 | 200 | 180.95 |
| | 60 | 96.13 | 124.90 | 150 | 99.75 | | 60 | 146.45 | 162.84 | 200 | 170.19 |
| | 70 | 97.01 | 126.19 | 150 | 85.56 | | 70 | 146.82 | 163.13 | 190 | 150.40 |
| | 80 | 97.28 | 127.01 | 150 | 70.73 | | 80 | 147.18 | 163.18 | 190 | 131.10 |
| | 90 | 99.35 | 129.33 | 150 | 58.86 | | 90 | 149.11 | 164.39 | 180 | 111.13 |
| 100 | 100.58 | 130.73 | 150 | 43.04 | 100 | 151.77 | 164.86 | 170 | 87.45 | | |
| PAAS3/ DGEBA/ CaCO ₃ | 0 | 108.25 | 131.92 | 231 | 167.05 | PAMS/ DGEBA/ CaCO ₃ | 0 | 93.16 | 125.20 | 207 | 196.80 |
| | 10 | 108.45 | 132.15 | 170 | 165.46 | | 10 | 95.56 | 125.24 | 160 | 194.83 |
| | 20 | 108.74 | 132.65 | 170 | 163.46 | | 20 | 96.75 | 125.56 | 160 | 190.76 |
| | 30 | 108.85 | 132.73 | 160 | 157.42 | | 30 | 98.76 | 125.64 | 160 | 183.95 |
| | 40 | 109.13 | 133.09 | 150 | 152.63 | | 40 | 98.92 | 125.64 | 160 | 177.10 |
| | 50 | 109.77 | 133.21 | 150 | 146.48 | | 50 | 102.75 | 125.64 | 160 | 170.19 |
| | 60 | 110.01 | 133.66 | 150 | 138.64 | | 60 | 108.63 | 125.83 | 150 | 160.40 |
| | 70 | 111.5 | 134.71 | 150 | 124.01 | | 70 | 109.61 | 126.99 | 150 | 144.48 |
| | 80 | 113.98 | 135.01 | 150 | 104.41 | | 80 | 110.28 | 128.29 | 150 | 122.13 |
| | 90 | 114.58 | 135.90 | 150 | 84.52 | | 90 | 110.43 | 129.46 | 150 | 97.45 |
| 100 | 115.33 | 136.76 | 150 | 52.26 | 100 | 111.32 | 130.07 | 150 | 66.94 | | |

TABLE 4 : Activation energy and reaction order of PAASx/DGEBA-CaCO₃ and PAMS/DGEBA/CaCO₃

| System | % CaCO ₃ | E (kJ/mole) | n | System | % CaCO ₃ | E (kJ/mole) | n |
|-----------------------------------|---------------------|-------------|------|-----------------------------------|---------------------|-------------|------|
| PAAS1/DGEBA/ CaCO ₃ | 0 | 161.01 | 2.22 | PAAS4/DGEBA/ CaCO ₃ | 0 | 151.36 | 2.11 |
| | 10 | 161.35 | 2.26 | | 10 | 152.05 | 2.16 |
| | 20 | 162.18 | 2.31 | | 20 | 153.28 | 2.21 |
| | 30 | 163.06 | 2.35 | | 30 | 154.16 | 2.30 |
| | 40 | 163.86 | 2.41 | | 40 | 155.29 | 2.37 |
| | 50 | 165.82 | 2.48 | | 50 | 157.25 | 2.48 |
| | 60 | 167.95 | 2.59 | | 60 | 159.22 | 2.59 |
| | 70 | 170.52 | 2.68 | | 70 | 162.08 | 2.68 |
| | 80 | 173.02 | 2.77 | | 80 | 165.70 | 2.77 |
| | 90 | 175.52 | 2.86 | | 90 | 169.46 | 2.86 |
| 100 | 176.90 | 2.99 | 100 | 175.10 | 2.99 | | |
| PAAS2/DGEBA/ CaCO ₃ | 0 | 148.10 | 2.00 | PAA/DGEBA/ CaCO ₃ | 0 | 188.94 | 2.52 |
| | 10 | 148.97 | 2.08 | | 10 | 190.06 | 2.60 |
| | 20 | 149.68 | 2.12 | | 20 | 191.01 | 2.67 |
| | 30 | 150.52 | 2.21 | | 30 | 192.82 | 2.75 |
| | 40 | 151.86 | 2.29 | | 40 | 194.54 | 2.81 |
| | 50 | 153.53 | 2.42 | | 50 | 196.42 | 2.90 |
| | 60 | 155.12 | 2.57 | | 60 | 199.09 | 3.09 |
| | 70 | 158.63 | 2.70 | | 70 | 201.94 | 3.28 |
| | 80 | 161.85 | 2.87 | | 80 | 206.28 | 3.47 |
| | 90 | 166.82 | 3.15 | | 90 | 213.26 | 3.76 |
| 100 | 174.43 | 3.38 | 100 | 221.04 | 3.99 | | |

