MATERIAL CHARACTERIZATION TO EVALUATE THE SUITABILITY OF OUT-OF-AUTOCLAVE SEMIPREGS FOR STRUCTURAL SPACE APPLICATIONS

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ABSTRACT

Due to the promise shown by Out-of-Autoclave (OOA) semipregs in the aircraft industry, the space industry is currently seeking to use and process these materials using Vacuum Bag Only (VBO) processing. Under the right conditions, VBO processing has been shown to yield components of similar quality to autoclave parts. In addition, their low production cost makes the process very attractive. Space structures, which can have complex geometries, experience a wide range of operating temperatures (-185°C to 185°C). Thus, it is required to produce parts that are dimensionally stable. These parts must have high glass transition temperatures (T_g), high flow numbers, low coefficients of thermal expansion, and low cure shrinkage.

With an understanding of these key parameters, it is possible to achieve the most robust manufacturing method attainable, while meeting the structural requirements. The objective of this paper is to provide a comparative study of five different prepregs as candidates for structural space applications, using VBO consolidation. As part of the study, resin characterization of four epoxies and one cyanate ester is first performed. Each thermoset resin's thermal stability, cure kinetics, rheological behaviour, shrinkage, T_g, and the coefficient of thermal expansion are measured. Semi-empirical models are then fitted to the experimental data and key parameters are extracted from each of the tests to be implemented in a simulation software Raven. Using Raven, the T_g, and flow numbers are simulated for each material using a representative cure cycle. The weighted decision method is used to evaluate and compare the materials. An epoxy-based OOA material is found to have the highest T_g and flow number, which would allow the part to perform at a wide range of temperatures and to minimize void formation during cure, respectively. On the other hand, the autoclave cyanate ester has the lowest cure shrinkage and lower coefficient of thermal expansion (CTE), which would yield parts with very high dimensional stability.

1. INTRODUCTION

Typical space structures must withstand harsh conditions through the life of the spacecraft, which can include a wide range of operating temperatures (-185°C to 185°C), vibration, exposure to ionizing radiation, and exposure to atomic oxygen [1,2,3]. The requirements for these structures include high strength-to-weight ratios, low thermal expansion, and high dimensional stability during the operational lifetime [4,5], thus making composite materials an ideal material for space applications.

Traditionally, cyanate ester resins using autoclave processing have been used due to their superior properties: they are radar transparent, have high toughness, suitable dielectric and higher heat resistance properties, low moisture absorption, low outgassing, high dimensional stability and resistance to micro-cracking [6]. However, the cost of these resins compared to epoxies is much higher, which has been the main driver to seek out other alternatives. Thus, it is of interest to explore epoxy resins that can be processed using Out-of-Autoclave (OOA) Vacuum Bag Only (VBO) consolidation. With VBO consolidation, it is possible to use conventional ovens with a diverse range of cure setups, thus reducing significantly the operation costs and high capital investment compared to using an autoclave [7].

In this paper, a comparative study of four off-the-shelf epoxy resins and one cyanate ester is performed to assess their feasibility to be used in structural space applications, using VBO consolidation. First, material characterization is performed and semi-empirical models are fit to the experimental data. Subsequently, key parameters are extracted and implemented in simplified process simulation software Raven. An evaluation is then performed based on relevant criteria to structural space applications. Finally, results and recommendations on the suitability of the materials are provided.

2. EXPERIMENTAL

In this paper, five off-the-shelf materials are studied. These materials, along with their recommended processing method and cure cycle as per their confidential data sheet, are summarized in Table 1. Materials B and C can be cured using two different cycles (Cure A and Cure B).

