CONTRIBUTION OF RESIN SHRINKAGE TO THE DEFORMATION OF LAMINATES MADE BY 4D PRINTING

Suong Van Hoa, Alan Victor Alfred Raju

Concordia Center for Composites
Department of Mechanical, Industrial and Aerospace Engineering
Concordia University
Center for Research in Polymers and Composites (CREPEC)
Montreal, Quebec, Canada H3G 1M8
hoasuon@alcor.concordia.ca
http://www.concordia.ca/research/composites/html

Keywords: 4D printing of composites, Unsymmetric laminates, Resin shrinkage, Deformation.

Abstract

The process of 4D printing of composites can make curved laminates without the need for curved molds [2]. This is due to the use of unsymmetric laminates. The curvature of these structures can be determined using laminate theory. Factors that contribute to the curvature are the shrinkage of the resin during curing, and the difference in coefficients of thermal expansion (contraction) of the different layers. The contribution of shrinkage onto the deformation of the laminates is not straight forward. This is because apart from the resin shrinkage, the resin modulus development also plays an important role. The resin shrinkage due to curing needs to be accompanied by the increase in modulus for the deformation to occur. In this work, the contribution of shrinkage onto the deformation of the laminate is investigated. Laminates made of [0/90] lay up sequence were made using autoclave. Subsequently, the curved solid laminates were heated up again. The curvatures of the laminate at intervals of temperature increase were measured. Plots of the curvature as function of temperature are obtained. If resin shrinkage does contribute to the deformation of the laminate, then there is still curvature at the cure temperature, and the laminate becomes flat at a temperature higher than the cure temperature. The result shows that, as compared to thermal effects, the contribution from resin shrinkage to the final shape of the structure at room temperature is insignificant.

1. Introduction

3D printing is a manufacturing process that has received widespread attention in many applications. In this process, materials in the form of viscous liquids or powders are deposited at strategic locations (by computer controlled) to build up complex structures. 4D printing is a process that combines 3D printing of the materials onto a flat surface, with the reconfiguration of the deposited material into a complex shape [1]. The materials used need to have special properties that can react with the application of some activation source such as heat, light, or the absorption of water. By strategic deposition of materials of different properties at strategic locations within the deposited layers, the flat configuration can change itself into controlled curved complex shapes. The materials used in 4D printing are usually soft in order to allow for significant shape reconfiguration. As such they may have limited application in engineering structures.

4D printing of composites utilizes the same concept as 4D printing, except that 4D printing of composites use composite materials that are strong and stiff, and can have applications in engineering structures. The process of 4D printing of composites uses the long continuous fiber composites that have been used in many aircraft structures such as carbon/epoxy, or glass/epoxy. These are commercially available. The process utilizes the anisotropy of the composite materials to provide the reconfiguration of a flat stack of composite prepregs upon curing. The concept of 4D printing of composites is given in [2]. One example of the curved laminates is shown in figure 1.

Figure 1: Example of curved laminates made by 4D printing

The reconfiguration of the laminate upon cooling from the cure temperature to room temperature can be attributed to two factors: One is due to the difference in the coefficients of thermal contraction in different directions in the individual layers in the laminate. The other is due to the difference in the degree of shrinkage along the different directions in the individual layers. The equations for the determination of the strains and curvatures developed are given as:

$$\begin{vmatrix} \varepsilon_x^o \\ \varepsilon_y^o \\ \gamma_{xy}^o \\ \kappa_x \\ \kappa_y \\ \kappa_{xy} \end{vmatrix} = \begin{bmatrix} a_{11} & a_{12} & a_{16} & b_{11} & b_{12} & b_{16} \\ a_{12} & a_{22} & a_{26} & b_{21} & b_{22} & b_{26} \\ a_{16} & a_{26} & a_{66} & b_{61} & b_{62} & b_{66} \\ b_{11} & b_{21} & b_{61} & d_{11} & d_{12} & d_{16} \\ b_{12} & b_{22} & b_{62} & d_{12} & d_{22} & d_{26} \\ b_{16} & b_{26} & b_{66} & d_{16} & d_{26} & d_{66} \end{bmatrix} \begin{bmatrix} N_x^T + N_x^S \\ N_y^T + N_y^S \\ N_{xy}^T + N_{xy}^S \\ M_x^T + M_x^S \\ M_y^T + M_y^S \\ M_{xy}^T + M_{xy}^S \end{bmatrix} \qquad (1)$$

