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Surface Degradation of Polymer Matrix Composites Under Different Low Thermal Cycling Conditions

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ABSTRACT

The principal effects of mass degradation on polymer matrix composites (PMCs) are the decay of mechanical properties such as strength, elongation, and resilience. This degradation is a common problem of the PMCs under thermal cycling conditions. In this article, composite degradation was investigated by measurement of total mass loss (TML) using the Taguchi approach. Thermal cycling tests were performed using a developed thermal cycling apparatus. Weight loss experiments were performed on the glass fiber/epoxy laminates under different number of thermal cycles and temperature differences. Also, The specimens had various fiber volume fractions and stacking sequences. Statistical analysis is performed to study contribution of each factor. Based on weight loss rates, a regression model was presented to evaluate the TML of laminated composite materials samples. It was found that the temperature differences and fiber volume fraction are the most effective factors of surface degradation with 61 and 22 percent contribution. Also, under the similar experimental conditions, the $[0]_8$ layups exhibits 44 and 35.7 percent more mass loss than the $[0/\pm45/90]_s$ and $[02/902]_s$ layups, respectively.

Keywords: Thermal cycling; Total mass loss; Polymer matrix composites (PMCs); Taguchi method; Stacking sequence.

1 INTRODUCTION

POLYMER matrix composites (PMCs) are being used in various engineering applications especially in aerospace engineering. The promise and potential of these materials are sometimes threatened because of their in-homogeneities and inherent susceptibility to degradation due to moist and thermal environments [1]. Virtually all the physical properties such as mass loss of the PMCs may change with the passage of time. So, there is a need to predict a reliable model of the maximum lifetime for the PMCs under aerospace service environments such as thermal cycling [2]. At normal temperatures, polymers react slowly with oxygen so oxidation only becomes apparent after a long time. The oxidative degradation in polymeric composites involves solid– gas reactions, and is associated with chain division [3]. As a result, these harsh components can cause the erosion and mass loss of polymers and the PMCs, and degradations of their material properties [4].

In-flight experiments are very expensive and time-consuming. Therefore ground simulation experiments have been widely performed to verify the effects of the thermal cycling environment [5-6]. As the different factors are simultaneously applied on composite structures at the in-flight conditions, aging behaviors were much complicated than the individual effective factor effects studies. Different researches are done to identify the effects of different factors on the mass loss degradation of the PMCs [6-11]. These effects are mainly radiation (ultra violet or electron)

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[6], resins [7], fiber angle and sample size [8,11], number of thermal cycling [9] and environmental atmospheres (oxidative or neutral) [7,10] conditions. Paillous et al. [6] subjected various graphite/epoxy laminate specimens to electron radiation combined with thermal cycling, or to oxygen atom fluxes. The results showed that the synergistic action of electrons and thermal cycling degrades the matrix by chain scission, cross-linking and micro crack damage, altering the composite's properties such as flexural stiffness. Zhang et al. [7] evaluated the mass change in two carbon/epoxy +60˚/0˚/-60˚ triaxial braided composites, T700s/3502 and T700s/PR520, as well as 3502 and PR520 pure resins were exposed to a thermal cycling environment. Based on the observations, the changes of mass for both composites and pure resins were small (less than 1% after 160 cycles) and the mass loss became almost flat after 160 cycles. It was also found that the composites exhibit larger mass loss than the pure resin. This was probably due to the more volatile products being trapped during the manufacturing process. Nam and Seferis [8] considered two different degradation mechanisms of unidirectional bismaleimide/carbon fiber composites. These mechanisms were polymer molecules-adjacent phase molecular interactions and the degradation behavior of polymer composites at elevated temperature in air environment due to the anisotropy of the composite. It was found that the different degradation mechanisms were operative in the different directions. Shin et al. [9] evaluated the changes in the mechanical properties, mass and coefficient of thermal expansion of composites in space. The mass of the graphite/epoxy composites after 80 thermal cycles of exposure under simulated conditions including ultraviolet radiation, thermal cycling and high vacuum was down almost 1.0% in comparison with the same mass loss under a vacuum environment with 125˚C. It was found that this mass loss was a direct result of matrix loss and material outgassing. The major outgassed products were H_2O, N_2 and hydrocarbon (C_6H_5).