Material	Resin +Fibre	Processing Method	Recommended Cure
Material A	Cyanate Ester, 5HS^1	A^3	30 min at 71°C + 3 h at 121°C
Material B	Toughened Epoxy, 5HS	OOA	1.1°C/min to 107°C for 1 h + 6 h at 135°C^4
Material C	Toughened Epoxy, PW^2	OOA	1.1°C/min to 107°C for 1 h + 2 h at 177°C^5
Material D	Toughened Epoxy, 5HS	A/OOA	1.7-2.8°C/min to 177°C for 1.5 h
Material E	Toughened Epoxy, 5HS	A	2 h at 135°C + 2 h at 163°C (optional)

1 – 5 Harness Satin, 2 – Plain Weave, 3 – Autoclave, 4 – Cure A, 5 – Cure B

Table 1: Five off-the-shelf materials to be studied

2.1 Material characterization methodology

As a first step in this comparative study, the materials are characterized in terms of thermal stability, cure kinetics, rheology, shrinkage, thermal expansion, and their glass transition temperature (T_g) evolution as per Figure 1 [8].

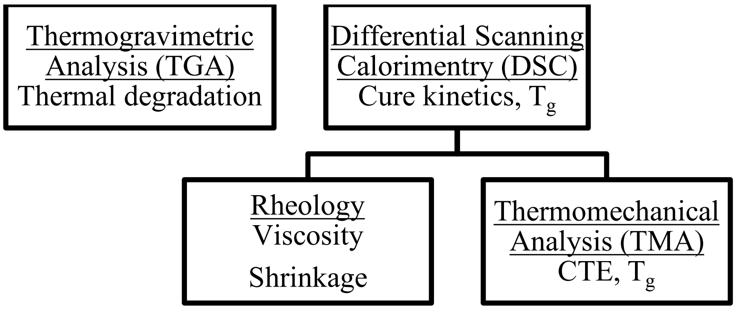

Figure 1: Material characterization methodology [8]

2.1.1 *Thermal degradation*

The first test performed is thermogravimetric analysis (TGA). A Q5000 IR TGA is used to determine the degradation temperature of each resin. This temperature establishes the ceiling of the cure window of each material to ensure the heat released during differential scanning calorimetry (DSC) is due to cure and not degradation. Resin samples of approximately 10 mg are loaded in a small platinum crucible that is suspended from the arm of a microbalance [8]. For each experiment, a ramp is performed from 20°C up to 550°C under nitrogen and from 550°C to 700°C under compressed air. The degradation temperature is chosen before there is a significant mass loss percent of less than 2.5%. This weight percent change is caused by evaporation of volatiles present in the resin. Table 2 shows the summary of the degradation temperature of each resin along with the percent weight loss.

Material	Degradation Temperature (°C)	Weight Loss (%)
Material A	350	1.3
Material B	320	1.4
Material C	320	1.6
Material D	350	2.5
Material E	315	1.7

Table 2: TGA degradation temperature for each resin

2.1.2 *Cure kinetics*

A Q100 from TA Instruments is used to perform DSC. The heat released during cure (dynamic scans) and the heat flow during isothermal cures (isothermal scans) determine the cure kinetics of the materials. Dynamic scans with heating rates of 10°C/min from -50°C up to the degradation temperature of each resin (Table 2) are performed. Similarly, at least three isothermal scans are performed for each material at a fast heating rate (>20°C/min). These isothermal scans are chosen near the dwell temperature of each material as per the manufacturer's specification. Table 3 shows the isotherm temperatures performed for each material.

Material	Isothermal Scan Temperatures (°C)
Material A	120, 140, 160
Material B	100, 110, 120, 140, 180
Material C	100, 110, 120, 140, 180
Material D	150, 160, 180, 190, 200
Material E	120, 140, 160, 180

Table 3: DSC Isothermal Runs Test Matrix

2.1.3 *Rheology*

The rheological behaviour is analyzed using an AR2000 rheometer from TA Instruments. Dynamic scans at heating rates of 1-3°C/min and isothermal scans at temperatures ranging 120-180°C are performed using 25 mm aluminum parallel plates in oscillatory mode at percent strains ranging from 0.05 to 0.7 % and a frequency of 1 Hz. The test matrix for each material is shown in Table 4.

Material	Dynamic Scan Ramp Rates (°C/min)	Isothermal Scan Temperatures (°C)
Material A	2	120, 140, 160
Material B	1	120, 140, 180
Material C	1	120, 140, 180
Material D	2	120, 140, 180
Material E	3	120, 140

Table 4: Rheology dynamic and isothermal scans

After each isotherm, shrinkage tests are conducted at isothermal temperatures by switching to force control after gelation to measure volumetric changes. A constant force of 0.01 N is applied. By keeping the sample at a constant temperature, the 25 mm plates do not undergo any expansion, thus isolating the shrinkage of the resin [8].

