Supporting Information to:

Biowaste Chicken Eggshell Powder as a Potential Cure Modifier for Epoxy/Anhydride: Competitiveness with Terpolymer-modified Calcium Carbonate at Low Loading Levels

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The unmodified $CaCO_3$ and eggshell samples were mainly composed of different elements (**Table S1**): traces of fluorine, silicon (detected as Si 2p peak at 102 eV and Si 2s peak at 154 eV), and chlorine (detected as Cl 2p peak at 198.7 eV and Cl 2s peak at 201 eV) were also found in the $CaCO_3$.

Table S1. Elemental surface composition of $CaCO_3$ and ES before and after modification with (**I**).

The atomic ratios $[X]:[C]|_{spec}$ determined from wide-scan XPS spectra shown in **Figure 3** (left column).

	$CaCO_3$	ES	$mCaCO_3$	mES
$[N]:[C]\|_{spec}$	–	0.096	0.108	0.115
$[O]:[C]\|_{spec}$	1.162	1.154	0.392	0.539
$[F]:[C]\|_{spec}$	0.016	0.018	0.010	0.015
$[Si]:[C]\|_{spec}$	0.006	0.024	0.004	–
$[P]:[C]\|_{spec}$	–	0.009	–	0.006
$[S]:[C]\|_{spec}$	–	0.006	0.004	0.006
$[Cl]:[C]\|_{spec}$	0.003	0.004	0.001	–
$[Ca]:[C]\|_{spec}$	0.134	0.125	0.029	0.045

As an example, Curing characteristics are extracted for epoxy/0.3-$CaCO_3$ system at different heating rates and compared in **Figure S1**. According to the figure, change of heating rate from 5 to 20 °C/min caused increase in both T_{ons} and T_P. This can be explained in this manner that higher rates of heating assist in promotion of kinetic energy of the system per molecule. It can be also speculated that the total curing process is prolonged in the same direction as signaled by a rise in ΔT at higher heating rates.

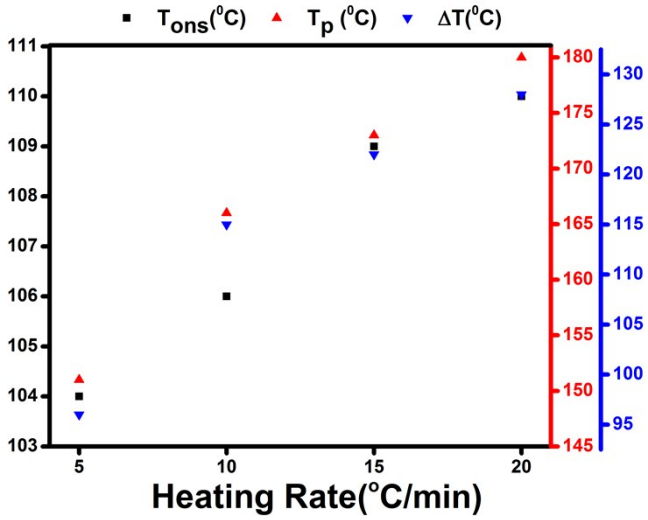

Figure S1: Alteration of T_{ons}, T_P, and ΔT for epoxy/0.3-$CaCO_3$ system as a function of heating rate

Nonisothermal cure kinetic of thermosetting resins is characterized by a general rate equation. This straightforward relation describes the cure reaction rate as a function of time and temperature and takes independently the contribution of temperature and conversion to the cure reaction, as follows [1]:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \qquad \text{(S1)}$$

where f(α) is the reaction model inspired from the reaction mechanism, and $k(T)$ is the reaction rate constant as a function of temperature taking as an Arrhenius form as:

$$k(T) = A\exp(-\frac{E_a}{RT}) \qquad \text{(S2)}$$

Substituting eq. (S2) into eq. (S1) yields:

$$\frac{d\alpha}{dt} = A\exp(-\frac{E_a}{RT})f(\alpha) \qquad \text{(S3)}$$

Epoxy curing process can be characterized by nth order or an autocatalytic reaction model:

$$f(\alpha) = (1-\alpha)^n \qquad \text{(S4)}$$

$$f(\alpha) = \alpha^m(1-\alpha)^n \qquad \text{(S5)}$$

Figure S2 shows the plot lnβ against $1000/T_p$ for the sample containing 0.1 wt.% ES, as a representative of the studied specimens. A very good linear regression (R-squared=0.998) is obtained by Ozawa model.

