# Cryogenic Properties of Epoxy Resin Matrix Composites prepared by RTM Process

Han-Qiao Shi, Kung Gao, Jian-Bo Sun, Qian Liu, Bao-Gang Sun and Yi Zhang

Aerospace Research Institute of Materials & Processing Technology, Beijing, 100076, China Email: <u>shihanqiao@126.com</u>

Keywords: Cryogenic, Epoxy resin, Composites, RTM, cycles

#### Abstract

For cryogenic application, M40-level braiding fabric/epoxy composites were prepared via a RTM process. The mechanical properties of M40-level braiding fabric/epoxy composite at 80°C, RT and -196°C were examined. And the effects of cryogenic temperature on the mechanical properties of the composite were studied. Then, 300 cryogenic-cycles were performed between 80°C and -196°C. And the effects of  $(80^{\circ}C \sim -196^{\circ}C)$  cryogenic-cycles on cryogenic mechanical properties of the composites were also studied. According to the results, the effect of cryogenic temperature on tensile strength of the composites was small; while as the decrease of temperature, the flexural strength, compression strength, interlaminate shear strength and impact strength were improved remarkably. The effect of ( $80^{\circ}C \sim -196^{\circ}C$ ) cryogenic-cycles on tensile strength of the composites was also small. After 100 cryogenic-cycles, the flexural strength, and impact strength of the composites decreased slightly; and after 300 cryogenic-cycles, these properties became stable. While, as the cryogenic-cycles increased, the compression strength and interlaminate shear strength decreased gradually.

#### 1. Introduction

With the rapid development of spacecraft, superconducting cable, and large cryogenic engineering projects, the application of fiber reinforced epoxy resin matrix composite materials under cryogenic temperature has attracted increasing attention[1-3]. Resin transfer molding (RTM) could prepare the composites with complex structures, and has been widely applied in the manufacture of may composite structures [4]. The development of epoxy resin matrix composites for RTM process will greatly promote the progress of cryogenic engineering.

Owing to their high mechanical properties, good thermal and corrosion resistance, and low curing shrinkage, epoxy resins have been widely used as matrix materials for structural composites[5-10]. However, the main drawback of epoxy resins is their inherent brittleness, leading to poor resistance to crack [11,12]. Therefore, epoxy matrix composites usually have low toughness, and are prone to impact damage and delamination, which limits their applications under cryogenic temperature [13-14].

Many approaches have been reported on the toughening of epoxy matrices. Most of them are based on the addition of a secondary phase such as liquid rubbers, thermoplastic, particulates or nanoparticles. However, the low viscosity was a prerequisite for epoxy resins to be applied in resin transfer molding (RTM). The viscosity of epoxy resin systems would be significantly increased as the rubber, thermoplastic, or particulate tougheners were added. The addition of even a small amount of nanoparticles could dramatically increase the viscosity of the resin systems. Moreover, during liquid resin infusion these toughening additives would be filtered by the reinforcing fabrics, and could not arrive at the effective toughening regions throughout the perform[15]. Besides, the thermal stress between epoxy phase and the secondary phase was disadvantage for the application under cryogenic temperature.

In the paper, the M40-level braiding fabric/R608 epoxy composites with excellent cryogenic mechanical properties and RTM processability were developed. The effects of cryogenic temperature and  $(-196^{\circ}C-80^{\circ}C)$  cryogenic-cycles (as shown in Figure 1) on the mechanical properties of the M40-level braiding fabric/R608 epoxy composites were studied systemically.



Figure 1. Cryogenic-cycle curve for one cycle

# 2. Results and Discussions

# 2.1. Mechanical properties of R608 resin

The tensile properties, flexural properties, and impact properties were investigated under 80°C, RT and -196°C, respectively. As shown in Table 1, the breaking elongation of R608 resin at RT was as high as 6.1%, and the breaking elongation of R608 resin at -196°C was as high as 2.3%. Under -196°C, the small moving units of the polymer have been frozen, leading to the increase of the brittleness. Therefore, the breaking elongation of the R608 resin under -196°C decreased remarkably compared with that under RT. The impact strength of R608 resin under -196°C was as high as 24.1 kJ/m<sup>2</sup>. While for may epoxy resin systems under-196°C, their breaking elongation was commonly lower than 2%, and their impact strength was generally lower than 20 kJ/m<sup>2</sup>. Therefore, R608 resin has a relatively high ductility and impact strength at cryogenic temperature.

 Table 1. Mechanical properties of R608 resin under different temperature.