| System | % CaCO ₃ | E (kJ/mole) | n | System | % CaCO ₃ | E (kJ/mole) | n |
|-----------------------------------|---------------------|-------------|------|----------------------------------|---------------------|-------------|------|
| PAAS3/DGEBA/ CaCO ₃ | 0 | 111.77 | 1.99 | PAMS/DGEBA/ CaCO ₃ | 0 | 120.30 | 1.90 |
| | 10 | 112.08 | 2.01 | | 10 | 121.18 | 1.96 |
| | 20 | 113.15 | 2.10 | | 20 | 122.43 | 2.01 |
| | 30 | 114.16 | 2.23 | | 30 | 123.64 | 2.12 |
| | 40 | 115.54 | 2.35 | | 40 | 125.57 | 2.23 |
| | 50 | 117.5 | 2.46 | | 50 | 127.82 | 2.35 |
| | 60 | 119.59 | 2.61 | | 60 | 130.79 | 2.46 |
| | 70 | 122.68 | 2.79 | | 70 | 135.56 | 2.61 |
| | 80 | 126.28 | 2.99 | | 80 | 141.07 | 2.79 |
| | 90 | 130.62 | 3.17 | | 90 | 147.54 | 2.99 |
| | 100 | 137.86 | 3.34 | | 100 | 153.07 | 3.17 |

Variation of the characteristics T_g, T_f and T_{max}

PAAS1/DGEBA/CaCO₃ systems: the T_g temperature increases from 108.92°C (0% of CaCO₃) until reaching gradually 115.86°C with 100% of CaCO₃.

T_{max} increases from 136.31°C (0% of CaCO₃) to 138.84°C with 100% of CaCO₃. This difference of the increasing of the two temperatures, gel temperature T_g and temperature at the maximum of the peak T_m, shows the higher reactivity of the system before the gel point.

However the final temperature, T_f, decreases considerably from 208°C at 0% to 160°C of 100% of CaCO₃ showing that the additive contribute to lower the global heat of the reaction. PAAS2/DGEBA-CaCO₃ the T_g temperature increases from 95°C until reaching gradually 100.58°C with 100% of CaCO₃. T_{max} increases from 121.81°C to 124.02°C of 100% of CaCO₃. T_f decreases considerably by 222°C to 150°C at 100% of CaCO₃.

PAAS3/DGEBA - CaCO₃ the T_g temperature increases 108.25°C until reaching gradually a value of 115.33°C with 100% of CaCO₃. T_{max} increases by 131.92°C with 136.76°C to 100% of CaCO₃. T_f decreases abruptly from 231°C to 150°C of 100% of CaCO₃.

PAAS4/DGEBA-CaCO₃; the T_g temperature increases 112.85°C until reaching gradually a value of 119.11°C with 100% of CaCO₃. T_{max} increases from 136.17°C to 140.39°C at 100% of CaCO₃. T_f decreases abruptly by 230.57°C to 165°C of 100% of CaCO₃.

PAMS/DGEBA - CaCO₃; the T_g temperature gradually increases 93.16°C until reaching a value of 111.32°C with 100% of CaCO₃. T_{max} increases by

125.20°C to 130.07°C at 100% of CaCO₃. T_f decreases abruptly by 230.57°C to 150°C at 100% of CaCO₃.