2.1.4 Thermal expansion

A Q400 by TA Instruments is used to perform thermomechanical analysis (TMA) to measure the coefficient of thermal expansion (CTE) of the materials. Neat resin samples are made using 40 mm parallel plates in the rheometer. The samples are then cured at 180°C. In addition, 101.6 mm by 101.6 mm 16-ply laminates with lay-up $[(0/90)_3/90/0]_2$ are manufactured and cured using a baseline cure cycle as per the cure kinetics data. The neat resin samples and laminates are then cut in pieces that are approximately 10 mm by 10 mm by 1 mm. The out-of-plane CTE is measured for the resin samples while both the out-of-plane and in-plane CTE is measured for the laminate samples. Three cycles are run for each sample from 25°C to 250°C at 5°C/min.

2.1.5 Glass transition temperature

To measure the T_g of the materials, DSC and TMA are used and the results are then compared. In DSC, the T_g of each material can be identified by a step change in the specific heat. In TMA, the CTE increases when there is a transition between glassy to rubbery phases, thus it is possible to extract the T_g from this test [8]. A relationship between the degree-of-cure of each resin and the T_g is modelled using the DiBenedetto equation as per (1):

$$\frac{T_g - T_g^0}{T_g^\infty - T_g^0} = \frac{\lambda\alpha}{1-(1-\lambda)\alpha} \tag{1}$$

Where T_g^0 is the glass transition of neat resin at degree-of-cure α=0, T_g^∞ is the highest measured T_g, and λ is a fitting parameter between zero and one.

2.1.6 Implementation in process simulation software

The material characterization data is processed and semi-empirical models are fit to obtain the parameters of interest for each test. These parameters are then implemented in the material database of simulation software Raven version 3.7.7 by Convergent Manufacturing Technologies [9]. Raven is a simplified process simulation software that is used as a tool to evaluate the evolution of degree-of-cure, cure rate, viscosity, and T_g with respect to a specific cure cycle.

3. RESULTS AND DISCUSSION

3.1 Material characterization results

3.1.1 Cure kinetics results

Polymerization reactions in thermoset resins exhibit a combination of n^th order (all the monomers start crosslinking at the beginning of the reaction) or autocatalytic behaviour (only a few monomers can react at the beginning of the reaction). The cure rate increases until it reaches a peak, representing the full reaction of the remaining monomers [10]. Using iso-conversional curves, it is possible to determine the type of reaction and model that best fits each material. A semi-empirical model developed by Cole et al. [11], and a model combination developed by Lee [12] and Cole [11] are selected as per Equation (2) and Equation (3), respectively.

$$\frac{d\alpha}{dt} = \frac{K\alpha^m(1-\alpha)^n}{1+\exp[C(\alpha-(\alpha_{C0}+\alpha_{CT}T))]} \tag{2}$$

$$\frac{d\alpha}{dt} = K_1\alpha^{m1}(1-\alpha)^{n1} + \frac{K_2\alpha^{m2}(1-\alpha)^{n2}}{1+\exp[C(\alpha-(\alpha_{C0}+\alpha_{CT}T))]} \tag{3}$$

α is the degree-of-cure, m and n are the first and second exponential constants, respectively; C is the diffusion constant, α_{C0} is the critical degree-of-cure at T = 0 K, and α_{CT} is the constant that accounts for the increase in the critical resin degree-of-cure with temperature. K can be defined as per the Arrhenius equation in (4):

$$K = Ae^{\frac{-Ea}{RT}} \tag{4}$$

Where A is the pre-exponential factor, R is the gas constant, and T is the temperature. The activation energy, E_a, is calculated as the slope of the iso-conversional curves. The models are fit using least squares non-linear regression between the cure rate and the degree-of-cure. Figure 2 shows the results for Material D.

