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Synergistic Evaluation of the Toughness of Calcium Carbonate Reinforced Epoxy Resin Plastic Based on their Input Ratios

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Abstract: Synergistic evaluation of the toughness of calcium carbonate ($CaCO_3$) reinforced epoxy resin plastic was carried out based on input ratios of its constituents; $CaCO_3$ and epoxy resin. Generated results from experiment, derived model and regression model show that the toughness of $CaCO_3$-epoxy resin composite increases with increase in epoxy resin addition and decrease in $CaCO_3$ addition. An empirical model derived, validated and used for the evaluation shows that the toughness of $CaCO_3$-epoxy resin composite is a combination of power and exponential functions of $CaCO_3$ and epoxy resin additions respectively. The validity of the derived model expressed as: $\mathfrak{z} = 1.3411\ \gamma^{-0.8774} + 0.0092\ e^{0.0307\varepsilon}$ was rooted in the model core expression $\mathfrak{z} - 0.0092e^{0.0307\varepsilon} = 1.3411\gamma^{-0.8774}$ where both sides of the expression are correspondingly approximately equal. Evaluated results indicated that the standard error incurred in predicting the toughness of $CaCO_3$-epoxy resin composite for each value of $CaCO_3$ & epoxy resin addition considered, as obtained from experiment, derived model and regression model were 0.0411, 0.0369 and 2.9277×10^{-5} & 0.0411, 0.037 and 2.9277×10^{-5} % respectively. Further evaluation indicates that $CaCO_3$-epoxy resin composite toughness per unit $CaCO_3$ and epoxy resin addition as obtained from experimental, derived model and regression model predicted results were (for each input material) 0.0051, 0.0051 and 0.0049 $MJ/cm^3\ \%^{-1}$ respectively. Comparative analysis of the correlations between toughness of $CaCO_3$-epoxy resin composite and $CaCO_3$ & epoxy resin addition as obtained from experiment, derived model and regression model indicated that they were all > 0.96. Deviational analysis revealed that the maximum deviation of model-predicted $CaCO_3$-epoxy resin composite toughness from the experimental results is 11.98%. These invariably translated into over 88% operational confidence for the derived model as well as over 0.88 dependency coefficients of $CaCO_3$-epoxy resin composite toughness on $CaCO_3$ and epoxy resin input ratios.

Key words: Evaluation · $CaCO_3$-Epoxy Resin Composite Toughness · $CaCO_3$ and Epoxy Resin Input Ratios

INTRODUCTION

The growing applicability of polymers for production of composites of better properties than its parent materials have raised the need for intensive research and development amply geared towards improving the processing techniques.

The relationship between reinforcing fillers and composite strength has been based on the use of short glass fibres [1]. However, to improve their young's modulus, polymers are filled by right inorganic particles [2]. Research [3] has shown that fillers also lead to reduction of the fracture strain and even to embrittlement of polymers.

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Earlier work [4] has revealed that synthetic silica samples show a reinforcing effect on the tensile strength of epoxy resin. This effect is due to the interaction with surface silanol groups on the silica and the polymer matrix. The researchers [4] observed in separate study of epoxy resin/ silica/$CaCO_3$ filler system that as the amount of filler increased there was a decrease in the ultimate tensile strength of the polymer. Similar studies [5] explained the interaction between the polymer matrix, the calcium carbonate and silica filler on the basis of Acid-Base interaction.

Silica (SiO_2) is acidic whereas $CaCO_3$ and Epoxy resin are basic. Epoxy resin synthetic marble is composed of $CaCO_3$, SiO_2 and a polymer system composed of epoxy resin as well as a polyamine catalyst.

It has been reported [6] that the strength of the marble is derived from the interplay of acid-base interactions of polymer/SiO_2 and $CaCO_3$/SiO_2 pairs, the polymer/$CaCO_3$ repulsion and the polymer network. The researchers revealed that, the level of adsorption of polymer and $CaCO_3$ depended on the available adsorption sites on the SiO_2. These sites increase with increasing diameter of the SiO_2 particles. The scientists [6] also indicated that more polymers were adsorbed as the SiO_2 particle size increased, while the induced $CaCO_3$/SiO_2 interaction increased at the expense of repulsion between the basic components.