PAA/DGEBA - CaCO₃; the T_g temperature increases from 143.05°C until reaching gradually a value of 151.77°C with 100% of CaCO₃. T_{max} increases by 161.53°C to 164.86°C at 100% of CaCO₃. T_f decreases abruptly from 255°C to 170°C at 100% of CaCO₃. We observe that for all systems T_g, T_{max} and T_f evolve in the same way. The percentage of acid groups in the copolymers seems have not a significant effect with the addition of CaCO₃. The effect of the CaCO₃ on the parameters T_g and T_{max} is quite marked only from 80-90% of CaCO₃, while it is much important on the temperature T_f with final conversion. A notable decreasing of T_f is yet observed at 10% of CaCO₃.

Variation of the enthalpy of reaction

PAAS1/DGEBA - CaCO₃ the enthalpy of reaction, ΔH, decreases slowly from 62.73 J/g to 54.16 J/g with 50% of CaCO₃ then quickly to 22.06 J/g with 100% of CaCO₃.

PAAS2/DGEBA - CaCO₃: ΔH decreases slowly from 127.77 J/g to 113.39 J/g with 50% of CaCO₃ then quickly to 43.04 J/g with 100% of CaCO₃.

PAAS3/DGEBA - CaCO₃: ΔH decreases slowly from 167.05 J/g to 146.48 J/g with 50% of CaCO₃ then quickly to 52.26 J/g with 100% of CaCO₃.

PAAS4/DGEBA - CaCO₃: ΔH decreases slowly from 193.63 J/g to 178.63 J/g with 40% of CaCO₃ then quickly to 69.9 J/g with 100% of CaCO₃.

PAMS/DGEBA - CaCO₃: ΔH decreases slowly from 196.8 J/g to 170.19 J/g with 50% of CaCO₃ then quickly to 66.94 J/g with 100% of CaCO₃.

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PAA/DGEBA - CaCO_3 : ΔH decreases slowly from 210.13 J/g to 180.95 J/g with 50% of CaCO_3 then quickly to 87.45 J/g with 100% of CaCO_3 .

We observe that for all the studied systems the enthalpy of reaction decreases with the percentage of CaCO_3 . For all systems, only modest effects has been observed on T_g et T_{max} parameters to 80-90% wt of CaCO_3 , whereas, an important decrease of T_f is observed from 10 % of CaCO_3 content.

The figure 1 represents the variation of the enthalpy according to % of CaCO_3 introduced into the formulation for the PAAS₃/DGEBA - CaCO_3 system, taking as typical of the other formulations.

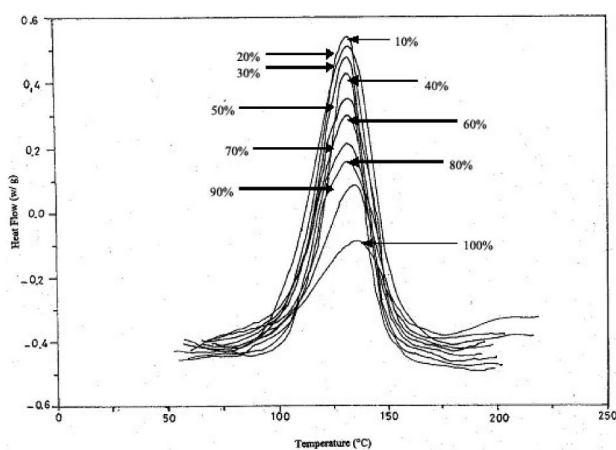


Figure 1 : DSC exotherms at different % of CaCO_3 for the PAAS₃/DGEBA/ CaCO_3

The curves present two distinct phases. In the first phase which is up to 50%, the enthalpy of reaction decreases slightly, then during the second phase beyond the 50%, the decreasing becomes faster. The effect of the introduction of the CaCO_3 on the enthalpy is weak in the first phase, beyond that, the system becomes less reactive. As the CaCO_3 percent increases, it forms a continuous glassy phase would hamper the mobility of the system. Therefore, the curing reaction is controlled by diffusion effect of functional groups through the cross linked spatial structure formed, resulting in a decrease of the heat of reaction as it is shown in figure 2.