Lafarie-Frenot et al. [10] carried out weight measurements of cross-ply laminates samples in oxidative and neutral environment. The main result obtained was that the test atmosphere: neutral (nitrogen) or oxidative (air or oxygen) has a very significant influence on the damage processes and degradation rates of the composite materials. Lafarie-Frenot et al. [11] also focused on the characterization and understanding the mechanisms of thermo-oxidation of the epoxy matrix alone, without and with mechanical stress. They placed each specimen in a neutral or oxidizing environment subjected to thermal ageing at 120˚C, 150˚C and 180˚C. The results showed that the mass loss rate depends strongly on the stacking sequences and fiber orientation with respect to the exposed surface. As the effective factors on the mass degradation are spread, performing a complete experiment that considers all the factors is impossible. Taguchi method is one of the designs of experiment (DOE) methods for designing and performing experiments to investigate processes where the output depends on many factors (variables, inputs) using minimum experiments [12]. Dobrzañski et al. [13] used this method in the optimization of filament winding of thermoplastic composites to find the optimum parameters to produce Twintex®. They used the machining parameters, number of layers and roving and fibers temperature as the design parameters. Ghasemi et al. [14-15] have been investigated nonlinear behavior of PMCs under cyclic thermal shock and effects on residual stresses, fracture and failure index, but did not focus on surface degradation and mass loss.

The goal of the present work is prediction of the mass loss of the PMCs as a function of environmental exposure and composite material properties. More specifically, the present work focuses on the different fiber volume fractions, stacking sequences, temperature difference and number of thermal cycles effects in the thermo-oxidative degradation behavior of the PMCs. For the experiment implementation of the Taguchi method, L9 scheme is extracted for four effective factors with three levels. E glass/epoxy composite specimen is prepared and subjected to thermal cycling at a developed thermal cycling apparatus. The weight loss measurement of specimens is performed and statistical approach is utilized to identify contribution of the effective factors. Based on this approach, a multiple linear regression model was obtained and sensitivity analysis of each parameter on the mass reduction is studied. This work provides an understanding of how the different condition of material and thermal cycling process are affect the long-term properties of the PMCs.

2 EXPERIMENTS

2.1 Experiment planning

Experiment design of this research is accomplished according to the four effective factors namely number of thermal cycles (N); temperature difference (dT), fiber volume fraction (V_f) and stacking sequence (S) of the laminated composite materials. Three different levels are also considered for each factor (Table 1), so, the *L9* orthogonal array type of the Taguchi method was used to experiment plan (Table 2). As shown in this table, three different stacking sequences are selected − $[0]_8$, $[0_2/90_2]_s$ and $[0/\pm45/90]_s$ that considers unidirectional, cross-ply and quasi-isotropic sequence, respectively.

For the study different temperature effect, three different cycles is considered that have the maximum temperature of 50˚C, 75˚C and 100˚C, respectively. The minimum temperature of the all cycles was selected 0˚C. The maximum temperature of the thermal cycle was also selected 100˚C to accelerate the damage processes. This value is much higher than the supported temperature of this material in the real applications. The fiber volume fractions of the composites were also 45,55 and 60% and the specimens are cycled up to 1,50 and 100 cycles.

Table 1
Level of experiment parameters.

Symbol	Factor	Level 1	Level 2	Level 3
A	Number of thermal cycles	1	50	100
B	Stacking sequence	$[0]_8$	$[0_2/90_2]_s$	$[0/\pm45/90]_s$
C	Temperature difference (˚C)	50	75	100
D	Fiber volume fraction (%)	45	55	60

Table 2
Taguchi´s *L9* (3^4) orthogonal array.