Research [7] on the acid-base interactions in polymer matrix/filler systems has shown that it depends on the pH, the size, composition, nature, distribution and compatibility of the components in the system.

The present work aims at carrying out a synergistic evaluation of the toughness of calcium carbonate reinforced epoxy resin plastic based on input ratios of its constituents; $CaCO_3$ and epoxy resin.

MATERIALS AND METHODS

$CaCO_3$-epoxy resin composite was produced using calcium carbonate ($CaCO_3$) with relative density of about 1.4, particle size of between 0.5-0.06 mm and manufactured by Kavitex Nigeria Limited, German made epoxy resin of relative density of 1.2 and polyamine catalyst.

A tertiary polyamine was used to catalyze epoxy resin prepolymer to produce a thermoset; epoxy plastic. Gradual build-up of the viscosity and increase in temperature of the mixture was indicative of the curing or cross linking process. Details of the experimental procedures are as stated in past report [8]. ASTM E1820 testing procedure was adopted for the toughness tests.

RESULTS AND DISCUSSIONS

Model Formulation: Computational analysis (using C-NIKBRAN: [10]) of results in Table 1 indicates that.

Table 1: Variation of $CaCO_3$-epoxy resin composite toughness with $CaCO_3$ and epoxy resin addition [9]

(ε)	(γ)	(ξ)
40	60	0.071
50	50	0.086
60	40	0.106
70	30	0.131
80	20	0.228
90	10	0.326

Table 2: Variation of $\xi - 0.0092\, e^{0.0307\varepsilon} = 1.3411\, \gamma^{-0.8774}$

$\xi - 0.0092\, e^{0.0307\varepsilon}$	$1.3411\gamma^{-0.8774}$
0.0396	0.0369
0.0433	0.0433
0.0480	0.0527
0.0521	0.0678
0.1207	0.0968
0.1802	0.1779

$$\xi - K\, e^{S\varepsilon} = N\, \gamma^{-ƀ} \quad (1)$$

Substituting the values of K, S, N and ƀ into equation (1) reduces it to;

$$\xi - 0.0092\, e^{0.0307\varepsilon} = 1.3411\, \gamma^{-0.8774} \quad (2)$$

$$\xi = 1.3411\, \gamma^{-0.8774} + 0.0092\, e^{0.0307\varepsilon} \quad (3)$$

where

K = 0.0092; S = 0.0307, N = 1.3411 and ƀ = 0.8774 are equalizing constants (Determined using C-NIKBRAN [10])

(ξ) = Toughness of $CaCO_3$-epoxy resin composite (MJ/cm^3)

(ε) = Epoxy resin (%)

(γ) = $CaCO_3$ addition (%)

Boundary and Initial Condition: The ranges of $CaCO_3$-epoxy resin composite impact strength, $CaCO_3$ addition and applied load are 0.071 – 0.326 MJ/cm^3, 10 - 60% and 40 – 90 (%) respectively.

Model Validation: The validity of the derived model was rooted in equation (2) where both sides of the equation are correspondingly approximately almost equal. Furthermore, equation (2) agrees with Table 2 following the values of $\xi - 0.0092e^{0.0307\varepsilon} = 1.3411\gamma^{-0.8774}$ evaluated from Table 1.

