Available online at www.sciencedirect.com
SCIENCE DIRECT®
Composite Structures 75 (2006) 261–266
COMPOSITE STRUCTURES
www.elsevier.com/locate/compstruct

Reduction of residual stresses in thick-walled composite cylinders by smart cure cycle with cooling and reheating

Jong Woon Kim [a], Ji Hyung Lee [b], Hyoung Geun Kim [b], Hak Sung Kim [a], Dai Gil Lee [a,*]

[a] *Department of Mechanical Engineering, Korea Advanced Institute of Science and Technology, ME3261 Guseong-dong, Yuseong-gu, Daejeon, 305-701, South Korea*
[b] *Agency for Defense Development, P.O. Box 35, Yuseong-gu, Daejeon, South Korea*

Abstract

The nozzle parts of solid rocket motors must endure both the internal pressure generated by high temperature exhaust gas and the mechanical load generated by steering operation. Therefore, the nozzle parts of solid rocket motors are fabricated with thick carbon fiber phenolic resin composites. When the thick-walled phenolic composite cylinder is cooled down from the curing temperature of about 155 °C to the room temperature, thermal residual stresses are created due to the anisotropic thermal deformation of the composite structure.

In this paper, a smart cure method with cooling and reheating was developed to reduce residual stresses in thick-wound composite cylinders made of carbon phenolic woven composite. The optimal cure cycle was obtained to reduce the residual stresses without increasing processing time and applied to fabrication of the thick-walled composite cylinder. From the residual stresses measured by the radial-cut-cylinder-bending method, it was found that the residual stresses were reduced 30% by using the smart cure method.

Keywords: Thick carbon phenolic composite; Residual stress; Smart cure; Degree of cure; Solidification temperature; Radial-cut-cylinder-bending

1. Introduction

The nozzle parts of solid rocket motors must endure both the internal pressure generated by high temperature exhaust gas and the mechanical load generated by steering operation of the nozzle. Therefore, the nozzle parts are usually made of thick carbon phenolic composites when the thick carbon phenolic composite cylinders made of many prepreg plies are cured at high temperatures and cooled to the room temperature, thermal residual stresses are developed due to large difference of CTE (coefficient of thermal expansion) between the in-plane direction and the transverse direction. As the radial thickness of composite cylinder increases, the tensile residual stress in the radial direction may increase up to the interlaminar tensile strength, which eventually causes delamination failures [1,2]. Therefore, a new manufacturing process for the thick-walled composite cylinder to reduce thermal residual stresses is necessary to avoid the interlaminar failure.

Since the magnitude of thermal residual stresses is proportional to the temperature difference between the cure temperature of composite and the room temperature, a lower cure temperature is beneficial to reduce the thermal residual stresses. But the low temperature curing is not recommended because it takes very long time to complete the cure reaction and obtain full consolidation. Although there are many researches to reduce temperature overshoot of thick composite structures due to the internal exothermic heat generation by cure reaction such as the autoclave cure cycle with cooling and reheating [3–5], cure temperatures for phenolic resin composites are still too high to reduce the thermal residual stresses.

Because the cure reaction and the thermal residual stresses due to shrinkage are chemical and physical phenomena,

---

[*] Corresponding author. Tel.: +82 42 869 3221; fax: +82 42 869 5221.
E-mail address: dglee@kaist.ac.kr (D.G. Lee).

0263-8223/$ - see front matter © 2006 Elsevier Ltd. All rights reserved.
doi:10.1016/j.compstruct.2006.04.029

respectively, the process for generating thermal residual stresses can be separated by controlling the viscoelastic behavior of thermosetting resins. Hodges et al. experimentally investigated the method for the reduction of residual stresses in epoxy curing [6]. They employed a rheometer, dilatometer, and DSC to investigate the influence of five different curing cycles on the characteristics of epoxy resin, from which the optimized dwell times and cure temperatures were suggested using a simple elasticity theory for the prediction of residual stresses. White and Hahn investigated an optimal cure cycle for the reduction of the fabricational residual stress in composite materials [7]. They investigated the effect of cooling rate, dwell time, and post-cure cycle on the fabricational thermal residual stress in the composite material considering the viscoelastic properties of resin during cure cycle. Kim et al. [8] devised a smart cure cycle with cooling and reheating for co-cure bonded steel/carbon epoxy composite hybrid strips, from which an optimal cooling temperature to reduce the thermal residual stress was found. However, research results either for the reduction of thermal residual stresses in thick composite structures or phenolic resin composites are rare.