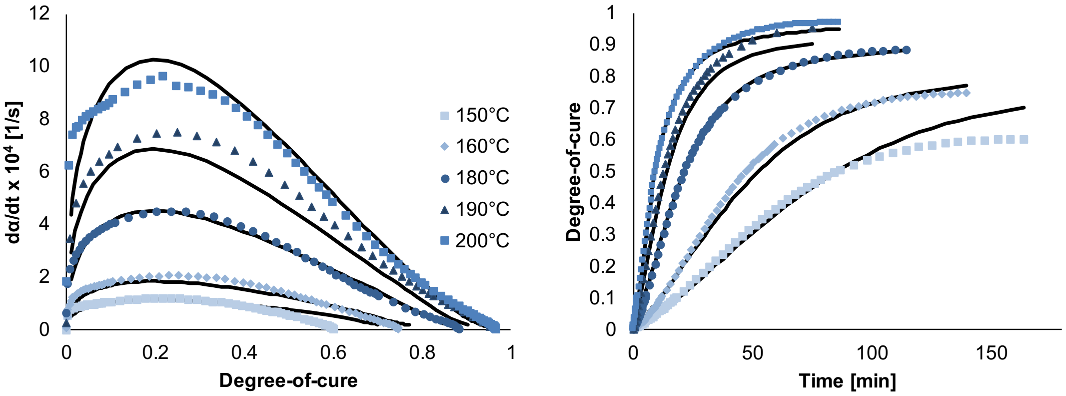

Figure 2: Comparison of the rate of cure (left) and degree of cure (right) between experiments and model predictions for material D in isothermal conditions

3.1.2 *Rheology results*

In terms of rheology, the model used to describe the evolution of resin viscosity is developed by Halley et al. [13] and is shown in Equation (5):

$$\mu = \mu_1(T) + \mu_2(T)\left(\frac{\alpha_{gel}}{\alpha_{gel}-\alpha}\right)(A' + B'\alpha + C'\alpha^2) \quad , \quad \mu_i(T) = A_{\mu_i}\exp\left(\frac{E_{\mu i}}{RT}\right), i = 1,2 \tag{5}$$

α_{gel} is the degree-of-cure at the gel point and $A_{\mu i}$, $E_{\mu i}$, A’, B’, C’ are constants. These are obtained using least squares non-linear regression and using the data obtained from the cure kinetics models. Cure shrinkage is calculated using Equation (6), and Equation (7) shows the model applied to fit the shrinkage data [14]:

$$\varepsilon_{\upsilon} = \left[1 + \frac{1}{3}\left(\frac{h-h_0}{h_0}\right)\right]^3 - 1 \tag{6}$$

$$\alpha \le \alpha_{gel}, \varepsilon_{\upsilon} = 0 \quad \alpha \ge \alpha_{gel}, \varepsilon_{\upsilon} = D(\alpha - \alpha_{gel}) \tag{7}$$

ε_v is the volumetric cure shrinkage, h_0 is the initial resin gap, h is the value of the gap at a given time, and D is a model constant. D is found using the least squares method for linear regression. Material A ramp results (left) and material D shrinkage plots (right) with their respective models are shown in Figure 3.