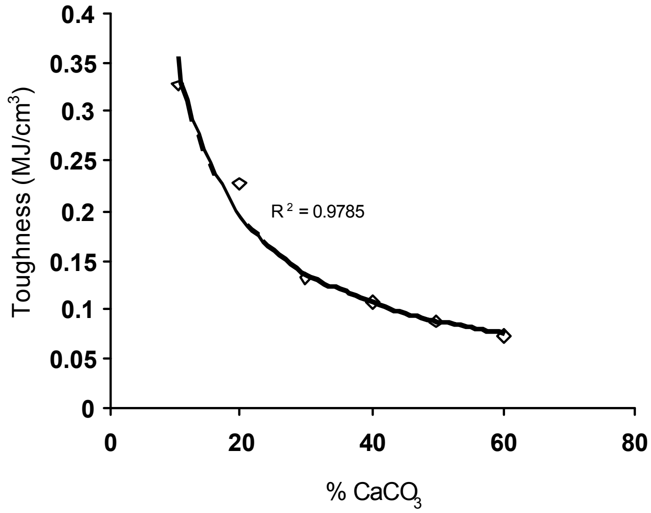

Fig. 1: Variation of $CaCO_3$-epoxy resin composite toughness with $CaCO_3$ addition as obtained from experiment [9]

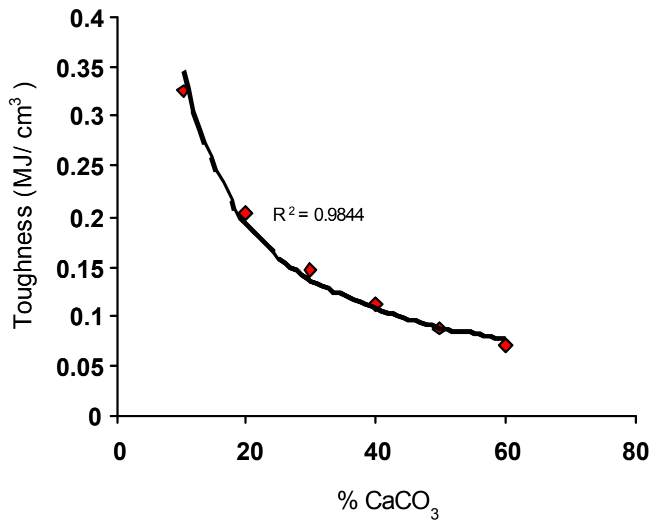

Fig. 2: Variation of $CaCO_3$-epoxy resin composite toughness with $CaCO_3$ addition as predicted by derived model

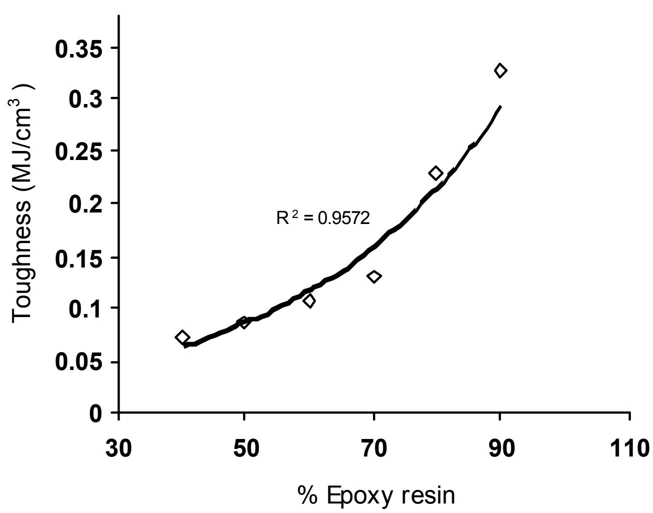

Fig. 3: Variation of $CaCO_3$-epoxy resin composite toughness with epoxy resin addition as obtained from experiment [9]