Test Group	Number of thermal Cycles	Stacking Sequence	Temperature Difference (˚C)	Fiber Volume Fraction(%)
Run-1	1	$[0]_8$	50	45
Run-2	1	$[0_2/90_2]_s$	75	55
Run-3	1	$[0/\pm45/90]_s$	100	60
Run-4	50	$[0]_8$	75	60
Run-5	50	$[0_2/90_2]_s$	100	45
Run-6	50	$[0/\pm45/90]_s$	50	55
Run-7	100	$[0]_8$	100	55
Run-8	100	$[0_2/90_2]_s$	50	60
Run-9	100	$[0/\pm45/90]_s$	75	45

2.2 Fabrication of specimens

The specimens were fabricated and tested according to the ASTM D3039 [16]. Stacking sequences of the specimens were $[0]_8$,$[0_2/90_2]_S$ and $[0/\pm45/90]_s$. The resins of composite material were formulated using a mixture of commercial epoxy resin and polyamine hardener. Unidirectional *E* glass fiber also used as the reinforcing material. The materials properties used to make the laminates are shown in Table 3. The composite thin laminates are fabricated using hand lay-up method and three different fiber volume fraction of V_f=45%, V_f=55% and V_f=60% of laminates were made for each layups. Then the laminates are allowed to cure for seven days at room temperature. The test specimens were cut from laminates according to the ASTM D3039. The thickness of each layer was 0.2 *mm* and the thicknesses of the specimens were 1.6±0.1 *mm*. The width of unidirectional and symmetric specimens was also15±0.5 *mm* and 25±0.5 *mm*, respectively.

Table 3
Mechanical and physical properties of epoxy resin and E-Glass fiber.

Material properties	ML506 Epoxy	E-Glass
Tensile modulus (GPa)	2.79	41
Shear modulus (GPa)	15.24	15.24
Poisson’s ratio	0.35	0.3
Density (g/cm^3)	1.11	2.48
Coefficient of thermal expansion (CTE)	62	4.9

2.3 Experimental setup

A thermal cycling apparatus was developed to simulate the aging of composites under the thermal cycling environment condition. This apparatus consisting of heating/cooling stainless steel chambers and a rail system for specimen displacement that can be simulated thermal cycling between -20˚C to 150˚C. Fig. 1 shows a picture of apparatus chambers and a thermal cycling profile of the simulation. This apparatus can be monitored the temperature of specimen using PT100 sensor and a user interface software. The cooling chamber can be cooled down to -20˚C by the refrigerant circulating system with temperature decreasing at the rate of 10˚C/min. Two heater elements were also used in the heating chamber. The chamber is able to warm up specimen to 150˚C at a rate of 20˚C/min. The period of one thermal cycle of 50˚C, 75˚C and 100˚C temperature difference were measured about 6.5, 9.5 and 12.5 minutes, respectively.