Where ε_{ij} are the in plane strains, k_i are the curvatures, a_{ij}, b_{ij}, d_{ij} are components of the compliance matrix of the laminate, N_i^T, M_i^T are the stress and moment resultants due to thermal effect, and N_i^S, M_i^S are the stress and moment resultants due to resin shrinkage.

And

$$N_x^T = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{11}}\alpha_x^T + \overline{Q_{12}}\alpha_y^T + \overline{Q_{16}}\alpha_{xy}^T \;)\Delta T \, dz$$

$$N_y^T = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{12}}\alpha_x^T + \overline{Q_{22}}\alpha_y^T + \overline{Q_{26}}\alpha_{xy}^T)\Delta T\, dz$$

$$N_{xy}^T = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{16}}\alpha_x^T + \overline{Q_{26}}\alpha_y^T + \overline{Q_{66}}\alpha_{xy}^T)\Delta T\, dz$$

$$M_x^T = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{11}}\alpha_x^T + \overline{Q_{12}}\alpha_y^T + \overline{Q_{16}}\alpha_{xy}^T)\Delta T z\, dz \quad (2)$$

$$M_y^T = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{12}}\alpha_x^T + \overline{Q_{22}}\alpha_y^T + \overline{Q_{26}}\alpha_{xy}^T)\Delta T z\, dz$$

$$M_{xy}^T = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{16}}\alpha_x^T + \overline{Q_{26}}\alpha_y^T + \overline{Q_{66}}\alpha_{xy}^T)\Delta T z\, dz$$

And

$$N_x^S = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{11}}\varepsilon_x^s + \overline{Q_{12}}\varepsilon_y^s + \overline{Q_{16}}\varepsilon_{xy}^s)\, dz$$

$$N_y^S = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{12}}\varepsilon_x^s + \overline{Q_{22}}\varepsilon_y^s + \overline{Q_{26}}\varepsilon_{xy}^s)\, dz$$

$$N_{xy}^S = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{16}}\varepsilon_x^s + \overline{Q_{26}}\varepsilon_y^s + \overline{Q_{66}}\varepsilon_{xy}^s)\, dz$$

$$M_x^S = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{11}}\varepsilon_x^s + \overline{Q_{12}}\varepsilon_y^s + \overline{Q_{16}}\varepsilon_{xy}^s)\, zdz \quad (3)$$

$$M_y^S = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{12}}\varepsilon_x^s + \overline{Q_{22}}\varepsilon_y^s + \overline{Q_{26}}\varepsilon_{xy}^s)\, zdz$$

$$M_{xy}^S = \int_{-\frac{H}{2}}^{\frac{H}{2}} (\overline{Q_{16}}\varepsilon_x^s + \overline{Q_{26}}\varepsilon_y^s + \overline{Q_{66}}\varepsilon_{xy}^s)\, zdz$$

The thermal effect can be considered as being controlled by the magnitude of the elastic constants of the laminate, the coefficients of thermal contraction and the difference in temperature. The resin shrinkage effect can be considered as being controlled by the magnitude of the elastic constants of the laminate, and the shrinkage strain of the resin (ε_s).

Effect of resin shrinkage:

The effect of resin shrinkage only occurs during the curing process of the composite, and this happens at the cure temperature. There is no effect of resin shrinkage on the reconfiguration of the laminate when the laminate is cooled from cure temperature to room temperature. As such, the reconfiguration of the laminate can be divided into two parts. Part 1 is during curing and this only happens at the cure temperature. Part 2 is after curing, and during cooling from the cure temperature to room temperature. Part 1 is due to resin shrinkage only and part 2 is due to the difference in thermal contraction only.