When cooling and reheating was applied to composite structures during curing process, calculation of the thermal residual stresses is complicated because the viscoelastic behavior of the resin should be considered. Therefore, the measurement of residual stresses in thick composite cylinders is preferable to the calculation. A plausible measuring technique for residual stresses in the thick-walled composite cylinder is the radial-cut method [9,10]. In this paper, the modified method for the radial-cut method which considered the radial variation of material properties in fabric composite cylinders with shear deformation was used [11].

Also, the smart cure method with an abrupt cooling to decrease the solidification temperature of the resin and a reheating to complete the cure reaction was developed to reduce thermal residual stresses in thick-wound composite cylinders made of carbon phenolic woven composite. The DSC method is generally used to obtain the cure rate of a thermosetting resin. In the DSC method, the degree of cure is calculated using the heat generated during cure of the material. The degree of cure of the carbon phenolic composite was measured by the dynamic and isothermal DSC tests to determine the optimum time to apply the cooling operation. The solidification temperatures, which induce the thermal residual stresses, were obtained by measuring the curvatures of steel/composite co-cured strips with respect to cooling temperature. Then the optimum cooling temperature to reduce the thermal residual stresses without increasing processing time was determined and applied to fabrication of the thick-walled composite cylinders. Finally, the residual stresses in the thick-walled composite cylinders fabricated with the manufacturer's recommended cycle and the optimum cooling and reheating cycle were measured by the radial-cut-cylinder-bending method.

2. Degree of cure of carbon phenolic composite

The carbon fabric phenolic composites are widely used for heat-resisting parts in solid rocket motors because of their excellent ablative property, high strength and dimensional stability. The specifications of PAN-based carbon fabric phenolic prepreg (CF3336, Hankuk Fiber Glass Co., Korea) and their laminate properties are shown in Tables 1 and 2, respectively. The conventional cure cycle recommended by the prepreg manufacturer is composed of dwelling for 30 min at 80 °C, temperature increment by a uniform rate of 1.0 °C/min, and curing for 2 h at 155 °C as shown in Fig. 1.

The degree of cure of the carbon fabric phenolic composite was measured with Thermal Analyst 2200 (TA

Table 1
Specifications of the carbon fabric phenolic prepreg

Woven pattern	8-harness satin
Number of fibers in a yarn	3000
Yarn width	2.2 mm
Uncompacted ply thickness	0.62 mm
Fiber volume fraction	62%

Table 2
Laminate properties of the carbon fabric phenolic composite

E_1	62.8 GPa
E_2	59.8 GPa
E_3	6.21 GPa
ν_{12}	0.0754
ν_{31}	0.0460
ν_{32}	0.0470
G_{12}	5.49 GPa
G_{13}	2.86 GPa
G_{23}	2.63 GPa
α_1	$1.2 \times 10^{-6}\,°C^{-1}$
α_2	$1.8 \times 10^{-6}\,°C^{-1}$
α_3	$41 \times 10^{-6}\,°C^{-1}$
Ply thickness	0.37 mm

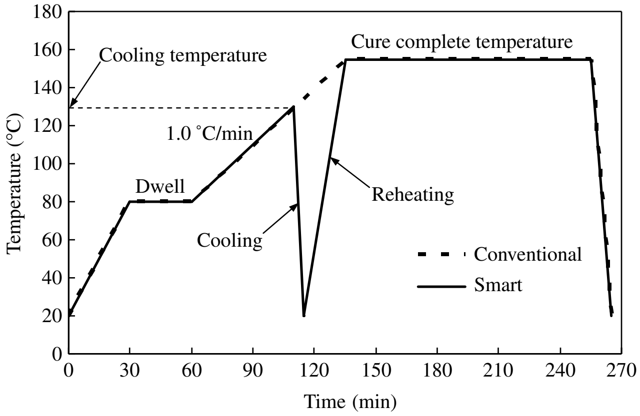

Fig. 1. Conventional cure cycle recommended by the prepreg manufacturer and smart cure cycle with cooling and reheating for the carbon phenolic composite.