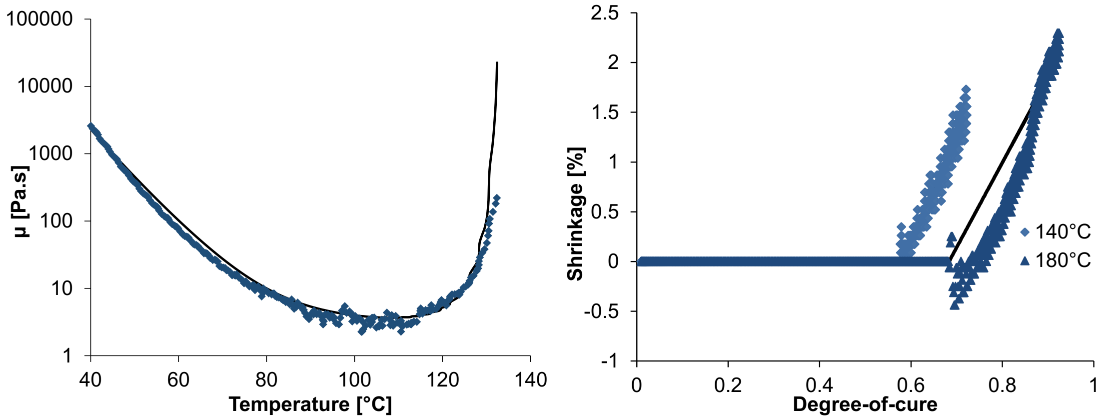

Figure 3: Comparison of measured and predicted viscosity evolution with temperature for material A under a temperature ramp(left), and comparison between the measured and predicted volumetric cure shrinkage for material D under isothermal conditions (right)

Table 5 shows a summary of the cure shrinkage percentage for each material.

Material	Shrinkage (%)
A	1.2
B	3.2-7.2
C	3.9-5.1
D	1.7-2.2
E	6.3

Table 5: Summary of cure shrinkage percent for all the materials

OOA prepregs contain partially impregnated fibre tows, which act as vacuum channels and allow gases in the laminate to escape in the early stages of processing [15]. As the cure progresses, the polymer chains cross-link until the resin can no longer move, and has thus gelled. Therefore, there is only a limited time and temperature window where the viscosity is low enough to flow and fill the space between the fibre tows. The flow number (FN) is proportional to the amount of resin flow possible at a given temperature and is defined as per Equation (8). $\mu(t)$ is the resin viscosity as a function time from the start of the test up to the gelation time (t_{gel}).

$$FN = \int_0^{tgel} \frac{1}{\mu(t)} dt \tag{8}$$

In VBO processing, the parts are cured at atmospheric pressure (1 atm), thus making OOA materials prone to void formation in comparison to autoclave parts. Therefore, to ensure full impregnation and minimize void content, it is desirable to have a high FN. The presence of voids has a negative impact in the transverse, compressive, and interlaminar properties [16,17]. The flow number for each material based on their recommended cure cycle is calculated and summarized in Section 3.1.4.

3.1.3 Thermomechanical analysis results and evolution of T_g

The evolution of T_g as a function of degree-of-cure is shown in Figure 4. DSC and TMA experimental data is included in the graph. The TMA samples are fully cured, thus showing agreement with the DSC measurements at a high temperature isotherm. Equation (1) is used to fit the relationship between the T_g and the degree-of-cure.

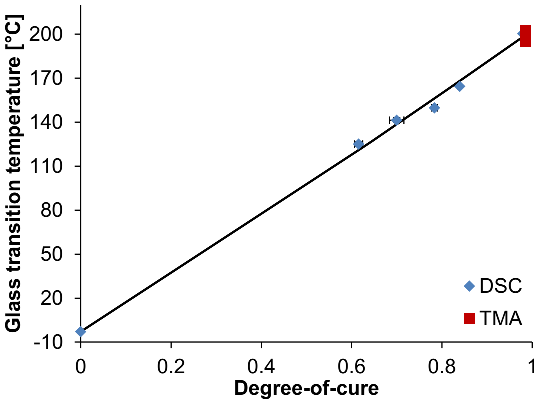

Figure 4: Evolution of T_g with respect to degree-of-cure of the resin of material B

The T_g of the material is an important parameter to evaluate the evolution of the CTE. Thus, the evolution of CTE is plotted as a function of T*, which is the difference between the instantaneous temperature and the T_g. The movement of the polymer chain is limited below the T_g, thus the CTE remains constant. However, as T_g is approached, the movement of the chains increase, causing the CTE to increase. To represent this physical phenomenon, the model in Equation (9) is used [8]:

$$\begin{aligned} CTE(T^*) &= CTE_{glass}, T^* < T' \\ CTE(T^*) &= A_0(T^* - T') + CTE_{glass}, T^* \geq T' \end{aligned} \tag{9}$$

Linear least squares regression is used to find constant A_o. T’ is taken as the inflection point in the data. The resulting plot is shown in Figure 5.