There are a few methods used to determine the shrinkage of the resin [3,4]. One method [5] utilizes the time of flight of ultrasonic signals through the material to determine the amount of shrinkage and the evolution of the modulus of the epoxy. The results show that the shrinkage and modulus development depend on the amount of curing agent. Two typical results are shown in figures 2 and 3. The total amount of shrinkage varies between 3% and 4%, depending on the amount of the curing agent. There is a discontinuity in the modulus development curve. This is due to the loss of the ultrasonic signal when the viscosity of the liquid resin is high. The modulus is doubled its initial value over the process time, but it is relatively low as compared to the E_2 value of the solid composite. (Note that the modulus as shown in figure 3 is more of a bulk modulus, rather than Young modulus).

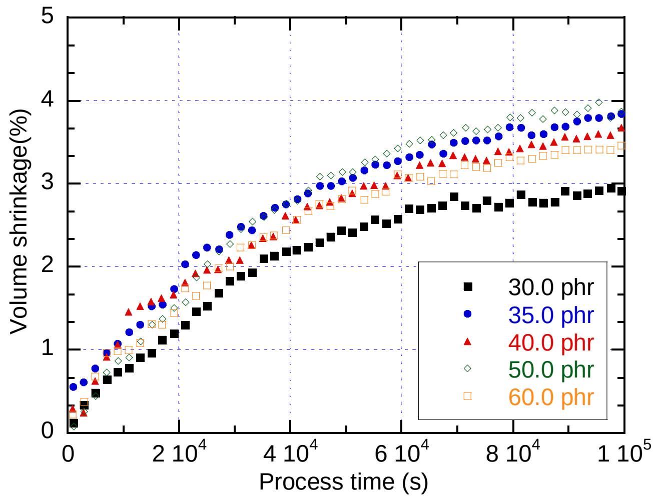

Figure 2: Shrinkage development of Shell Epon 828, Epicure 3046 epoxy resin- Different curves are for different amounts of curing agents [5]

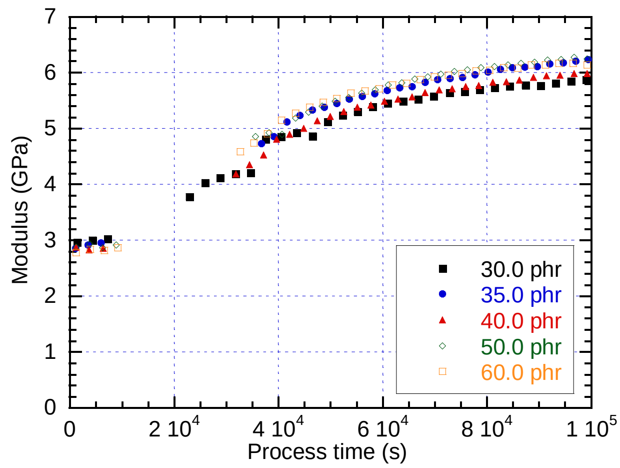

Figure 3: Modulus development of Shell Epon 828, Epicure 3046 epoxy resin- Different curves are for different amounts of curing agents [5]

Even though the total amount of shrinkage is about 3% or 4%, not the whole amount of shrinkage contributes to the reconfiguration of the laminate. This is because the modulus is relatively small during most of the curing process. It is difficult to extract the actual amount of shrinkage that makes contribution to the shape change. Using a value of volumetric shrinkage of 0.1% in the laminate equation seems to provide an agreement between the experimental radius of curvature and the calculated value. However this is a curve fitting method. It is desired to have another method for the determination of the amount of resin shrinkage that contributes to the reshaping of the laminate.

The experiment presented below is based on the concept that if a solid, curved, laminate of [0/90] is heated up to the cure temperature, it will flatten. At the cure temperature, whatever is the contribution to the reshaping due to the difference in coefficient of thermal contraction would be nullified. If at the cure temperature, the laminate still has curvature, that curvature must be due to the contribution from resin shrinkage.