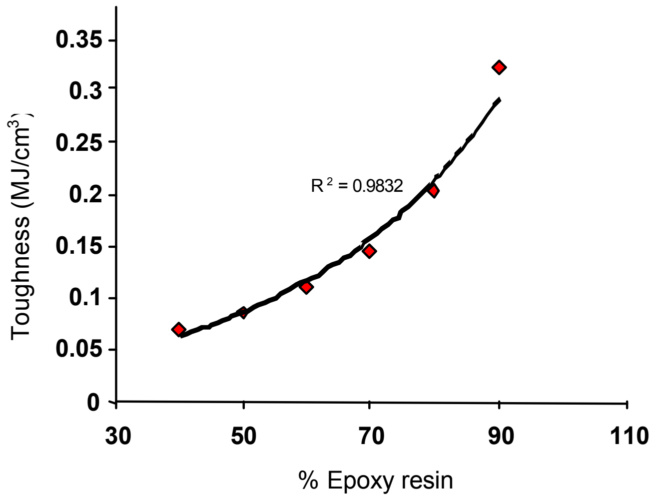

Fig. 4: Variation of $CaCO_3$-epoxy composite toughness with epoxy resin addition as predicted by derived model

Furthermore, the derived model was validated by comparing the model-predicted toughness of $CaCO_3$-epoxy resin composite and that obtained from the experiment. The fourth Degree Model Validity Test Techniques (4^{th} DMVTT); statistical graphical, computational and deviational analysis were used for the validation.

Statistical Analysis: The standard errors incurred in predicting the toughness of $CaCO_3$-epoxy resin composite for each value of the $CaCO_3$ & epoxy resin additions considered as obtained from experiment and derived model were 0.0411 and 0.0369 & 0.0411 and 0.0370 % respectively. The standard error was evaluated using Microsoft Excel version 2003.

The correlation coefficient between toughness of $CaCO_3$-epoxy resin composite and $CaCO_3$ and epoxy resin addition were evaluated (using Microsoft Excel Version 2003) from results of the experiment and derived model. These evaluations were based on the coefficients of determination R^2 shown in Figs. 1-4.

$$R = \sqrt{R^2} \quad (4)$$

The evaluated correlations are shown in Tables 3 and 4. These evaluated results indicate that the derived model predictions are significantly reliable and hence valid considering its proximate agreement with results from actual experiment.

Graphical Analysis: Graphical analysis of Figures 5 and 6 show very close dimension of covered areas, shapes and alignment of the curves from the experimental (ExD) and model-predicted (MoD) toughness of $CaCO_3$-epoxy resin composite.

It is strongly believed that the degree of closeness of shapes dimension and alignment of these curves are indicative of the proximate agreement between both experimental and model-predicted values of the $CaCO_3$-epoxy resin composite.

Comparison of Derived Model with Standard Model: The validity of the derived model was further verified through application of the Least Square Method (LSM) in predicting the trend of the experimental results.

Comparative analysis of Figures 7 and 8 show very close dimension of covered areas, shapes and alignment of curves by the toughness of $CaCO_3$-epoxy resin composite, which precisely translated into significantly similar trend of data point's distribution for experimental (ExD), derived model (MoD) and regression model-predicted (ReG) results of toughness of $CaCO_3$-epoxy resin composite.

The calculated correlations (Figures 7 and 8) between the toughness of $CaCO_3$-epoxy resin composite and $CaCO_3$ & epoxy resin addition for results obtained from regression model gave 1.0000 & 1.0000 respectively. These values are in proximate agreement with both experimental and derived model-predicted results. Comparative analysis of the correlations between toughness of $CaCO_3$-epoxy resin composite and $CaCO_3$ & epoxy resin addition as obtained from experiment, derived model and regression model indicated that they were all > 0.96.

Table 3: Comparison of the correlations evaluated from derived model predicted and experimental results based on $CaCO_3$ addition

	Based on $CaCO_3$ addition	
Analysis	ExD	D-Model
CORREL	0.9892	0.9922

Table 4: Comparison of the correlations evaluated from derived model predicted and experimental results based on epoxy resin addition