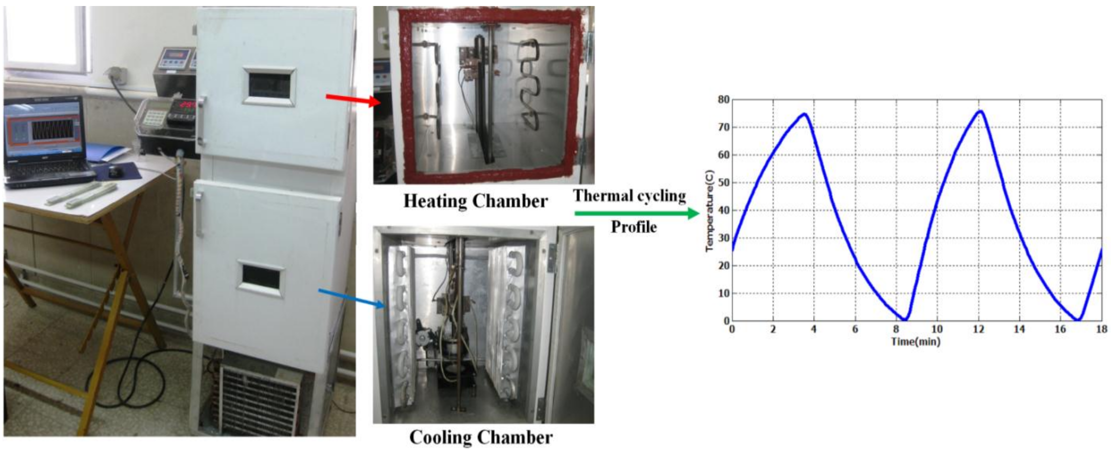

Fig.1
Thermal cycling apparatus and its temperature profile.

3 RESULTS

3.1 Mass loss results

Mass loss can be expressed in various forms that combine initial composite weight (M_0) and transient composite weight (M): normalized weight ($M/M0$), extent of weight loss (α-1-M/M_0); and total weight loss ($Q=M_0-M=\alpha M_0$). These expressions are easily converted to one another with the knowledge of the initial weight [2]. Here for each specimen, Total Mass Loss (TML) was calculated as follow:

$$\%TML = \frac{M_0 - M}{M_0} \times 100 \quad (1)$$

where M_0 and M are the mass of specimen before and after thermal cycling test. Nine different experiment groups according the plan of tests (Table 2) were performed using the design parameter combinations in the specified orthogonal array. Three specimens were fabricated for each of the parameter combinations.

The average results and Standard Deviations Values (SDV) of the three mass losses for each test group are reported in Table 4. The results show that the test group Run-7 ($[0]_8$ layups, N=100, dT=100˚C and V_f=55%) has 0.283% mass loss as the highest mass reduction. By obtaining the results of the mass loss test; it is required to find the contribution of each factor on the mass reduction.

In order to study the contribution ratio of each factor, pareto ANOVA (ANalysis of VAriance) [12] was performed for this results. Statistical analysis of the mass loss based on the Taguchi method is obtained using “MINITAB R17” [17] as the statistical software. Table 5. shows variance analysis and the impact factor of each level of the factors. Degree of Freedom (DOF) and difference of the maximum and minimum value of each factor (Delta) are also indicated in this table. As shown in Table 5, temperature difference is the main effective factor on the mass loss of specimens by 61% contribution.

Table 4
Average mass loss of the various test groups designed based on the Taguchi method.

Test Group	Total Mass Loss (%) (±SVD)
Run-1	0.056 (0.001)
Run-2	0.136 (0.094)
Run-3	0.239 (0.018)
Run-4	0.229 (0.133)
Run-5	0.133 (0.029)
Run-6	0.056 (0.002)
Run-7	0.283 (0.034)
Run-8	0.071 (0.019)
Run-9	0.079 (0.016)

Table 5
ANOVA for the mass loss test.

Factors	Level 1	Level 2	Level 3	Delta	DOF	Contribution (%)	Rank
Number of thermal cycles	0.144	0.139	0.144	0.005	2	0.08	4
Stacking sequence	0.189	0.113	0.125	0.076	2	16.55	3
Temperature difference (˚C)	0.061	0.148	0.218	0.157	2	61.32	1
Fiber volume fraction (%)	0.089	0.158	0.180	0.091	2	22.05	2
Total					8	100	

3.2 Analysis of surface degradation

Study the failure regions of the specimens at different thermal cycling condition showed that surface matrix loss can be observed at high number of thermal cycling (Fig. 2). Increment of the temperature difference also makes the surface matrix loss to be more significant. It should be considered that this surface matrix loss could be an initial region for matrix de-bonding and crack propagation.

