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OPTIMIZATION OF EPOXY NANOCOMPOSITE ON GLASS TRANSITION TEMPERATURE CHARACTERISTICS UTILIZING EXPERIMENTAL DESIGN METHOD

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An experimental study of the thermal performance characteristics of TMA glass transition temperature is developed. Three kinds of nanopowder, namely, alumina, silica and carbon black, are selected and mixed with reactive diluent to prepare a novel epoxy nanocomposite. By analysis of variance, it is found that the control factors are significant factors to qualify the glass transition temperature of the nanocomposite. In the study, the glass transition temperature is effectively optimized by using Taguchi method. As a result, the optimum composition is to adding 2 wt.% of Al_2O_3, 2 wt.% of SiO_2, and 2 wt.% of carbon black of the nanocomposite. The multiple regression equation can be established from the experiment to determine the weighted coefficient of control factors and quality characteristics. The error between the experimental value and the prediction value, which is calculated by the regression equation, is only 0.06%. It confirms the reliability of this study.

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Keywords: Nanopowder; epoxy; Glass transition temperature; Optimization; multiple regression equation

1.Introduction

In recent years, several studies were attracted to nanomaterial by considerable potential characteristics of reinforcing material [1-5]. This is due to the nanoscale reinforcing material has good dispersion and interaction in the substrate that enable the composite material to has better stability in the overall performance, thereby improving the performance of materials.

Several studies have examined the preparation and thermal characterization of epoxy resins using a range of inorganic fillers. Omrani et al. investigated the reinforcing effects of alumina nanoparticle in a diglycidyl ether of bisphenol A (DGEBA) type epoxy resin. They found that a relatively low concentration of Al_2O_3 nanoparticle led to an impressive improvement of

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dynamic mechanical, mechanical, and thermal properties [6]. Chen et al. found, when the γ-Al_2O_3 content was increased from 1phr to 5phr, results revealed that γ-Al_2O_3 nanoparticles were effective to enhance both the stiffness and toughness of epoxy resin [7].

The rigidity and toughness of epoxy composite have been significantly improved by adding silica nanoparticles preparation. However, its thermal properties, thermal expansion coefficient decreased with the addition of silica [8]. When 3wt% of nanosilica added into the epoxy resin, the new composite material has the highest glass transition point temperature [9]. The reason is a high content of silica nanoparticles will cause the crosslinking density of polymer material falling. Barabanova et al. studied epoxy resin with silica nanoparticles and found that the glass transition point temperature of the nanocomposite materials can be higher when compared to pure epoxy under the same conditions [10]. Hasnaoui et al. investigated the thermal properties of a mixture of the copolymer and carbon black by differential scanning calorimetry (DSC). The results showed that the glass transition temperature rises as the content of carbon black increasing [11].

From above literatures, it can be known that a composite of nanomaterials can improve the overall performance of the substrate. In order to promote applications of epoxy resin, researchers usually consider how the composite type of materials can improve its properties and overall performance. In this study, an experimental study of the thermal performance characteristics of TMA glass transition temperature of a new composite material is attempted. Three kinds of nanopowder materials, namely, alumina, silica and carbon black, are selected and mixed with diluent to prepare a new epoxy composite. As this way, it is due to the reinforcing material has good dispersion and interaction in the substrate that enable the composite material to has better stability in the overall performance, thereby improving the performance of materials. The multiple regression equation can be established from the experiment to predict the weighted coefficient of control factors and quality characteristics. Thus, the derived formulae provide a quick and convenient means of predicting the thermal response of organic-inorganic materials with a known composition without the need for experimental investigation.

2. Experiment

2.1 Materials

The bisphenol-A novolac epoxy resin (an epoxide equivalent weight of 190-210 g/equiv.) and reactive diluent (alkyl glycidyl ether has an epoxide equivalent weight of 275-290 g/ equiv. and viscosity of 5-20c.p. at 25℃) were purchased from Chang Chun Plastics Co. Ltd. Taiwan. The hardener (methyl hexahydrophthalic anhydride) was purchased from Nan Ya Plastics Co. Ltd. Taiwan. The γ-Alumina powder with an average primary particle size is 50 nm. The silica powder of particle diameter 14 nm which is hydrophobic fumed silica powder treated by the alkyl polydimethyl silicone. The surface area of silicon powder is $120m^2/g$. The average primary particle size of Carbon black is 28 nm. Note that all the purchased materials were used as-received without further purification.