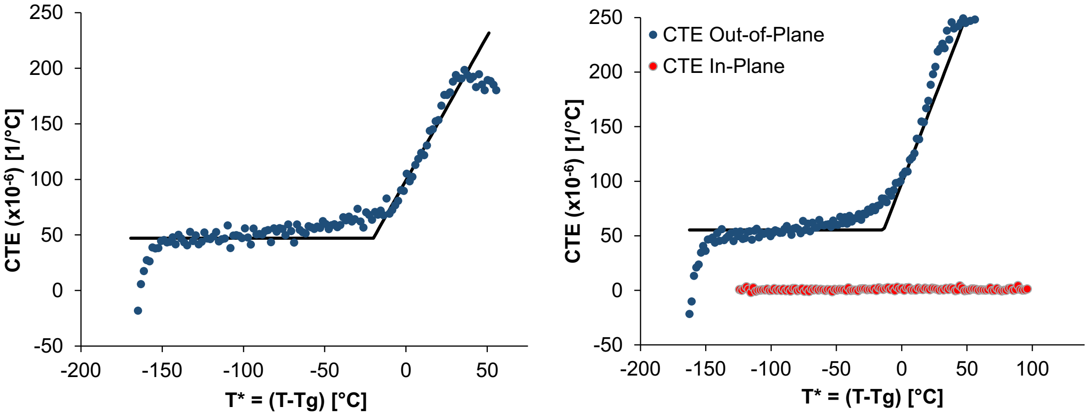

Figure 5: Comparison of measured and predicted out-of-plane CTE for resin of material A(left), and comparison between the measured and predicted out-of-plane and in-plane CTE of material A cured laminate with their respective models (solid line)

Table 6 shows a summary of the results obtained with the TMA, which includes the out-of-plane CTE of the resin and laminate, the in-plane CTE of the laminate and the T_g of each material. The CTE of materials B and C are different due to their fibre configuration (5HS vs. PW), despite of having the same resin. Typically, the in-plane CTE of harness satin fibre is higher than PW [18, 19]. It has been demonstrated, however, that fabric with lower strand crimp result in lower CTE values. It is possible that the 5HS woven fibre in this study (material B) has low strand crimp, thus resulting in lower in plane CTE values [20].

Material	T_g (°C)	CTE^1 (1/°C) x10^{-6}	CTE^2 (1/°C) x10^{-6}	CTE^3 (1/°C) x10^{-6}
A	201	47.1	55.4	0.41
B	202	51.8	71.0	0.52
C	204	51.8	68.2	1.25
D	209	51.0	68.2	0.52
E	185	43.2	64.5	0.60

1 – Resin out-of-plane CTE, 2 – Laminate out-of-plane CTE, 3 – Laminate in-plane CTE

Table 6: Summary of TMA results, including T_g

3.1.4 Summary of characterization results and implementation into Raven

Key model parameters are implemented into the Raven material database software. Using the suggested cure cycles in Table 1, the cure kinetics, T_g, and rheology information is obtained for each material. Table 7 shows a summary of results using Raven for the five materials presented in this study. It is observed that the cure cycles (except for cure cycle B for materials B and C) could be further optimized as the materials have not yet reached their maximum T_g and degree-of-cure.

Material	T_g (°C)	Degree-of-cure α	Flow number (1/Pa s)
A	126	0.71	411
B	184*	0.91*	27*
	203**	1.00**	27**
C	178*	0.88*	60*
	204**	1.00**	60**
D	183	0.86	3380
E	159	0.90	1500

* - Cure cycle A, ** - Cure cycle B

Table 7: Summary of values obtained using Raven

4. RECOMMENDATIONS

In structural space applications, it is required to have a T_g at least 28°C above the expected service temperature [21]. This is a conservative value that is selected to account for the variability in the T_g measurement techniques. To prevent voids when using OOA semipregs, it is desirable to have a high FN as explained previously in Section 3.1.2. On the other hand, it is required to have materials with near zero CTE's [22] and low cure shrinkage. Shrinkage influences residual stresses which can cause deformation in the final part. The weighted property method (WPM) [23] is used to evaluate each material in terms of T_g^{∞}, T_g and FN obtained from Raven that is specific to each cure cycle, shrinkage, out-of-plane and in-plane CTE. The digital logic approach is used by evaluating only two of these properties at a time. A value of one (1) and zero (0) is assigned to the most and least important property, respectively. These values are then added and divided by the total number of decisions, N, resulting in the emphasis coefficient, β. N is calculated as per Equation (10), where n is the number of criteria under consideration. In this case, the number of decisions is 15.