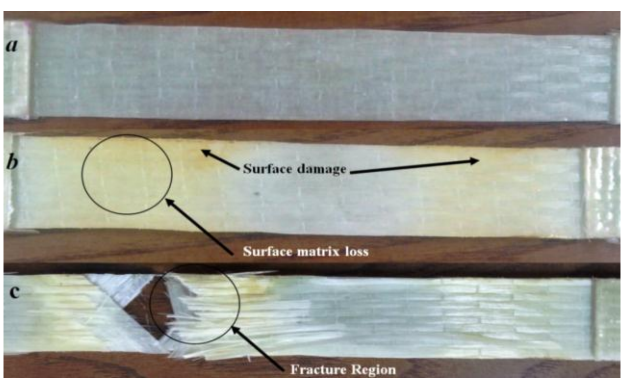

Fig.2
Surface of the $[0/\pm45/90]_s$ layup, V_f=45% specimen a) before and b) after thermal cycling (dT=100˚C) c) after tensile test.

3.3 Multiple polynomial regression models

Different models were presented to evaluate the mass loss of the polymers and polymeric composites [2,11,18]. Chung et al. [2] modeled the mass loss considering surface dependent oxidative degradation based on the shrinking core model. Considering that the weight change is the result of mass loss from the surface of specimen, total weight loss can be defined as a summation of the weight loss per unit surface area. The suggested model considers the anisotropic degradation of polymer composites. Difficult constants determination for different material is the most problem of this model.

Lafarie-Frenot [11]also developed a mechanistic coupled diffusion-reaction-oxidation model based on chemical reaction. This model predicts mass loss and thermo-oxidation induced matrix shrinkage in pure resins and unidirectional (UD) composites, but does not include coupling with mechanics. This model could be evaluate the trends of mass loss but does not predict the mass loss value. The result showed that the effect of anisotropy should be taken into account in a predictive model. It has been clearly shown that [18], in most cases, oxidation is the predominant ageing process. Its kinetic study is especially difficult for many reasons:

i. Oxidation is a branched radical chain process. There is not yet a consensus on a kinetic scheme.
ii. Oxidation kinetic is diffusion controlled. A realistic model must take into account the reaction-diffusion coupling.
iii. Analytical investigations are especially difficult in thermosets (and in composites) owing to their insolubility and structural complexity.

Due to the complexity of the oxidation process and robustness of statistical approach, a multiple polynomial regression model is obtained using MINITAB software. This model established the quadratic correlation between the four effective factors on the mass loss during thermal cycling. This method has high flexibility to specify expectation functions and determines the function with the optimal fit for the data. The statistically significant terms are included in the model. Stacking sequences also used as a categorical predictor and the other factors used as continuus predictors. The regression function defined here is as follows:

$$TML(\%) = A(S) + BV_f + CV_f^2 + DN + EN^2 + FdT + GdT^2 \tag{2}$$

where S, V_f, N and dT are stacking sequence, fiber volume fraction, number of thermal cycles and temperature difference, respectively. A(S) is a categorical constant and differ for each layups. C, D, E, F and G are also the other constant and are unique for different layups. For better comparison, thermal cycles and temperature differences are divided to their high level values and they changed to the dimensionless parameters as follow:

$$\begin{cases} N = \dfrac{number\ of\ thermal\ cycles}{100} \\ dT = \dfrac{temperature\ difference}{100} \end{cases} \tag{3}$$

The values of coefficients for this correlation are given in Table 6.

Table 6
The values of correlation coefficient of the model.

Properties	A	B	C	D	E	F	G
TML (%)	$A = \begin{cases} -0.9174 & [0]_8 \\ -0.9933 & [0_2/90_2]_s \\ -0.9820 & [0/\pm45/90]_s \end{cases}$	2.472	-1.78	-0.002	0.02	0.51	-0.13

4 SENSITIVITY ANALYSIS OF THE EFFECTIVE FACTORS ON MASS LOSS

4.1 Temperature difference effects

The mass loss behaviors of the PMC under different thermal cycling conditions are obtained (Figs. 3-6) using the presented model (Eq. (2)) and the model coefficients (Table 6). As shown in the statistical analysis, temperature difference is the main effective factor of mass loss under the thermal cycling process. Fig. 3 shows the mass loss changes based on this parameter. This figure indicates that increase of temperature difference causes to increase the mass loss at different thermal cycling conditions. Increment of oxidative reaction of composite molecular components with the harsh environment can be reason of this increment. This degradation in polymeric composites involves solid–gas reactions, and is associated with chain division. It is also found that the mass loss and temperature difference has the linear relationship and the maximum mass loss occurs at the high temperature difference.