	Based on epoxy resin addition	
Analysis	ExD	D-Model
CORREL	0.9784	0.9916

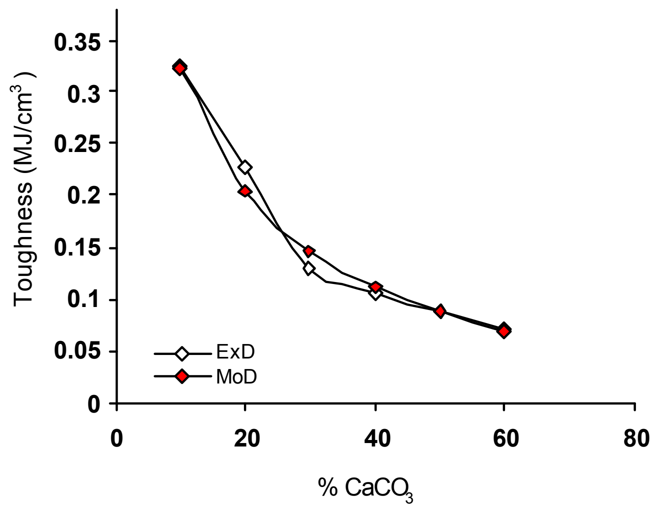

Fig. 5: Comparison of $CaCO_3$-epoxy resin composite toughness (relative to $CaCO_3$ addition) as obtained from experiment and derived model

The standard errors incurred in predicting the toughness of $CaCO_3$-epoxy resin composite for each value of the $CaCO_3$ and epoxy resin addition considered as obtained from regression model were 2.9277 $x10^{-5}$ and 2.9277 $x10^{-5}$% respectively.

Computational Analysis: Computational analysis of the experimental and model-predicted toughness of $CaCO_3$-epoxy resin composite was carried out to ascertain the degree of validity of the derived model. This was done by comparing the toughness of $CaCO_3$-epoxy resin composite per unit $CaCO_3$ and epoxy resin addition obtained from evaluation of experimental and model-predicted results.

Toughness of $CaCO_3$-epoxy resin composite per unit $CaCO_3$ and epoxy resin addition.

The toughness of $CaCO_3$-epoxy resin composite per unit $CaCO_3$ and epoxy resin addition were calculated from the expression;

$$\xi_C = \Delta\xi / \Delta\gamma \tag{5}$$

Equation (5) is detailed as;

$$\xi_C = \xi_2 - \xi_1 / \gamma_2 - \gamma_1 \tag{6}$$

where

$\Delta\xi$ = Change in toughness at two values of $CaCO_3$ addition.

γ_2, γ_1.

Considering the points (60, 0.071) & (10, 0.326), (60, 0.0683) & (10, 0.3237) and (60, 0.0347) & (10, 0.2813) as shown in Figure 8, then designating them as (ξ_1, γ_1) & (ξ_2, γ_2) for experimental, derived model and regression model predicted results respectively and also substituting them into equation (6), gives the slopes: - 0.0051, - 0.0051 and - 0.0049 MJ/cm^3 $\%^{-1}$ as their respective $CaCO_3$-epoxy resin composite toughness per unit $CaCO_3$ addition.

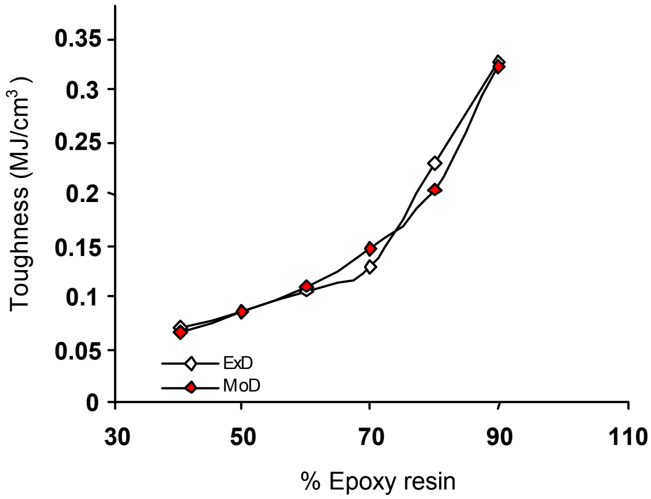

Fig. 6: Comparison of $CaCO_3$-epoxy resin composite toughness (relative to epoxy resin addition) as obtained from experiment and derived model