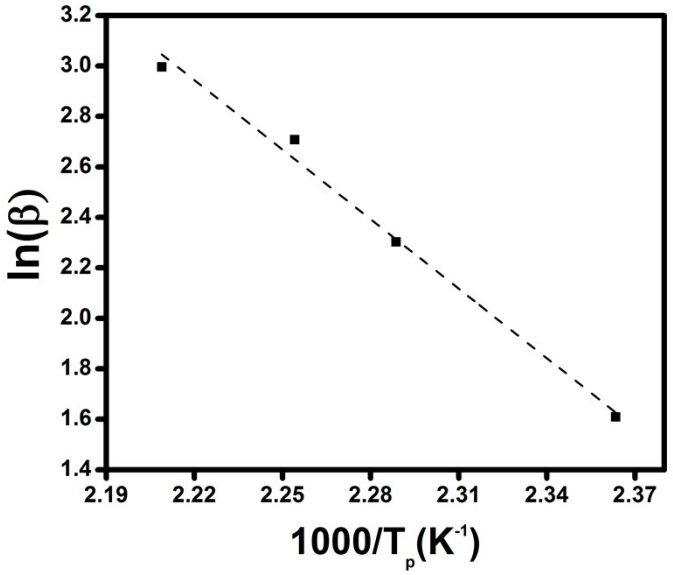

Figure S2: Plot of lnβ against$1000/T_p$ for the composite containing 0.1 wt.% ES

Typical curves are plotted for sample with 0.1 wt.% ES under heating rate of 5 °C.min^{-1} (**Figure S3**).

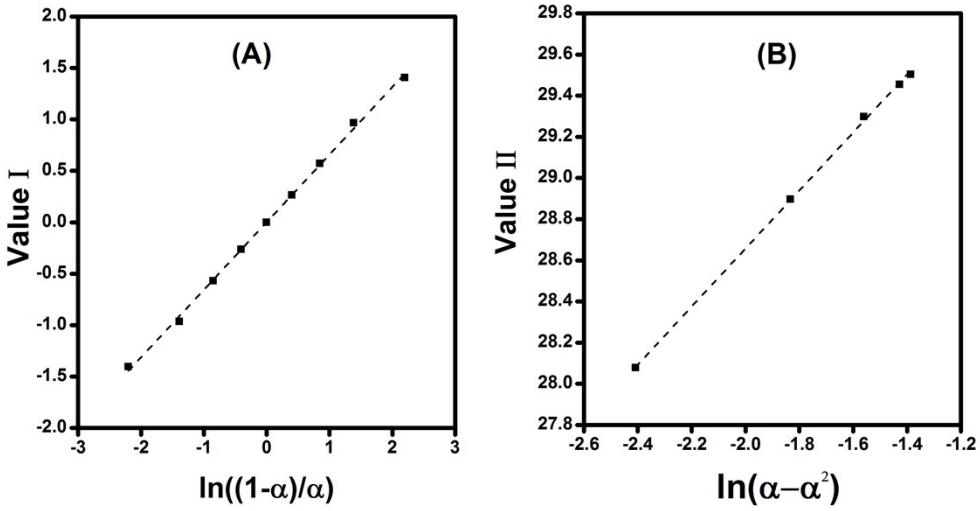

Figure S3: Plots of *Value* I (A) and *Value* II (B) calculated using DSC data for the sample containing 0.1 wt.% ES under heating rate of 5 °C.min^{-1}

Figure S4 shows a typical plot of ln(dα/dt) vs. 1000/T for the sample containing 0.1 wt.% ES.