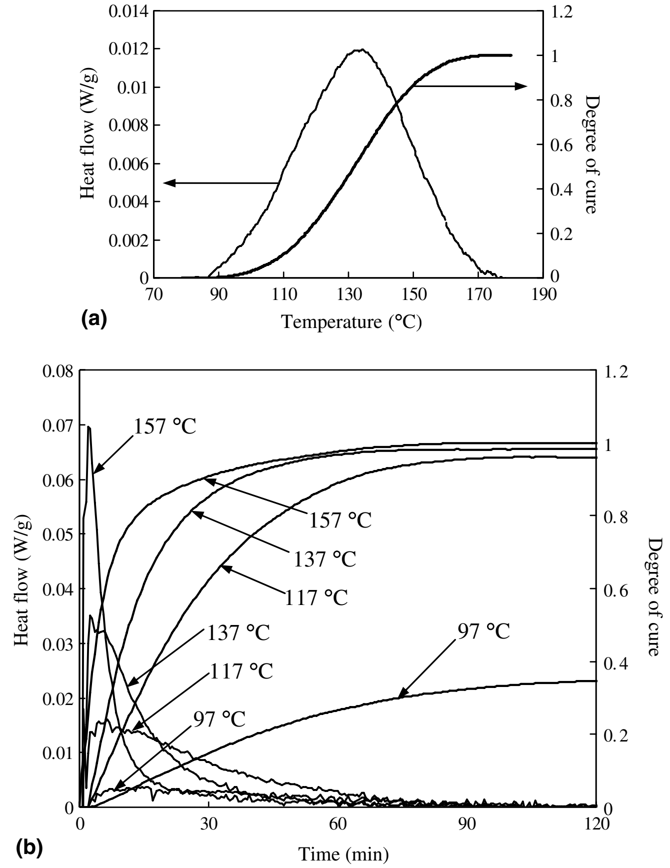

Fig. 2. Heat generation rate and the absolute degree of cure of the carbon fabric phenolic composite from the DSC tests: (a) dynamic scanning with the temperature increasing rate of 1.0 °C/min and (b) isothermal scanning at the temperature of 97, 117, 137, and 157 °C.

Table 3
Total heat generation of carbon fabric phenolic composite during the dynamic and isothermal scannings

Dynamic scanning	
1 °C/min	30.3 J/g
Isothermal scanning	
97 °C	10.5 J/g
117 °C	29.1 J/g
137 °C	29.8 J/g
157 °C	30.3 J/g

Instruments, USA). Small samples of 6–8 mg of the prepreg were used for DSC measurements under both the dynamic scanning and isothermal scannings. In the isothermal scanning, the heat generation rates were measured with respect to time at the constant temperatures of 97, 117, 137, and 157 °C for 2 h. In the dynamic scanning, the heat generation rates were measured with respect to time at the uniformly increasing temperature rate of 1.0 °C/min.

The dynamic cure rate $d\xi/dt$ is expressed as follows [12]:

$$\frac{d\xi}{dt}=\frac{1}{H_U}\left(\frac{dH}{dt}\right)_T, \tag{1}$$

where ξ is the dynamic degree of cure (or absolute degree of cure), $(dH/dt)_T$ is the heat generation rate during the dynamic scanning (W/g), and H_U is the total heat generation during dynamic scanning (J/g). Eq. (1) can be rewritten using the isothermal cure rate $d\zeta/dt$:

$$\frac{d\xi}{dt}=\frac{H_T}{H_U}\frac{d\zeta}{dt}, \tag{2}$$

where ζ is the isothermal degree of cure and H_T is the total heat generation during isothermal scanning (J/g). On integrating Eq. (2), the dynamic degree of cure ξ can be expressed as follows:

$$\xi=\frac{H_T}{H_U}\int_0^t\left(\frac{d\zeta}{dt}\right)dt. \tag{3}$$

Fig. 2 shows heat generation rate and the absolute degree of cure during the dynamic scanning and the isothermal scanning. Table 3 shows the total heat generation during the dynamic scanning and the isothermal scanning.

3. Solidification temperature

The solidification temperature of the carbon phenolic composite was estimated with respect to cure cycles by measuring curvatures induced by the thermal residual stress in the steel/composite co-cured strips cured with smart cure cycles with cooling and reheating, isothermal cure cycles, and the conventional cure cycle as in Fig. 1 [8]. The dimensions and stacking sequence of steel/composite co-cured strips are shown in Fig. 3 and mechanical properties of the steel strip are shown in Table 4. The cure assembly with a dummy laminate for monitoring temperature at the strip during fabrication is shown in Fig. 4.