$$N = \frac{n(n-1)}{2} \tag{10}$$

Each property is then scaled as per Equation (11) for when high (T_g, FN), and low (shrinkage, CTE) values are required, respectively. The highest scaled value, Y, is 100.

$$Y_{High} = \frac{value \quad of \quad property}{\max \quad value \quad in \quad the \quad list} \times 100 \qquad Y_{Low} = \frac{\min \quad value \quad in \quad the \quad list}{value \quad of \quad property} \times 100 \tag{11}$$

The resulting values are then multiplied by β. These values are summed to obtain a performance index, γ. The material with the highest γ is the optimum for structural space applications. Table 8 shows each material with their corresponding β, γ, and ranking based on the criteria of interest. The resulting β for the out-of-plane CTE is zero, suggesting that this property could be removed from this analysis when using the WPM as outlined in this paper.

Criteria	**β**	**Material A**	**Material B**	**Material C**	**Material D**	**Material E**
		Scaled Values Y•β				
T_g^{∞} (°C)	0.33	32.06	32.22	32.54	33.33	29.51
T_g Raven (°C)	0.27	18.26	26.67	25.80	26.52	23.04
FN (1/Pa)	0.20	2.43	0.16	0.36	20.00	8.88
Shrinkage (%)	0.07	6.67	2.50	2.05	4.71	1.27
CTE^1 (1/°C) $x10^{-6}$	0.00	0.00	0.00	0.00	0.00	0.00
CTE^2 (1/°C) $x10^{-6}$	0.13	13.33	10.51	4.37	10.51	9.11
γ		72.75	72.06	65.11	95.07	71.81
Ranking		**2**	**3**	**5**	**1**	**4**

1 – Out-of-plane CTE, 2 – In-plane CTE

Table 8: WPM matrix, including the emphasis coefficient, performance index and ranking of each material

The material with the highest ranking is epoxy-based material D, followed by the autoclave cyanate ester (material A). Material D ranked highest in terms of T_g^{∞} and FN, whereas material A ranked highest in terms of cure shrinkage and in-plane CTE. The other materials ranked more closely to the cyanate ester, however, a significant difference can be observed between them and material D.

5. CONCLUSION

Four different off-the-shelf epoxies and one cyanate ester are characterized to evaluate their suitability to VBO processing and structural space applications. The simulation software Raven by Convergent Manufacturing Technologies is used to obtain information on the cure kinetics, viscosity, and T_g specific to the cure cycle of each resin. The autoclave cyanate ester in the study (material A) has the lowest cure shrinkage and the lowest in-plane CTE. However, material A did not have a high T_g, which is very important for space applications. On the other hand, OOA epoxy resin (material D) has the highest T_g as measured by DSC and TMA, and the highest FN, which is important to ensure full impregnation and low void content for high performance structures. Material D also rated as the second highest in terms of in-plane CTE and cure shrinkage, which in terms of the evaluated criteria, makes it the best selection for the application of interest. The approach presented herein demonstrates that material characterization is an effective way to compare and assess the materials based on specific criteria prior to implementation into large scale industrial components.

6. ACKNOWLEDGEMENTS

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7. REFERENCES

[1] J. Ajaja. “Damage accumulation in composite materials subjected to thermal cycles in space environments” Master’s Thesis. McGill University. Montreal, 2013.

[2] S.P. Rawal, J.W. Goodman. “Composites for spacecraft.” *Comprehensive Composite Materials*. Vol 6, pp 279-315, 2000.

[3] A.B Strong. “Fundamentals of composites manufacturing: Materials, methods and applications”. Dearborn, Mich: Society of Manufacturing Engineers, 2008.