Test Temperature	80°C	RT	-196°C
Tensile Strength/MPa	50.3	86.8	65.7
Tensile Modulus/GPa	2.54	3.00	4.02
Breaking Elongation /%	5.1	6.1	2.3
Flexural Strength/MPa	98.6	134	221
Flexural Modulus/GPa	2.56	3.10	7.00
Impact Strength/kJ·m-2	33.8	27.5	24.1

#### 2.2 Effects of cryogenic temperatrue on mechanical properties of composites

To find the effects of temperature on mechanical properties of M40-leve braiding fabric/R608 composites, the tensile properties, flexural properties, compression properties, interlaminar shear properties and impact properties was tested under  $80^{\circ}$ C,RT and -196°C, respectively.



Figure 2. Tensile strength of M40-level braiding frabic/R608 composites under different temperature.

From Figure 2, it is obvious that the tensile strength of M40-level braiding frabic/R608 composites under different temperature keep stable. While as shown in Figur 3, as the temperature dropped form  $80^{\circ}$ C to  $-196^{\circ}$ C, the flexural strength of M40-level braiding frabic/R608 composites improved about 44%. Moreover, as the temperature reduced form  $80^{\circ}$ C to  $-196^{\circ}$ C, the flexural strength of M40-level braiding frabic/R608 composites greatly improved about 75% as given in Figure 4.



Figure 3. Flexural strength of M40-level braiding frabic/R608 composites under different temperature.



Figure 4. Compression strength of M40-level braiding frabic/R608 composites under different temperature.

The impovement of interlaminate shear strength and impact strength under cryogenic temperature has also been found in Figure 5 and Figure 6. As the temperature falled form  $80^{\circ}$ C to  $-196^{\circ}$ C, the interlaminate shear strength of M40-level braiding frabic/R608 composites increased about 23%. And as the temperature dropped form  $80^{\circ}$ C to  $-196^{\circ}$ C, impact strength of M40-level braiding frabic/R608 composites increased about 23%.



Figure 5. Interlaminar shear strength of M40-level braiding frabic/R608 composites under different temperature.



Figure 6. Impact strength of M40-level braiding frabic/R608 composites under different temperature.

Flexural strength, compression strength, interlaminate shear strength and impact strength of composites can be greatly influenced by resin matrix. The effects of cryogenic temperature on mechanical properties of composites were mainly through resin matrix. In other word, the effects of cryogenic temperature are large for the mechanical properties which are greatly influenced by resin matrix. Therefore, Flexural strength, compression strength, interlaminate shear strength and impact strength of M40-level braiding frabic/R608 composites could be greatly influenced by cryogenic temperature.

#### 2.3 Effects of cryogenic-cycle on mechanical properties of composites

To investigate the effects of cryogenic-cycle on the mechanical properties M40-level braiding frabic/R608 composites, 300 cryogenic-cycles have been performed between  $80^{\circ}$ C and  $-196^{\circ}$ C according to the cryogenic-cycle curve in Figure 1. Tensile strength, Flexural strength, Compression strength, Interlaminate shear strength, and Impact strength of M40-level braiding frabic/R608 composites before cryogenic-cycle, after 100 cryogenic-cycles, and after 300 cryogenic cycles have been tested and the results were summarized in Figure 7-11.



Figure 7. Tensile strength of M40-level braiding frabic/R608 composites after different numbers of the cryogenic-cycles.

As shown in Figure 7, after 100 cryogenic-cycles, the tensile strength of M40-level braiding frabic/R608 composites was improved; and after 300 cryogenic-cycles, the tensile strength of M40-level braiding frabic/R608 composites decreased slightly, but stil hiher than that before cryogenic-cycles.



**Figure 8.** Flexural strength of M40-level braiding frabic/R608 composites after different numbers of the cryogenic-cycles.

From Figure 8, it is obvious that after 100 cryogenic-cycles, the flexural strength of M40-level braiding frabic/R608 composites declined; and after300 cryogenic-cycles, the flexural strength of M40-level braiding frabic/R608 composites increased slightly.



**Figure 9.** Compression strength of M40-level braiding frabic/R608 composites after different numbers of the cryogenic-cycles.

As presented in Figure 9, after 100 cryogenic-cycles, the compression strength of M40-level braiding frabic/R608 composites was improved; and after 300 cryogenic-cycles, the compression strength of M40-level braiding frabic/R608 composites kept stable. Besides, after 100 and 300

cryogenic-cycles, interlaminate shear strength of M40-level braiding frabic/R608 composites has no obvious change as given in Figure 10.



Figure 10. Interlaminate shear strength of M40-level braiding frabic/R608 composites after different numbers of the cryogenic-cycles.