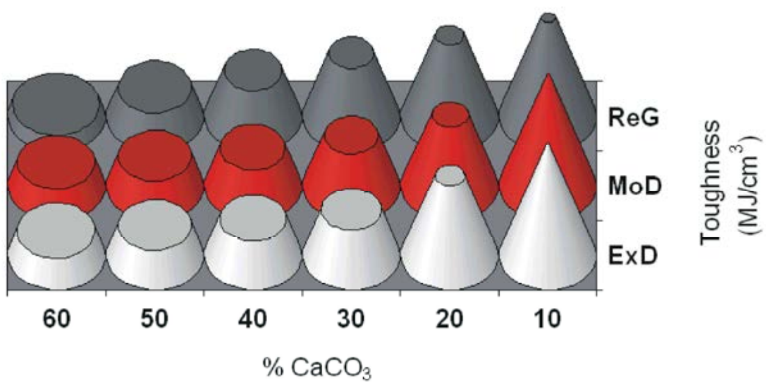

Fig. 7: 3-D Comparison of $CaCO_3$-epoxy resin composite toughness (relative to $CaCO_3$ addition) as obtained from ExD, MoD and ReG

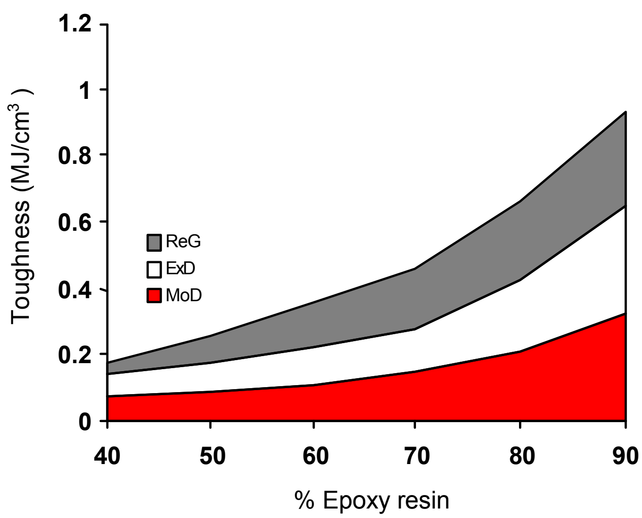

Fig. 8: 3-D Comparison of $CaCO_3$-epoxy resin composite toughness (relative to epoxy resin addition) as obtained from ExD, MoD and ReG

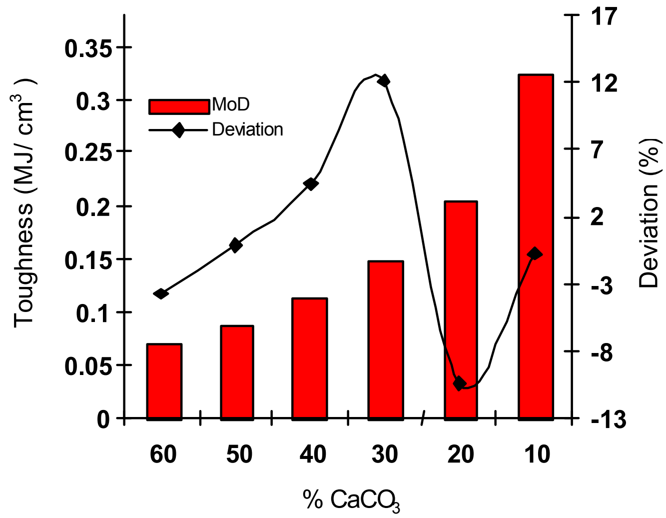

Fig. 9: Variation of model-predicted toughness of $CaCO_3$-epoxy resin composite (relative to CaCO $_3$addition) with associated deviation from experiment.