In the smart cure cycle with cooling and reheating, the temperature was controlled by the conventional cure cycle until the temperature at the dummy laminate reached the specified cooling temperature. Then the specimen was cooled abruptly by quenching the cure assembly into a water tank in order to stop the cure reaction. Finally, the strip was post-cured at 155 °C for 2 h to complete the cure

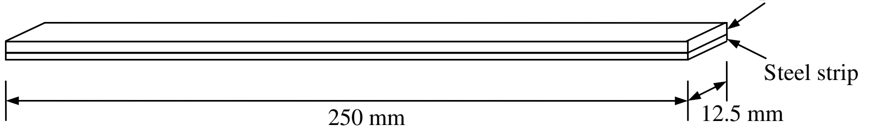

Fig. 3. Dimensions of the steel/composite co-cured strip before curing; thicknesses of the composite layer and the steel strip are 0.37 and 0.20 mm, respectively.

Table 4
Mechanical properties of the steel strip

E	207 GPa
G	72 GPa
v	0.30
α	11×10^{-6} °C^{-1}

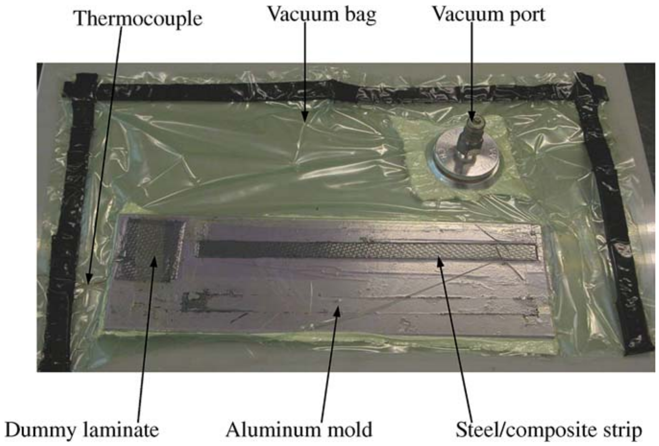

Fig. 4. Photograph of the assembly of the steel/composite co-cured strip for cure.

reaction. The smart cure cycle took less curing time than the conventional cycle as shown in Fig. 1. Several cooling temperatures such as 95, 115, 120, 125, 130, and 135 °C were used in the smart cure cycle, while the temperatures in the isothermal cure cycles were maintained for 2 h at 120, 125, and 130 °C.

When the temperature of the strip was cooled down from the cure temperatures to the room temperature, the strip bent due to the thermal residual stress created by the temperature difference ΔT between the solidification temperature T_{solidify} and the room temperature T_{room} was calculated using the measured curvature R of the curved strip and the principle of bimaterial thermometers [13] as follows:

$$\Delta T = T_{\text{solidify}} - T_{\text{room}} = \frac{t\left[3(1+m)^2 + (1+mn)(m^2 + 1/mn)\right]}{6R(1+m)^2(\alpha_{\text{steel}} - \alpha_{\text{composite}})}, \tag{4}$$

where $m = t_{\text{composite}}/t_{\text{steel}}$ is the thickness ratio of the composite to the steel; $n = E_{\text{composite}}/E_{\text{steel}}$ is the modulus ratio of the composite to the steel; $t = t_{\text{composite}} + t_{\text{steel}}$ is the total thickness of the strip; and α_{steel} and $\alpha_{\text{composite}}$ are CTE's of the steel and composite in the length direction, respectively.

Fig. 5(a) and (b) show the curved strips cured under the smart cure cycles with the different cooling temperatures at the room temperature of 15 °C before and after post-cure, respectively. The solidification temperatures estimated by Eq. (4) in the steel/composite co-cured strips fabricated under the smart cure cycles and the conventional cure cycle are shown in Fig. 6(a) and (b) with respect to cooling tem-