Figure 11. Impact strength of M40-level braiding frabic/R608 composites after different numbers of the cryogenic-cycles.

After 100 cryogenic-cycles, the impact strength of M40-level braiding frabic/R608 composites was increased slight; and after 300 cryogenic-cycles, the impact strength of M40-level braiding frabic/R608 composites decline slightly.

From the result above, it seems that after 100 cryogenic-cycles, the mechanical properties of M40-level braiding frabic/R608 composites generally changed slight ; and after 300 cryogenic-cycles, the mechanical properties of M40-level braiding frabic/R608 composites became stable. The similar results also be found in fracture toughness  $G_{\rm IC}$  and  $G_{\rm IIC}$  of M40-level braiding frabic/R608 composites. Both  $G_{\rm IC}$  and  $G_{\rm IIC}$  were improved slight after 100 cryogenic-cycles, while after 300 cryogenic-cycles, they all decreased slight, but still higher than that before cryogenic-cycles.



Figure 12.  $G_{1C}$  of M40-level braiding frabic/R608 composites after different numbers of the cryogenic-cycles.



Figure 13.  $G_{IIC}$  of M40-level braiding frabic/R608 composites after different numbers of the cryogenic-cycles.

Excerpt from ISBN 978-3-00-053387-7

9

# 2.4 Fracture features



**Figure 14.** SEM images of factrue features for M40-level braiding frabic/R608 composites after (a) 0, (b) 100, and (c) 300 cryogenic-cycles .

The facture feature of M40-level braiding frabic/R608 composites before cryogenic-cycles and after 100 and 300 cryogenic-cycles were measured by SEM. As shown in Figure 14, the micro-morphologies have not changed obviously after 100 and 300 cryogenic-cycles, indicating a good resistibility for the cryogenic-cycles.

# **3** CONCLUSIONS

The epoxy resin matrix composites with excellent cryogenic mechanical properties and RTM processability were developed. The cryogenic temperature had no obvious effect on tensile strength of the M40-level braiding frabic/R608 composites. While as the temperature dropped from  $80^{\circ}$ C to - 196°C, the flexural strength, compression strength, interlaminate shear strength and impact strength were improved remarkably. After 300 cryogenic-cycles, the mechanical strength and fracture toughness of M40-level braiding frabic/R608 composites have no obvious decline, indicating that the composites could effectively resist the (-196°C— $80^{\circ}$ C) cryogenic-cycles.

#### References

- [1] Evans D, Canfer SJ. Adv Cryog Eng Mater 2000, 46, pp. 361-8.
- [2] Chen Q, Gao BJ, Chen JL. *J Appl Polym Sci* 2003, **89**, pp. 1385.
- [3] Fabian PE, Schutz JB, Hazelton CS, Reed RP. Adv Cryog Eng Mater 1994, 40, pp. 1007.
- [4] Fu, X., Zhang, C., Liang, R., Wang, B. & Fielding, J. C. High Temperature Vacuum Assisted Resin Transfer Molding of Phenylethynyl Terminated Imide Composites. *Polymer Composites* 32, 2011, pp. 52-58.

- [5] Pingkarawat K. Bhat T. Craze DA. Wang CH. Warley RJ. Mouritz AP. *Polym Chem* 2013, **4**, pp. 5007.
- [6] He YX. Li Q. Kuila T. Kim NH. Jiang TW. Lau KT. Lee JH. *Compos Part B: Eng* 2013, **44**, pp. 533.
- [7] Bai N. Saito K. Simon GP. *Polm Chem* 2013, **4**, pp. 724.
- [8] Khan SU. Munir A. Hussain R. Kim JK. Compos Sci Technol 2010, 70, pp. 2077.
- [9] Yu JH. Huang XY. Wang LC. Peng P. Wu C. Wu XF. Jiang PK. Polym Chem 2011, 2, pp. 1380.
- [10] Yang G. Fu SY. Yang JP. Polymer 2007, 48, pp. 302.
- [11] Wong WY. Lin L. McGrail PT. Peijs T. Hogg PJ. Composties Part A 2010, 41, pp. 759.
- [12] Cicala G. Recca G. Carciottto S. Restuccia CL. Polym Eng Sci 2009, pp. 577.
- [13] Nograro FF. Llano-Ponte R. Mondragon I. Polymer 1996, 37, pp. 1589.
- [14] Mujika F. Benito AD. Fernández B. Vázquez A. Llano-Ponte R. Mondragon I. *Polym Compos* 2002, **23**, pp. 372.
- [15] Saalbrink A. Lorteije A. Peijs T. Composites Part A 1998, 29, pp. 1243.