2.2 Sample preparation

According the components of the designed material in this study, firstly, mix the epoxy resin and diluent by proportion. The weight content of the each nanopowder was varied from 0 to 2wt%. Add nanometer powder of different amounts for mechanical mixing and ultrasonic vibration to disperse the agglomerates [12]. Subsequently, the hardener was added into the mixture and stirred evenly; it was followed by using the methods of centrifugal mixer and vacuum to eliminate the air in the sample. The bubble free mixture was poured into a preheated mold, which had previously been sprayed with a mold release agent. The curing cycle was performed at 130℃ for 1h and at 160℃ for 2hr in an oven.

2.3 Characterization

Thermal mechanical analyzer (TMA) is mainly used to measure the thermal expansion coefficient and glass transition temperature of a material. The operation principle of the device for the analytes is as the following. The analytes is placed on the heated device. A probe is used to withstand against the analytes by some specific strength. Set up the temperature change procedure and rate, the relationship between material size change and temperature, time and the mechanical load can be obtained. Samples were heated at 10℃/min from 30 up to150℃in a first scan and at 5 ℃/min up to 180℃in a second scan, which was used for the calculations. The Tg was determined from the expansion curves as the crossover of the two tangents above and below the change of slope.

3. Experiment method

In this study, the thermal property test is designed by using Taguchi method. The best parameter combination of glass transition temperature characteristics can be found through the analysis of Taguchi method. Taguchi method is proposed and developed by G. Taguchi in order to improve the efficiency of experiment planning [13]. Taguchi method solves problem from the point of view of engineering. It is mainly a combination of engineering management and statistical methods makes the design of products and manufacturing processes to achieve the best conditions, thus improving the cost and quality. It is a high quality and efficient system design tool. Taguchi method utilizes the design of orthogonal array and analysis of variance to find out the significant control factors and the interaction of factors. It can observe the negative effect of these factors on target value or output value. It is a simple and efficient way to study the quality, performance and cost calculation for optimum design.

Taguchi method mainly goes through three steps to solve a problem, i.e. concept design, parameter design and tolerance design. For the system design, the process examined completing technologies for producing a product for production. Then, the designer used this information to generate a basic prototype design, and design parameters can be found in the best process parameters to improve quality characteristics of the product. The purpose is to optimize the parameter value setting process. Tolerance design is for the identification and analysis of tolerance and the parameter design is proposed by the best configuration for confirmation and analysis of tolerance. Several researchers utilized this method to optimize the parameters for system design [14, 15].

The purpose of this study is to improve the glass transition temperature of the experimental variables to find the best parameters, so the use of signal to noise ratio (Signal-to-Noise Ratio; referred to as S/N ratio). The ratio of signal to noise, the value is bigger is better. In this study, the glass transition temperature of the quality characteristics test is the kind. In addition to the S/N ratio, the analysis of variance can also be used from the statistics (ANOVA) to observe the influence of the experimental factors on the glass transition temperature characteristics and find out the significant factors affecting the experiment to calculate the optimal experimental factor level [16]. For the case of maximizing the performance characteristic, which is higher-is-better, refereed as HB, the following definition of the S/N ratio for higher-is-better (HB in short) case is:

$$S/N_{LTB} = -10 \times \log_{10}\left(\frac{1}{n}\sum_{i=1}^{n}\frac{1}{y_i^2}\right) \tag{1}$$

Where n is the number of experiment. y_i is the mean of experimental parameter values. The unit of S/N ratio is Decibel, denoted as db.

3.2 Confirmation experiment

It can be known from the S/N factor response diagram that the best combination of composite materials can be found to compute the predictive value of y_p. To ensure that the set of experimental design factor levels really affected the material properties and comply with the reliability of experiments, it needed to confirm the experiment and compare with the predicted values. Let the confirmation experiment with 95% confidence interval be Cl_e and the predictive value of the optimal factor level with 95% confidence intervals is denoted as Cl_p. Then if Cl_e and Cl_p overlapped, the experimental results are said be with confidence. The equations are as the following:

$$y_p = \bar{y} + \sum(y-\bar{y})_{sig} \tag{2}$$

$$Cl_p = \left| N_{\frac{\beta}{2}} \times \frac{S}{\sqrt{m_e}} \right| \tag{3}$$

$$Cl_e = \left| N_{\frac{\beta}{2}} \times \frac{S}{\sqrt{m_e + \frac{1}{r}}} \right| \tag{4}$$