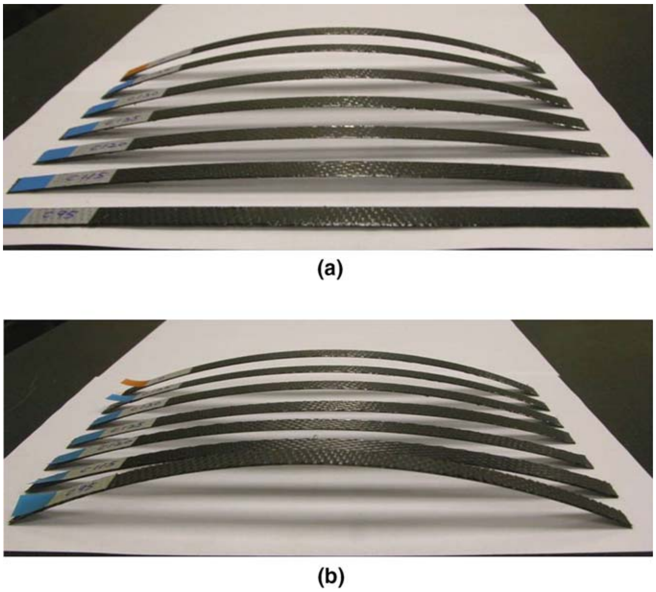

Fig. 5. Curved steel/composite co-cured strips at 15 °C: (a) before post-cure and (b) after post-cure.

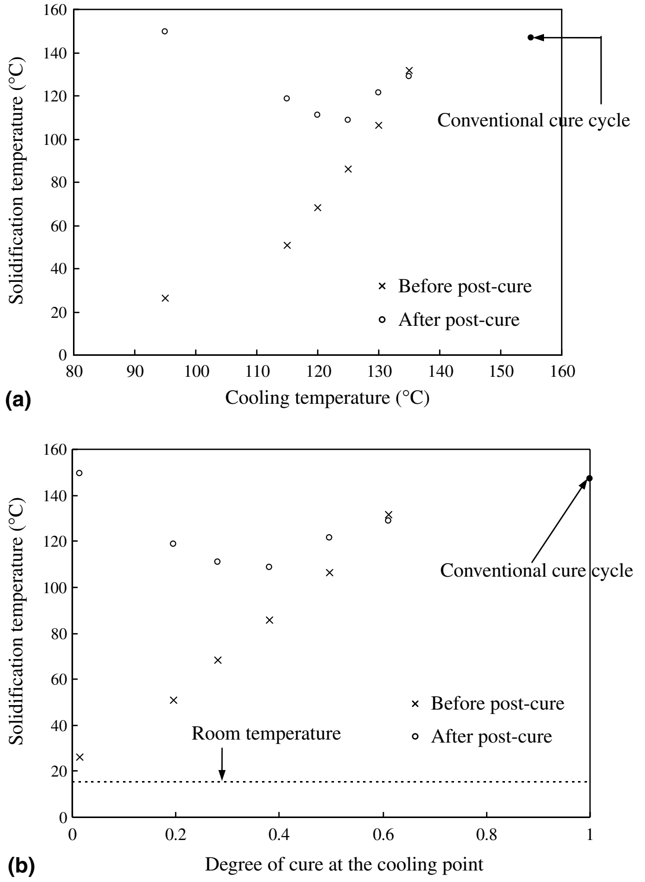

Fig. 6. Measured solidification temperatures in the steel/composite co-cured strips cured under the smart cure cycles and the conventional cure cycle: (a) with respect to cooling temperature and (b) with respect to degree of cure at the cooling point.

Table 5
Measured solidification temperatures of the steel/composite co-cured strips cured under the isothermal cure cycles

Curing temperature (°C)	Solidification temperature (°C)
120	122
125	124
130	129

perature and degree of cure at the cooling point, respectively. The degree of cure at each cooling point was obtained from Fig. 2(a) under the assumptions that the cure reaction stopped immediately at the cooling point and the 80 °C dwelling step affected little the degree of cure. The solidification temperature before post-cure increased as the degree of cure at the cooling point increased, while the solidification temperature after post-cure had the minimum value of 108 °C when the cooling temperature was 125 °C, where the degree of cure was 0.38. The measured solidification temperatures in the steel/composite co-cured strips cured under the several isothermal temperatures are shown in Table 5. The solidification temperatures were similar to the isothermal curing temperatures when the cure reactions were not fully completed.

Therefore, to minimize the thermal residual stresses without increasing the processing time, the smart cure cycle was determined as the cycle with abrupt cooling at 125 °C and reheating to the final post-cure temperature of 155 °C, where ΔT was reduced by 29% compared to the conventional cure cycle.