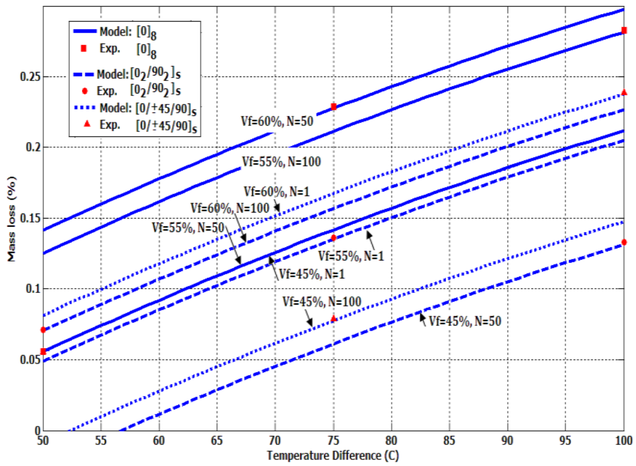

Fig.3
Variation of the mass loss as a function of the temperature difference.

4.2 Stacking sequences effects

Similar to the temperature difference, the mass loss change of the layups under the different condition is obtained (Fig. 4). The results show that the $[0]_8$ layups have more mass loss than the other layups at similar condition. The mass loss change in the $[0/\pm45/90]_s$ and $[0_2/90_2]_s$ are close together but the $[0_2/90_2]_s$ layup has less mass reduction than the other layups. The $[0]_8$ layups have 44% and 35.7% more mass loss than the $[0_2/90_2]_s$ and $[0/\pm45/90]_s$ layups, respectively.

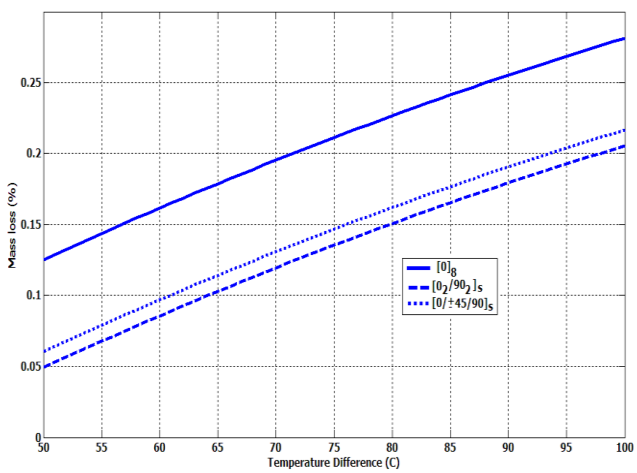

Fig.4
Variation of the mass loss for different layups (Vf=55% and N=100).

4.3 Fiber volume fraction effects

The mass loss changes in different fiber volume fraction indicate that increment of the fiber volume fraction causes to increase of the mass loss for different thermal cycling condition (Fig. 5). A reason of this increment could be the weakness of the surface molecular bonding at the higher fiber volume fraction. It is also found that the maximum mass loss occurs at V_f=60%.