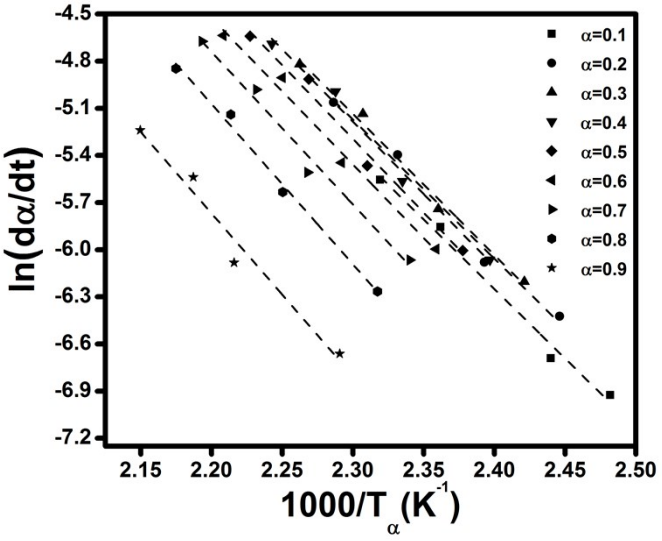

Figure S4: Plots of ln(dα/dt) vs. 1000/T for the sample containing 0.1 wt.% ES

Figure S5 shows plots of E_a and ln(Af(α)) against α. Different values obtained for the E_a at equivalent levels of α approves the dependence of E_a on the fractional extent of cure α.

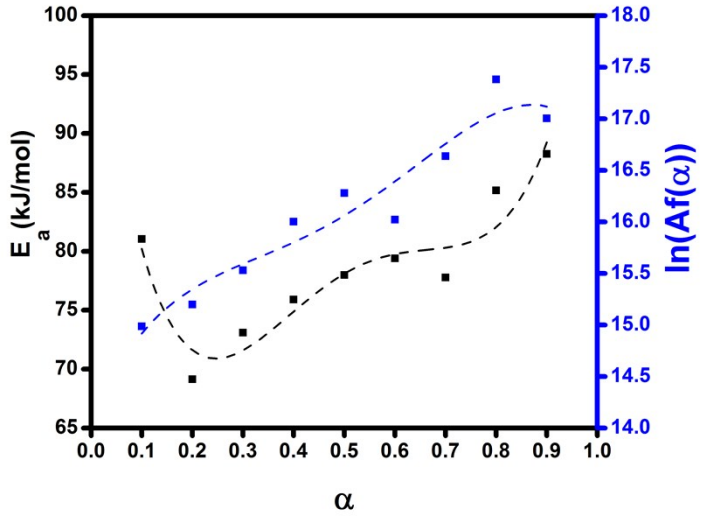

Figure S5: Plots of E_a and ln(Af(α)) vs. α for the sample containing 0.1 wt.% ES calculated using *Friedman*'s method

Among polynomials of different order passed through the data in **Figure S5**, the fourth-degree ones revealed the best fitting. Since the kinetic parameters are determined by selecting a rate equation followed by fitting to experimental data, the trustfulness of the interpretations based on kinetic parameters depends on whether the selected rate equation takes adequately the essential features of the process mechanism into account. The disadvantage of the adequateness of a rate equation to a curing mechanism roots in the improperness of statistical fit. Normally, an excellent data fit can be accomplished by using a physically meaningless equation such as that of a polynomial function.

A representative figure illustrating the linear plots at different conversions for the typical sample is provided based on KAS model (**Figure S6**).

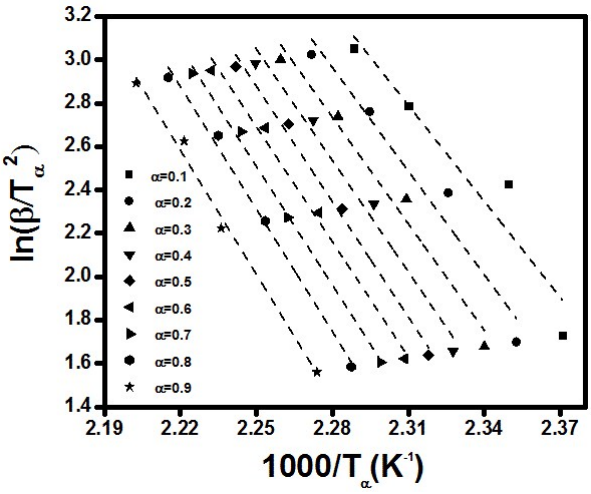

Figure S6: Plots of $\ln(\beta/T^2_\alpha)$ vs. $1000/T_\alpha$ for containing 0.1 wt.% ES

Reference

S1. M. Ghaffari, M. Ehsani, H. A. Khonakdar, G. Van Assche and H. Terryn, *Thermochimica Acta*, 2012, **549**, 81-86.