Experiment:

Three laminates [0/90] made of carbon/epoxy and 4D printing were heated in an oven from room temperature in increments of 20 ^{o}C. Inside the oven, along with the curved laminate, there is also a scale for calibration purpose. Figure 4 shows the configuration. At different increments of temperature, a photograph of the configuration of the laminate is taken through a glass window of the oven. A method called Digimizer [6] is used to determine the radius of curvature of the laminate. In this method, after calibration using the scale, the ‘center of circular path’ tool in the software is used mark various points around the curvature of the samples in the image file. After marking the various points along the curvature of the samples, the software finds an average radius and center of the arc formed by the points around the curve.

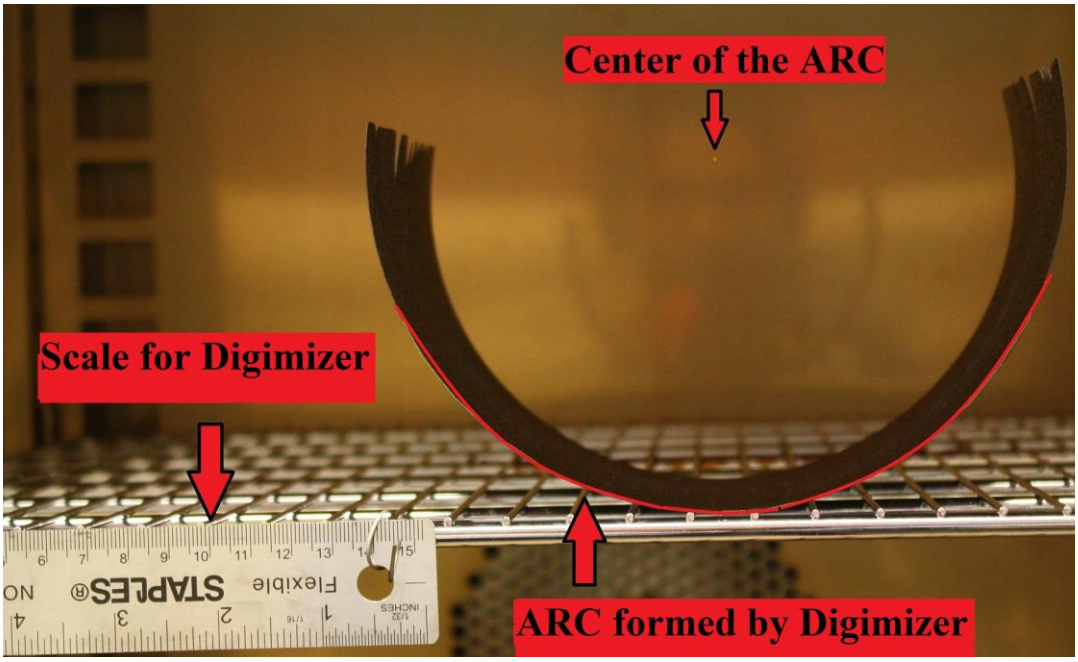

Figure 4: Experimental set up

Figure 5 shows the configurations of the laminate at different temperatures. The laminate becomes more flat as the temperature increases. At the cure temperature of 177 ^{o}C, the laminate appears flat but there is some curvature at the edges. The experimental radius of curvature at the cure temperature (177 ^{o}C) was found to be 137 cm. Substituting this value into equation (1) gives a value of ε_s of 0.000064.