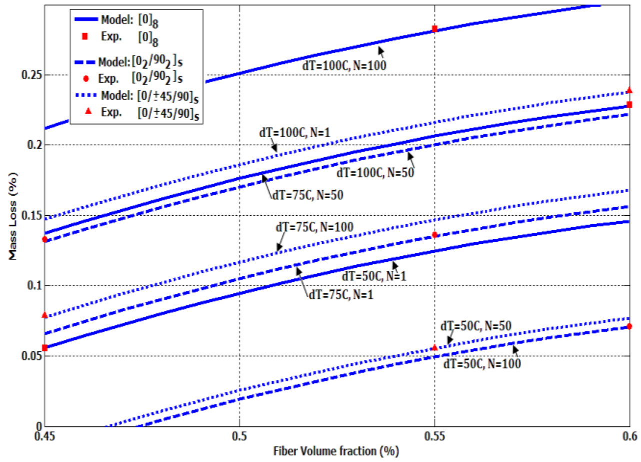

Fig.5
Variation of the mass loss as a function of the fiber volume fraction.

4.4 Number of thermal cycling effects

As shown in Fig. 6, compared to the other factors, increment of the number of thermal cycling has low effect on the mass loss of the specimens. When the number of thermal cycling increases, the mass loss increases slightly. This figure also shows that mass loss at high temperature differences is more than the low temperature differences. Mass loss of the $[0]_8$ layups are also more than the other layups.

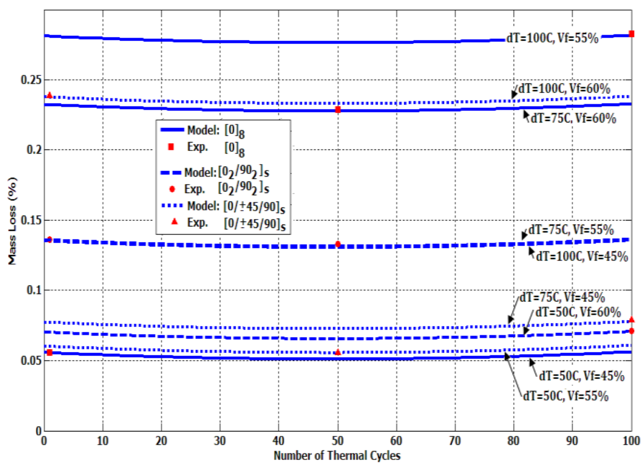

Fig.6
Variation of the mass loss as a function of the number of thermal cycles.

5 CONCLUSIONS

The Taguchi method was utilized to identify contribution of the main effective factors on the mass loss of the glass fiber/epoxy composite materials. The orthogonal array of L9 type was used to reduce the number of experiments to the nine run. The mass loss of each sample varied according to the fiber volume fraction, stacking sequence, temperature difference and number of thermal cycles. The thermal cycling tests were performed using the developed two chamber apparatus and mass of the specimens were measured before and after thermal cycling test. Using a statistical approach, it was found that the temperature difference and fiber volume fraction of the glass/epoxy composite with 61% and 22% contribution are the main effective factors under the thermal cycling conditions. Stacking sequence is also the next effective factor with 16% contribution. Next, a regression model was developed to predict the overall mass degradation. The proposed model took into account the four effective factors containing a categorical and three continous predictors. Model prediction was found to match the experimental data successfully, and it is accurately expressed the mass degradation effect over the experimental temperature, fiber volume fraction and thermal cycle range. Finally, sensitivity analysis of the parameters on the mass loss was studied. The studies showed that increment of temperature difference and fiber volume fraction cause to increase the mass loss under different thermal cycling condition. The results also showed the maximum mass loss occurs at dT=100˚C and V_f=60%. The sensitivity analysis showed that the mass loss of $[0]_8$ layups is 44% and 35.7% more than the $[0_2/90_2]_s$ and $[0/\pm45/90]_s$ layups, respectively. It is also found that compare to the other factors increment of the number of thermal cycling has low effect on mass loss of the glass/epoxy composite. Presented approach is essential to develop the knowledge of the long-term performances and effects of thermo-mechanical cyclic loading and long-term ageing of polymer matrix composites.