This phenomenon is comforted by the activation energy behaviour. The activation energy increases modestly with the percent of acid content in the copolymer/ DGEBA systems and then levelled, (see typical figure 2).

The low value of activation energy indicates a high reactivity. The important presence of CaCO_3 in the

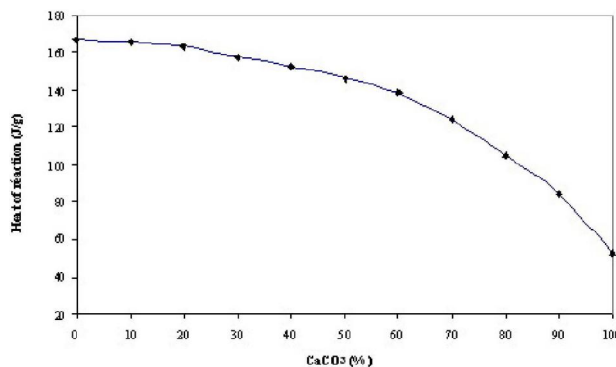


Figure 2 : Heat of reaction $f(\% \text{CaCO}_3)$ in the PAAS₃/DGEBA system

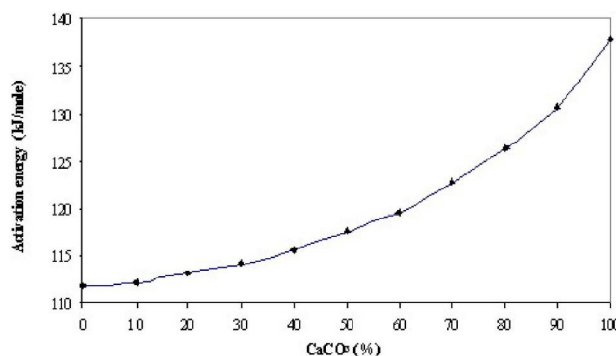


Figure 3 : Activation energy $f(\% \text{CaCO}_3)$ in the PAAS₃/DGEBA system

systems generates a steric hamper of reactive groups which are trapped. This contributes both to reducing their reactivity. Higher activation energy is necessary to relaxing polymer chains leading to their reacting.

The reaction order increases slowly with the percent of CaCO_3 content in the systems to 40% and then levelled. This comforts that the mechanism of hardening becomes more complex.

CONCLUSION

The effect on introducing a mineral filler on cure kinetics of high molecular weight poly-(acrylic acid-styrene) at different contents of styrene and a poly-(maleic anhydride-alt-styrene) used as hardener for a commercial epoxy resin (DGEBA) systems were studied by DSC technique. The exploitation of the obtained thermograms, made it possible to determine various parameters; enthalpy of reaction ΔH , the temperature at the gel point T_g , and the temperature (T_f) with final conversion as well as the temperature at the maximum of the peak T_{max} . Only modest effects has been observed on T_g and T_{max} parameters to 80-90% of

CaCO₃, whereas, an important decrease of Tf is observed from 10 % of CaCO₃ content.

The effect of introducing the carbonate calcium on the heat of curing (ΔH) is very low up to 50%, above this amount, the values of the heat of reaction decreases. The activation energy increases slowly with the percent of CaCO₃ content in the systems to 40% and then levelled. The reaction order increases slowly with the percent of CaCO₃ content in the systems to 40% and then levelled. The reactivity of all studied systems should depend on the acid functions present in the polymer vis à vis the epoxy groups of DGEBA. The decreasing on the reaction enthalpy in a way more marked from 50% in CaCO₃, shows that a part of the sites is not accessible during hardening the phase. The particles of CaCO₃ contribute to reduce the diffusion of the reactive.

So, according to our results, the content of CaCO₃ should not exceed the 40% level.

In a forthcoming work we will study, by FT-IR, the residual functions and the effect of the characteristics (size, porosity, specific surface) of the particles on the reactivity.

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