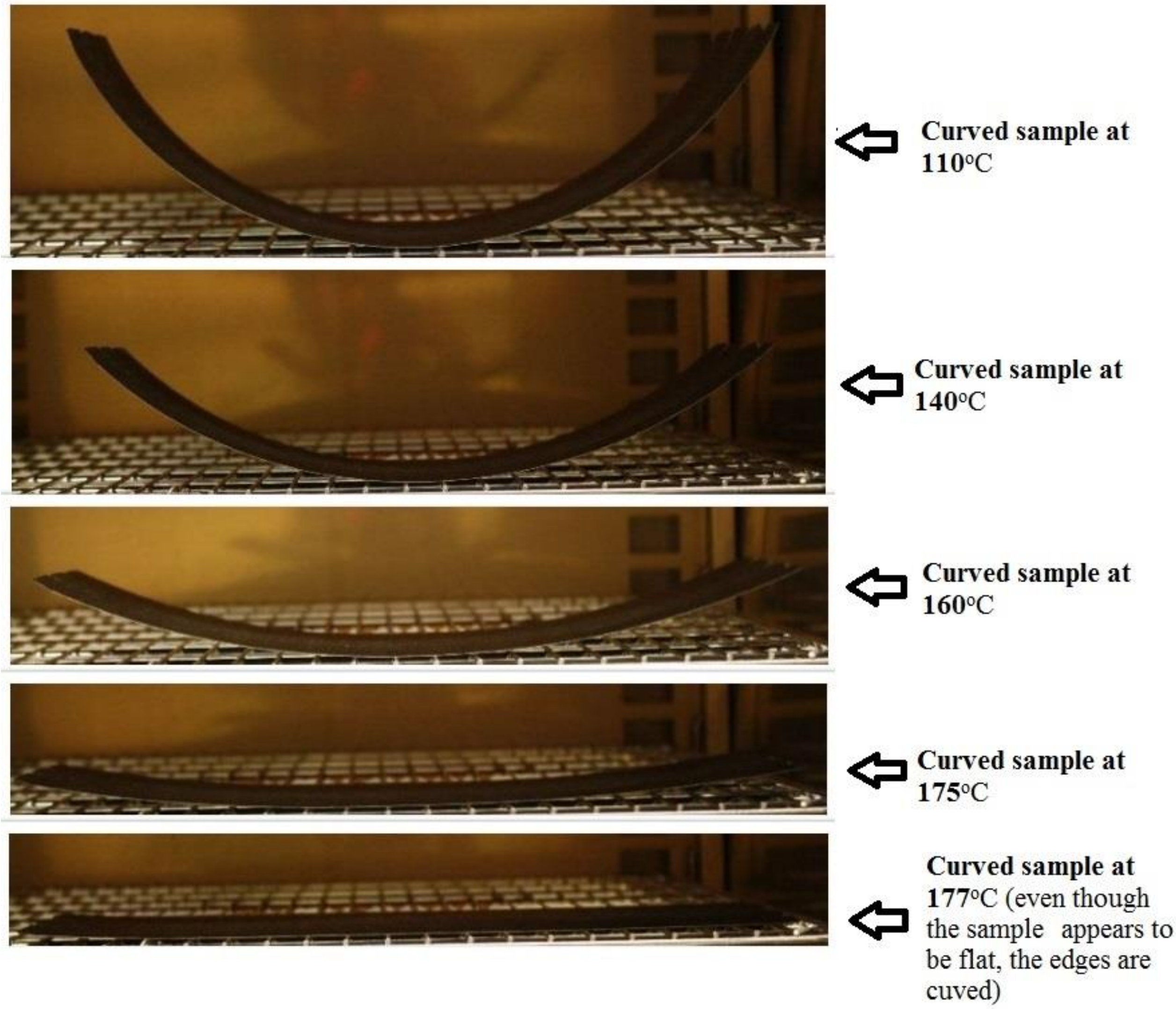

Figure 5: Configuration of laminate at different temperatures

The change in the experimental radius of the laminate as a function of temperature is shown as the blue line in figure 6 (one with error bars). The values calculated using laminate theory and diffrerent amounts of resin shrinkage are also calculated and plotted in figure 6. Good agreement is obainted until about 140 ^{o}C. Actually there is no significant difference in all the curves up to about 140 ^{o}C. Above this temperature, differences occur. This can be attributed to the reduction in the elastic constants of the composite material (reduction in E_2 and G_{12}). The values of E_2 and G_{12} were reduced to be a percentage of the values at room temperature. These were used to calculate the radius again using laminate theory. The results are shown in Figure 7. For reduction of the two elastic constants down to about 40% or more of the values at room temperature, there is no significant difference in the radius of curvature at low temperatures. For ΔT less than 40 ^{o}C (Actual temperature more than 137^{o}C), the change in radius becomes more pronounced.