REFERENCES

[1] Sethi S., Ray B.Ch., 2014, Environmental effects on fibre reinforced polymeric composites: Evolving reasons and remarks on interfacial strength and stability, *Advances in Colloid and Interface Science* **217**: 43-67.

[2] Chung K., Seferis J.C., Nam J.D., 2000, Investigation of thermal degradation behavior of polymeric composites: prediction of thermal cycling effect from isothermal data, *Composites: Part A* **31**: 945-957.

[3] Meyer M.R., Friedman R.J., Schutte H.D.J., Jr L.R.A., 1994, Long-term durability of the interface in FRP composites after exposure to simulated physiologic saline environments, *Journal of Biochemical Materials Research* **28**: 1221-1231.

[4] Yu Q., Chen P., Gao Y., Mu J., Chen Y., Lu Ch., Liu D., 2011, Effects of vacuum thermal cycling on mechanical and physical properties of high performance carbon/bismaleimide composite, *Materials Chemistry and Physics* **130**: 1046-1053.

[5] Moon J.B., Kim M. G., Kim Ch. G., Bhowmik Sh., 2011, Improvement of tensile properties of CFRP composites under LEO space environment by applying MWNTs and thin-ply, *Composites: Part A* **42**: 694-701.

[6] Paillous A. Pailler C., 1994, Degradation of multiply polymer–matrix composites induced by space environment, *Composites* **25**(4): 287-295.

[7] Chao Zh., Binienda K.W., Morscher G.N., Martin R.E., Kohlman L.W., 2013, Experimental and FEM study of thermal cycling induced microcracking in carbon/epoxy triaxial braided composites, *Composites Part A: Applied Science and Manufacturing* **46**: 34-44.

[8] Nam J.D., Seferis J.C., 1992, Anisotropic thermo-oxidative stability of carbon fiber reinforced polymeric composites, *SAMPE Quarterly* **24**: 10-18.

[9] Shin K.B., Kim C.G., Hong C.S., Lee H.H., 2000, Prediction of failure thermal cycles in graphite/epoxy composite materials under simulated low earth orbit environments, *Composites Part B* **31**(3): 223-235.

[10] Lafarie-Frenot M.C., 2006, Damage mechanisms induced by cyclic ply-stresses in carbon–epoxy laminates: Environmental effects, *International Journal of Fatigue* **28**(10): 1202-1216.

[11] Lafarie-Frenot M.C., Grandidier J.C., Gigliotti M., Olivier L., Colin X., Verdu J., Cinquin J., 2010, Thermo-oxidation behaviour of composite materials at high temperatures: A review of research activities carried out within the COMEDI program, *Polymer Degradation and Stability* **95**(6): 965-974.

[12] Taguchi G., Konishi S., 1987, *Taguchi Methods, Orthogonal Arrays and Linear Graphs, Tools for Quality Engineering*, American Supplier Institute Dearborn.

[13] Dobrzañski L.A., Domaga J., Silva J.F., 2007, Application of taguchi method in the optimization of filament winding of thermoplastic composites, *Archives of Materials Science and Engineering* **28**(3): 133-140.

[14] Ghasemi A.R., Baghersad R., Sereshk M.R.V., 2011, Non-linear behavior of polymer based composite laminates under cyclic thermal shock and its effects on residual stresses, *Journal of Polymer Science and Technology* **24**(2): 133-140.

[15] Ghasemi A.R., Baghersad R., 2012, Analytical and experimental studies of cyclic thermal shock effects on nonlinear behavior of composite laminates, *Journal of Aeronautical Engineering* **14**(2): 11-16.

[16] ASTM, D. D 3039M-95a, 1997, Standard test method for tensile properties of polymer matrix composite materials.

[17] MINITAB 17 statistical software, Minitab Inc, 2013.

[18] Colin X., Marais C., Verdu J., 2002 , Kinetic modelling and simulation of gravimetric curves: application to the oxidation of bismaleimide and epoxy resins, *Polymer Degradation and Stability* **78**: 545-553.