Where $\sum(\mathbf{y}-\bar{\mathbf{y}})_{\mathbf{sig}}$ is the effect caused by a significant factor; $\mathbf{N}_{\frac{\beta}{2}}$ is the cumulative probability of the standard normal distribution; β is 0.05 at 95% confidence; **S** is the standard deviation of the results by ANOVA; $\mathbf{m_e}$ is the total freedom divided by the freedom of predicted function; **r** is the number of confirmation experiment. The optimization of the resulting parameter set is conducted prediction calculation and the final simulation. If the error between the experiment results and prediction values is acceptable, the reliability of this optimization is thus determined.

3.3 Regression Analysis

In statistics, regression analysis is a statistical process for estimating the relationships among variables. It includes many techniques for modeling and analyzing several variables, when the focus is on the relationship between a dependent variable and one or more independent variables. The researchers must first consider the independent variables and the dependent variable whether there is a direct correlation between, as well as the independent variables with the explanatory variables are appropriate. In this study, control factors are selected as independent variables, including X_A is the weight percentage of alumina powder, X_B is weight percentage of silica powder, X_C is weight percentage of carbon black powder, X_D is weight percentage of diluent. From the factor response plot by Taguchi method, a quadratic curve estimates should be most consistent with the observed distribution of values. This study utilizes the factors forced entry method with the Levenberg-Marquardt method of iterations to get the most appropriate regression model.

This study established a multiple regression model of the quality characteristics. The interaction between the factors will not be considered in this case. Assumed control factor weight percentage and quality characteristic Y is a quadratic relationship, the equation is expressed as follows:

$$\mathbf{Y = i_n X_i^n + C} \qquad , n=1, 2 \qquad , i=A, B, C, D \tag{5}$$

Where, C is constant, i_n … are regression coefficients; Y is quality characteristic. Even if the non-linear relationship can be transformed to a linear model by elementary mathematical conversion, the model may also cause changes in the nature of random errors. In this case, the model is analyzed and compared favorably as nonlinear models.

Assess the suitability of the regression model can be judged by the coefficient of determination R^2. It evaluates the ability to explain the regression model of the independent variables to the dependent variables. The higher the value of the coefficient of determination R^2 is, on behalf of the explanatory ability of the model for the higher variation. Regression coefficient of determination is defined as the proportion of variation to the total variation. It also represents the variation in the Y, which a function is defined by a number of variables X and reveals percentage level as explained. So whether regression model is appropriate can be examined by utilizing the degree of variation in the dependent variable. If the total variance of the dependent variable and regression variance is close, it means that changes in the dependent variable can be fully explained by the regression model. The coefficient of determination R^2 is between the interval 0 and 1. If R^2 is closer to one, it means that the better the explanatory ability of regression models[17]. R^2 can be calculated from equation (6) as the following:

$$\mathbf{R^2 = \frac{SS_T}{SS_R}} , \ \mathbf{0 < R^2} < 1 \tag{6}$$

Where $\mathbf{SS_T}$ is total variation; $\mathbf{SS_R}$ is regression variation.

4. Results and discussion

This study investigated the control factors affecting the epoxy nanocomposite to find out the important factors that influenced the thermal properties by Taguchi method. The control factor level table was as shown in Table 1. The orthogonal array is a L_9 orthogonal array as shown in table 2. The test was repeatedly carried out in accordance with the orthogonal array. The TMA (to find glass transition temperature) of the sample was categorized finishing in Table 3.

Table 1 The level of control factors for the nanomaterials

Factor		Level 1	Level 2	Level 3
A.	Alumina powder	0wt.%	1 wt.%	2 wt.%
B.	Silica powder	0 wt.%	1 wt.%	2 wt.%
C.	Carbon black	0 wt.%	1 wt.%	2 wt.%
D.	Diluent	0 wt.%	2.7 wt.%	5.4 wt.%

The quality characteristics of this experiment are higher-is-better. According to equation (1) to calculate the value of quality characteristics, the results were organized into factor response plot to obtain the optimum combination of parameters. TMA glass transition temperature S/N factor response diagram is as shown in Figure 1. It can be found that the epoxy resin doped with 2wt.% of $Al_2O_{3,}$ 2wt.% of SiO_2 and 2wt.% of carbon black is the optimum combination for TMA glass transition temperature characteristic.