4. Residual stresses in the thick-walled composite cylinder

In order to reduce the interlaminar tensile thermal residual stress in the thick-walled composite cylinder, the smart cure cycle with cooling and reheating was used to fabricate the thick-walled carbon fabric phenolic composite cylinder. The inside-out one-step compaction method [11] was employed since the insufficient compaction of fabric laminates resulted in the large interlaminar through-thickness CTE and high void content [14]. The stacked composite cylinders were cured under the conventional manufacturer's recommended cycle and the optimal smart cure cycle with abrupt cooling at 125 °C and reheating. The measured temperature distributions showed that there was little temperature deviation through thickness due to high thermal conductivity of the carbon fabric phenolic composite as shown in Fig. 7. In the conventional cure cycle of the thick-walled composite cylinders, longer dwelling times at 80 °C and 105 °C were applied for good consolidation. The fully cured cylinders were machined to the dimensions of the cylindrical specimen shown in Fig. 8.

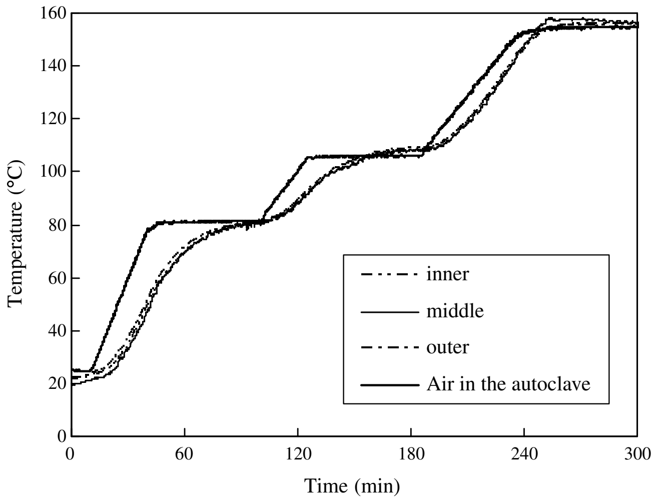

Fig. 7. Measured temperature distributions in the thick-walled carbon fabric phenolic composite cylinder during the conventional cure cycle.

The thermal residual stresses in the thick-walled cylinders at the room temperature of 15 °C were experimentally obtained by the radial-cut-cylinder-bending method [11] as shown in Figs. 9 and 10. The stress distributions in the hoop and radial (interlaminar tensile) direction in the thick-walled composite cylinders were calculated from the

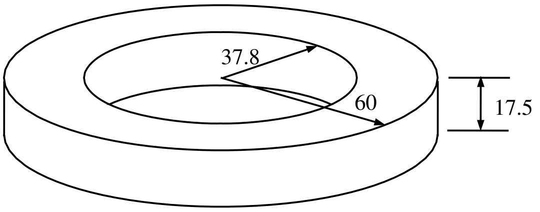

Fig. 8. Dimensions of the thick-walled composite cylinder (units in mm).

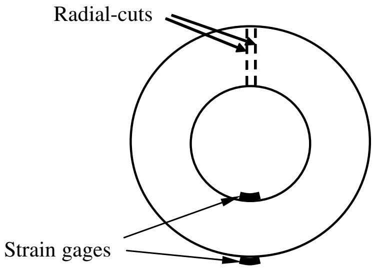

Fig. 9. Schematic drawing of the radial-cut test of composite cylindrical specimens.

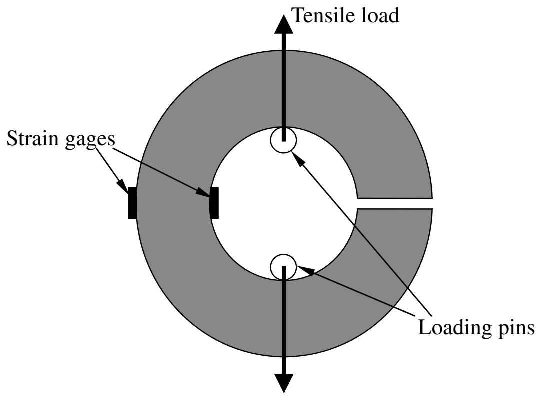

Fig. 10. Schematic drawing of the bending test of the radial cut composite cylinder.