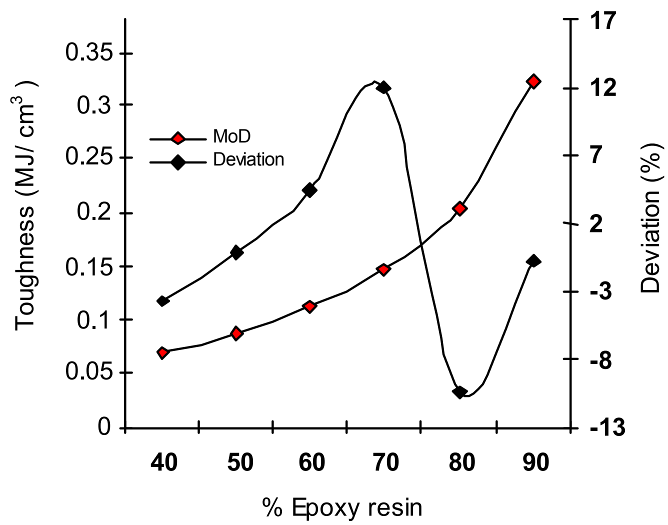

Fig. 10: Variation of model-predicted toughness of $CaCO_3$-epoxy resin composite (relative to applied load) with associated deviation from experiment.

Similarly, considering the points (40, 0.071) & (90, 0.326), (40, 0.0683) & (90, 0.3237) and (40, 0.0347) & (90, 0.2813) as shown in Figure 8 and Table 1, then designating them as ($ʒ_1$, ε_1) & ($ʒ_2$, ε_2) for experimental, derived model and regression model predicted results respectively and also substituting them into equation (6), gives the slopes: 0.0051, 0.0051 and 0.0049 MJ/cm^3 %$^{-1}$ as their respective $CaCO_3$-epoxy resin composite toughness per unit epoxy resin addition.

It is very important to state that the actual $CaCO_3$-epoxy resin composite toughness per unit $CaCO_3$ addition (as obtained from experiment and derived model) is just the magnitude of the signed value. The associated sign preceding these values signifies that the associated slope tilted to negative plane. Based on the foregoing, the toughness of $CaCO_3$-epoxy resin composite per unit $CaCO_3$ addition as obtained from experimental, derived model and regression model predicted results are also 0.0051, 0.0051 and 0.0049 MJ/cm^3 %$^{-1}$ respectively.

Deviational Analysis: Analysis of the toughness of $CaCO_3$-epoxy resin composite obtained from experiment and derived model reveal low deviations on the part of the model-predicted values relative to values obtained from the experiment. This was attributed to the fact that the surface properties of the $CaCO_3$ and epoxy resin as well as the physico-chemical interactions between the carbonate and the epoxy resin plastic which played vital roles during processing were not considered during the model formulation. This necessitated the introduction of correction factor, to bring the model-predicted toughness of $CaCO_3$-epoxy resin composite to those of the corresponding experimental values.

The deviation Dv, of model-predicted toughness of $CaCO_3$-epoxy resin composite $ʒ_{MoD}$ (from the corresponding experimental result $ʒ_{ExD}$) is given by;

$$Dv = \left(\frac{ʒ_{MoD} - ʒ_{ExD}}{ʒ_{ExD}}\right) x\,100 \qquad (7)$$

Deviational analysis of Figures 9 and 10 indicate that the maximum deviation of model-predicted $CaCO_3$-epoxy resin composite toughness from the experimental results is 11.98%. This invariably translated into over 88% operational confidence for the derived model as well as over 0.88 dependency coefficients of $CaCO_3$-epoxy resin composite toughness on $CaCO_3$ and epoxy resin addition.

Equation (7) and Figures 9 & 10 show that the least and highest magnitudes of deviation of the model-predicted $CaCO_3$-epoxy resin composite toughness (from the corresponding experimental values) are 0 and + 11.48%. Figure 9 and 10 indicate that these deviations correspond to $CaCO_3$-epoxy resin composite toughness: 0.086 and 0.1467 MJ/cm^3, $CaCO_3$ addition: 50 and 30 % as well as epoxy resin addition: 50 and 70 %respectively.