ANOVA for TMA glass transition temperature resulting from the experiment was organized into a table as shown in Table 4. The reliability of Confidence factor in 95% above is considered as an important factor, while Significant is in accordance with the conditions for determining the credibility in front of an important factor. From Table 4, it can be seen that the confidence level of the control factor of Al_2O_3, SiO_2, carbon black and diluent reached up to 95% by ANOVA for characteristic of TMA glass transition temperature. It confirmed that the three factors are significant factors for this experiment.

Table 2 Orthogonal array for the thermal experiment

Sample name	A	B	C	D
T1	1	1	1	1
T2	1	2	2	2
T3	1	3	3	3
T4	2	1	2	3
T5	2	2	3	1
T6	2	3	1	2
T7	3	1	3	2
T8	3	2	1	3
T9	3	3	2	1

Table 3 Glass transition temperatures obtained from the experiment

Sample Name	Y_1 (°C)	Y_2 (°C)	Y_3 (°C)	Y_{Avg} (°C)	C.O.V. (%)	S/N (db)
T1	119.78	121.17	119.92	120.29	0.64	41.60
T2	113.92	114.93	115.16	114.67	0.58	41.19
T3	109.05	110.63	110.88	110.19	0.90	40.84
T4	108.02	110.10	109.51	109.21	0.98	40.76
T5	123.89	123.42	124.24	123.85	0.33	41.86
T6	116.62	115.89	116.97	116.49	0.47	41.33
T7	118.84	118.60	118.30	118.58	0.23	41.48
T8	109.17	110.55	111.26	110.33	0.96	40.85
T9	124.32	124.11	124.34	124.26	0.10	41.89

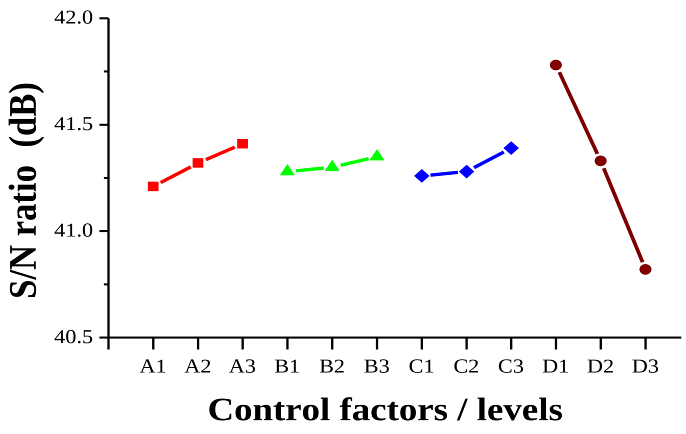

Fig 1 S/N factor response graph for the TMA glass transition temperature

Table 4 ANOVA of TMA glass transition temperatures

Factor	SS	DOF	MS	F	Confidence	Significant
A	32.24	2	16.12	29.94	99.99%	Yes
B	4.37	2	2.19	4.06	96.49%	Yes
C	17.15	2	8.57	15.92	99.98%	Yes
D	748.12	2	374.06	694.66	100.00%	Yes
Error	9.69	18	0.54		S =0.73	
Total	811.58	26		*At least 95% confidence		

Table 5 shows the comparison chart of the TMA glass transition temperature from the prediction and the confirmation experiment. According to equation (2), it can predict the best TMA glass transition temperature y_p=125.75, which confirmed the transition temperature y_e=125.51, the mean of experiment values. The experimental mean of glass transition temperature for each sample was plotted as Fig. 2.

Table 5 TMA glass transition temperatures from the confirmation experiment

item	Y1(℃)	Y2(℃)	Y3(℃)	YAvg(℃)	C.O.V.(%)
Prediction value			125.75		—
Value form Confirmation experiment	125.46	125.32	125.76	125.51	0.18