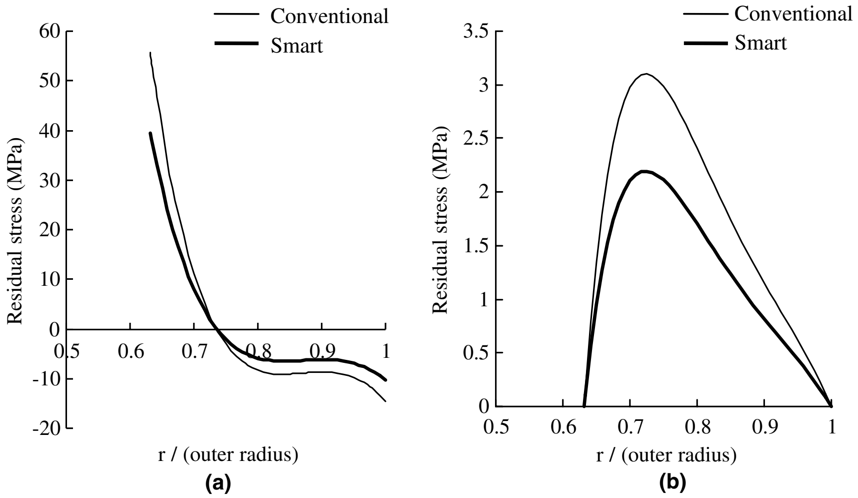

Fig. 11. Measured residual stresses in the thick-wound composite cylinders fabricated under the conventional cycle and the smart cure cycle: (a) hoop stresses and (b) radial stresses (interlaminar tensile stresses).

results of the bending tests of the radial-cut composite cylindrical specimens as shown in Fig. 11. The residual stresses in the cylinder manufactured under the smart cure cycle were 30% lower than those under the conventional cure cycle.

5. Conclusion

In this work, thick-walled carbon fabric phenolic composite cylinders were cured with the smart cure cycle with cooling and reheating to reduce thermal residual stresses. The stresses in the composite were estimated by thermal analysis and curvature experiments. Using the developed smart cure cycle, thick-walled carbon fabric phenolic composite cylinders were fabricated and the residual stresses in the cylinders were measured by the radial-cut-cylinder-bending method. From the experiments, it was found that the interlaminar tensile thermal residual stress in the composite cylinder cured under the smart cure cycle was reduced 30% compared the tensile stress in the composite cylinder cured under the conventional cure cycle.

Acknowledgements

This work has been performed by the fund of BK21 Project and NRL of MOST of Korean Government.

References

[1] Guemes JA. Curing residual stresses and failure analysis in composite cylinders. J Reinf Plast Compos 1994;13:408–19.

[2] Corden TJ, Jones IA, Jones DT, Middleton V. The mechanisms of interlaminar cracking in thick resin transfer moulded composite cylinders. Compos Part A – Appl Sci Manuf 1998;29A:455–64.

[3] Kim JS, Lee DG. Development of an autoclave cure cycle with cooling and reheating steps for thick thermoset composite laminates. J Compos Mater 1997;22:2264–82.

[4] Oh JH, Lee DG. Cure cycle for thick glass/epoxy composite laminates. J Compos Mater 2002;36:19–45.

[5] Smartt Z. A study of upgraded phenolic curing for RSRM nozzle rings. In: 36th AIAA/ASME/SAE/ASEE joint propulsion conference and exhibit, July 2000, Huntsville, Alabama.

[6] Hodges J, Yates B, Darby MI, Wostenholm GH, Clement JF, Keates TF. Residual stresses and the optimum cure cycle for an epoxy resin. J Mater Sci 1989;24:1984–90.

[7] White SR, Hahn HT. Cure cycle optimization for the reduction of processing induced residual stresses in composite materials. J Compos Mater 1993;27:1352–78.

[8] Kim HS, Park SW, Lee DG. Smart cure cycle with cooling and reheating for co-cure bonded steel/carbon epoxy composite hybrid structures for reducing thermal residual stress. Compos Part A – Appl Sci Manuf, in press.

[9] Fourney WI. Residual strain in filament-wound rings. J Compos Mater 1968;2:408–11.

[10] Aleong C, Munro M. Evaluation of the radial-cut method for determining residual strains in fiber composite rings. Exp Tech 1991; 15:55–8.

[11] Kim JW, Lee DG. Measurement of residual stresses in thick composite cylinders by the radial-cut-cylinder-bending method. Compos Struct, in press, doi:10.1016/j.compstruct.2005.07.020.

[12] Kwon JW, Chin WS, Lee DG. In situ cure monitoring of adhesively bonded joints by dielectrometry. J Adhes Sci Tech 2003; 16:2111–30.

[13] Timoshenko SP. The collected papers. New York: McGraw-Hill; 1953.

[14] Kim JW, Kim HG, Lee DG. Compaction of thick carbon/phenolic composites with autoclave method. Compos Struct 2004;66:467–77.