[4] N. Nayak, “Composite materials in aerospace applications”. *International Journal of Scientific and Research Publications.* Vol 4, No. 9, pp 1-10. 2014.

[5] O.V. Startsev, and E. F. Nikishin. “Aging of polymer composite materials exposed to the conditions in outer space”. *Mechanics of Composite Materials*. Vol 29, No. 4, pp. 338-346, 1993.

[6] C.P.R Nair, D. Mathew, and K.N. Ninan. “Cyanate ester resins, recent developments”. New Polymerization Techniques and Synthetic Methodologies.” Vol 155, 2001.

[7] T. Centea, L.K Grunenfelder, S.R Nutt. “A review of out-of-autoclave prepregs-Material properties, process phenomena, and manufacturing considerations” *Composites: Part A.* Vol 70, pp. 132-154, 2015.

[8] L. Khoun, T. Centea, et al. “Characterization methodology of thermoset resins for the processing of composite materials – Case Study: CYCOM 890RTM Epoxy Resin”. *Journal of Composite Materials*. Vol 44, No. 11, pp. 1397-1415, 2010.

[9] Convergent Manufacturing Technologies. Products. http://www.convergent.ca/products. Retrieved on 22-Mar-17.

[10] D. Dykeman, "Minimizing uncertainty in cure modeling for composites manufacturing". Ph.D Thesis. University of British Columbia, Vancouver, 2008.

[11] K. Cole, J. Hechler and D. Noel, "A new approach to modeling the cure kinetics of epoxy/amine thermosetting resins" *Macromolecules*, Vol 24, No. 11, pp. 3098-3110, 1991.

[12] S.N Lee, M.T Chiu, et al. “Kinetic model for the curing reaction of a tetraglycidyl diamino dihenyl methane/diamino diphenyl sulfone (TGDDM/DDS) epoxy resin system”. *Polymer Engineering and Science***.** Vol 32, No 15, pp. 1037-1046, 1992.

[13] P.J Halley, and M.E Mackay. “Chemorheology of thermosets: An overview”. *Polymer Engineering and Science*, Vol 36, No. 5, pp. 593-609, 1996.

[14] M, Haider, P. Hubert, and L Lessard. “Cure shrinkage characterization and modeling of a polyester resin containing low profile additives”, *Composites: Part A.* Vol 38, No. 3, pp. 994-1009, 2007.

[15] T. Centea. “Material-processing-quality relationships during the consolidation of out-of-autoclave prepregs”. Ph.D Thesis. McGill University, Montreal, Quebec, 2013

[16] B. D. Harper, G. H. Staab, and R. S. Chen, "A note on the effects of voids upon the hygral and mechanical properties of AS4/3502 Graphite/Epoxy," *Journal of Composite Materials*. Vol. 21, pp. 280-289, 1987.

[17] P. Olivier, J.P. Cottu, and B. Ferret. “Effects of cure cycle pressure and voids on some mechanical properties of carbon/epoxy laminates”, *Composites*. Vol 26, pp. 509-515, 1995.

[18] R. B. Deo, C. R. Saff. “Woven and braided fabric composites”. Composite Materials: Testing and Design. *ASTM International*. Vol. 12, pp 255, 1996.

[19]T. Vu-Khanh, B. Liu. “Thermo-elastic behaviour of deformed woven fabric composites at elevated temperatures”. *American Society of Composites, 9th International Conference Proceedings*, Newark, DE, Vol. 36, pp. 133-140,1994.

[20] L. Khoun, K. Challagulla, P. Hubert. “Thermo-mechanical properties of 5-harness satin fabric composites”. *Journal of Composite Materials*. Vol 46, No. 25, pp. 3121-3136, 2012.

[21] R.J Seyler. “Assignment of the glass transition”. *American Society for Testing and Materials*. STP 1249. 1994.

[22] M. Kutz. “*Handbook of materials selection*” John Wiley & Sons, pp. 1159, 2002.

[23] B. Dehghan-Manshadi, H. Mahmudi, et al. “A novel method for materials selection in mechanical design: Combination of non-linear normalization and a modified digital logic method”. *Materials and Design.* Vol 28, pp 8-15, 2007.