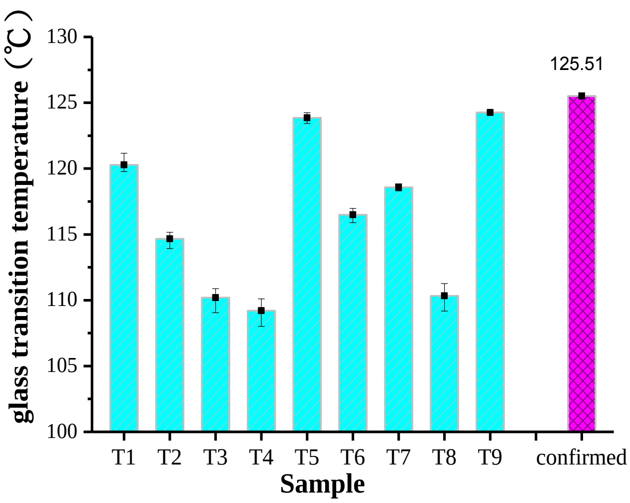

Fig. 2 The comparison of the TMA glass transition temperatures from different sample and the confirmation experiment

With Equations (3) and (4), it can be obtained the trust interval for the control factor prediction of the TMA glass transition temperature is 125.75 ± 0.85 ℃, the value from the confirmation experiment is 125.51 ± 1.19 ℃, as shown in Figure 3. Figure 3 showed that the TMA glass transition temperature from the prediction and the confirmation experiment had the confidence interval of 95% overlap. It verified that the experimental and predicted values overlap interval was over 95%. The result of this study presents its reproducibility and robustness.

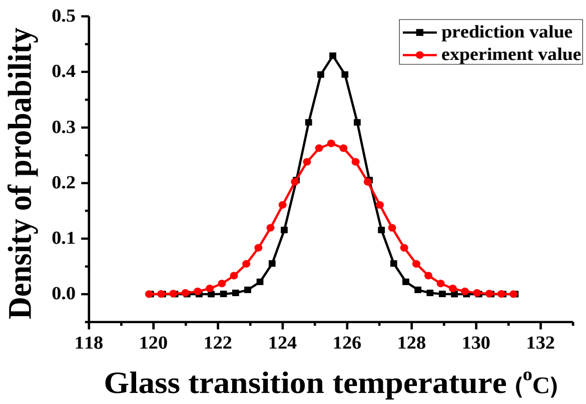

Fig. 3 The comparison of the TMA glass transition temperatures for prediction and the confirmation experiment

By statistical analysis software SPSS regression analysis, the empirical equation can be established by the target characteristics and control factors. According to the multiple regression equation shown as Equation (5), the added item quality characteristics regression coefficient can be obtained. The regression coefficient was as shown in Table 6. The coefficient of determination R^2 of the regression equation of TMA glass transition temperature reached to 100%.

Table 6 Coefficients of regression model

Quality characteristics	TMA glass transition temperature
A_1	1.760
A_2	-0.205
B_1	0.068
B_2	0.181
C_1	-0.105
C_2	0.485
D_1	-2.202
D_2	-0.039
Constant	120.29

The composition of parameters obtained from Taguchi method was substituted into the regression model to obtain the predictive value, namely 125.58 ℃ . The experimental mean value from the confirmation experiment is 125.51℃. The difference between them is only 0.06%. The above experimental results proved that the regression model on the glass transition temperature has a considerable degree of accuracy.

5. Conclusion

In this study, the thermal properties of TMA glass transition temperature characteristics are investigated by using Taguchi method. The study intends to explore the important factors how sensitively affect the thermal properties of the epoxy nanocomposite. The study utilizes Taguchi method to search the optimum combination of parameters to enhance the thermal properties of the epoxy nanocomposite material.

According to the results, it can be concluded that the best combination of parameters is 2wt.% of Al_2O_3 and 2wt.% of SiO_2 and 2wt.% of Carbon black for enhancing the glass transition temperature of the epoxy resin in the thermal test. In accordance with the equations of the glass transition temperature prediction and confidence interval, the value is y_p=125.75 ± 0.85 ℃, which confirms that the average TMA glass transition temperature and the confidence interval y_e=125.51 ± 1.19 ℃. The error between two values, i.e. y_p and y_e, is 0.19%. Substituting the values obtained from Taguchi-method experiment into the regression model to calculate the TMA glass transition temperature, the predictive value is 125.58 ℃. This compares with the mean value, y_e=125.51℃, obtained from the confirmation experiment, that the difference is only 0.06%. The comparison is further conducted by the value resulting from the original combination of parameters. It can confirm that the thermal properties of epoxy nanocomposite materials have been enhanced after optimization by Taguchi method. The multiple regression equation can be established from the experiment to predict the weighted coefficient of control factors and quality characteristics. Thus, the derived formulae provide a quick and convenient means of predicting the thermal response of organic-inorganic materials with a known composition without the need for experimental investigation.

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