By using the values of E_2 and G_{12} to be 50% those at room temperature, and the linear shrinkage strain of 0.00033, the value of the radius at cure (ΔT= 0) is indeed equal to 125 cm, which is close to the experimental value.

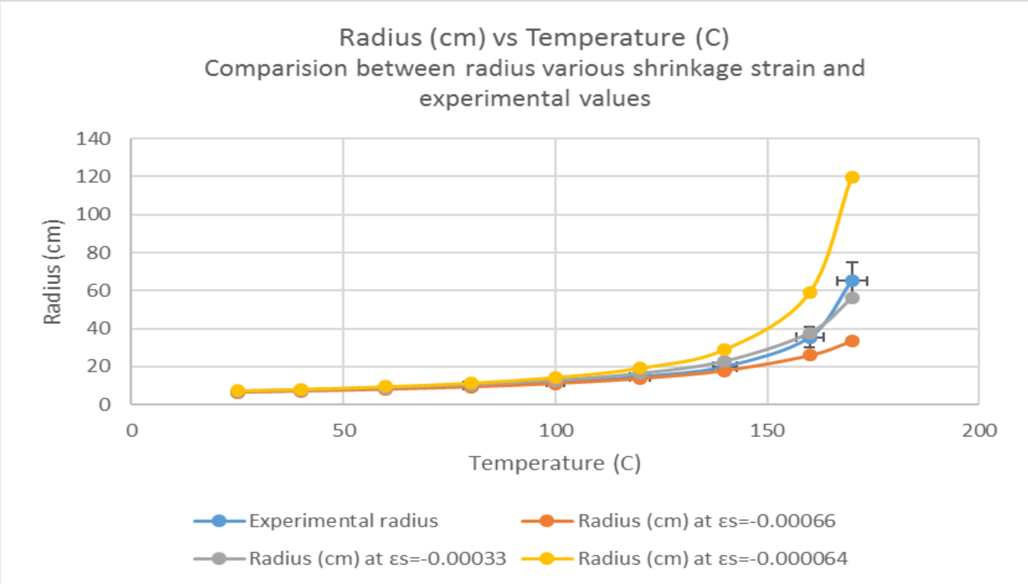

Figure 6:Variation of radius of curved laminate

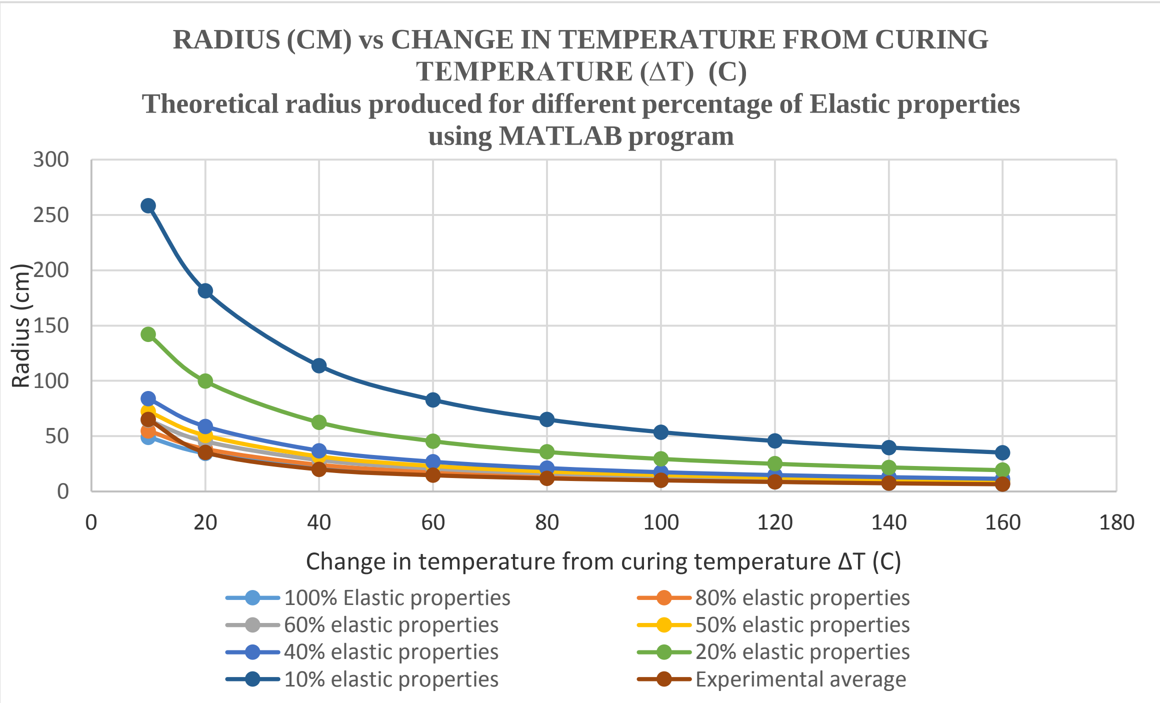

Figure 7: Effect of reduction in E_2 and G_{12} on the radius of curvature of [0/90] laminates

Also plotted in figure 6 are calculated values of the radii at different temperature increments and different values of assumed ε_s. It seems that the curve for linear shrinkage strain of ε_s = 0.00033 (0.033%) fits very well with the experimental curve. A linear shrinkage strain of 0.033% corresponds to a volumetric shrinkage strain of 0.1%.

It is also observed from figure 6 that at low temperatures (below 100 °C), the radius does not change with the amount of resin shrinkage. This is because at low temperatures, the difference between the actual temperature and the cure temperature (ΔT) is high and this makes the contribution due to thermal effect much larger than the contribution due to resin shrinkage. At high temperatures, ΔT is small and this makes the relative contribution from resin shrinkage to be more significant.

Conclusion:

A method for the determination of the amount resin shrinkage that contributes to the reconfiguration of [0/90] laminates made by 4D printing has been developed and presented. This method shows that the actual amount of shrinkage that contributes to the reconfiguration of the laminate is a very small fraction of the total amount of shrinkage. The amount found for this particular study is 0.1% volumetric strain (as compared to between 3% to 4% total resin shrinkage strain). Compared to the contribution from thermal effects, the contribution from resin shrinkage to the reconfiguration of the laminate at low temperatures (less than 100 ^oC) is not significant.

Acknowledgments

Financial support from the Natural Sciences and Engineering Research Council of Canada is appreciated.

References

[1] Farhang Momeni, Seyed M. Mehdi, Hasani N., Xun Liu, and Jun Ni, "A review of 4D printing", Materials and Design, 122, 2017, pp. 42-79.
[2] Suong Van Hoa, "Factors affecting the properties of composites made by 4D printing (moldless composites manufacturing", Journal of Advances Manufacturing: Polymer & Composites Science, Vol. 3, No. 3, 2017, pp. 101-109.
[3] Kinkelaar M., and Lee L.J., "Development of a dilatometer and its application to low shrink unsaturated polyester resin", J. Appl. Polym. Sci, 45, 37-50, 1992.
[4] Li C., Potter K., Wisnom M.R., and Stringer G., "In situ measurement of chemical shrinkage of MY750 epoxy resin by a novel gravimetric method", Comp. Sci. Tech., 64, 55-64, 2004.
[5] Hoa S.V., Ouellette P., and T.D. Ngo, "Determination of shrinkage and modulus development of thermosetting resins", J. Composite Materials, Vol. 43, No. 7, pp. 783-803, 2009.
[6] www.digimizer.com.