Correction factor, Cf to the model-predicted results is given by;

$$Cf = -\left(\frac{ʒ_{MoD} - ʒ_{ExD}}{ʒ_{ExD}}\right) x\,100 \qquad (8)$$

Comparative analysis of Figures 9, 10 and Table 5 indicates that the evaluated correction factors are negative of the deviation as shown in equations (7) and (8).

Table 5 shows that the least and highest correction factor (to the model-predicted toughness of $CaCO_3$-epoxy resin composite) are 0 and – 11.48%, being the negative of deviation as shown in equations (7) and (8). Table 5, Figures 9 and 10 indicate that these highlighted correction factors correspond to CaCO3-epoxy resin composite toughness: 0.086 and 0.1467 MJ/cm$_3$, $CaCO_3$ addition: 50 and 30 % as well as epoxy resin addition: 50 and 70 % respectively.

Table 5: Variation of correction factor (to model-predicted toughness of $CaCO_3$-epoxy resin composite) with $CaCO_3$ and epoxy resin addition

(ε)	(γ)	Correction factor (%)
40	60	+3.80
50	50	0
60	40	-4.43
70	30	-11.98
80	20	+10.48
90	10	+0.71

The correction factor took care of the negligence of operational contributions of the surface properties of the $CaCO_3$ and epoxy resin as well as the physico-chemical interactions between the carbonate and the epoxy resin plastic which actually played vital role during processing.

The model predicted results deviated from those of the experiment because these contributions were not considered during the model formulation. Introduction of the corresponding values of Cf from equation (8) into the model gives exactly the corresponding experimental values of $CaCO_3$-epoxy resin composite toughness.

It is very pertinent to state that the deviation of model predicted results from that of the experiment is just the magnitude of the value. The associated sign preceding the value signifies that the deviation is a deficit (negative sign) or surplus (positive sign).

CONCLUSIONS

Synergistic evaluation of the toughness of calcium carbonate ($CaCO_3$) reinforced epoxy resin plastic was carried out based on $CaCO_3$ and epoxy resin addition. The toughness of $CaCO_3$-epoxy resin composite increases with increase in epoxy resin addition and decrease in $CaCO_3$ addition. An empirical model derived, validated and used for the evaluation shows that the toughness of $CaCO_3$-epoxy resin composite is a combination of power and exponential functions of $CaCO_3$ and epoxy resin additions respectively. The validity of the derived model is rooted in the model core expression $ʒ - 0.0092e^{0.0307\varepsilon} = 1.3411\gamma^{-0.8774}$ where both sides of the expression are correspondingly approximately equal. The standard error incurred in predicting the toughness of $CaCO_3$-epoxy resin composite for each value of $CaCO_3$ & epoxy resin addition considered, as obtained from experiment, derived model and regression model were 0.0411, 0.0369 and 2.9277×10^{-5} & 0.0411, 0.037 and 2.9277×10^{-5} % respectively. $CaCO_3$-epoxy resin composite toughness per unit $CaCO_3$ and epoxy resin addition as obtained from experimental, derived model and regression model predicted results were (for each input material) 0.0051, 0.0051 and 0.0049 $MJ/cm^3\ \%^{-1}$ respectively. Comparative analysis of the correlations between toughness of $CaCO_3$-epoxy resin composite and $CaCO_3$ & epoxy resin addition as obtained from experiment, derived model and regression model indicated that they were all > 0.96. Deviational analysis revealed that the maximum deviation of model-predicted $CaCO_3$-epoxy resin composite toughness from the experimental results is 11.98%. These invariably translated into over 0.88% operational confidence for the derived model as well as over 0.88 dependency coefficients of $CaCO_3$-epoxy resin composite toughness on $CaCO_3$ and epoxy resin additions.

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