Effects of post-treatment for meta-aramid nanofiber mats on the adhesion strength of epoxy adhesive joints

Seung Yoon On and Seong Su Kim

Department of Organic Materials and Fiber Engineering, Chonbuk National University, Jeonju 561-756, Republic of Korea
Email: osy1471@jbnu.ac.kr, Web Page: http://ascl.jbnu.ac.kr

Keywords: Adhesion strength, Electrospun nanofiber, Single lap joint, Nanofiber reinforcement

Abstract

The mismatch of coefficient of thermal expansion (CTE) between adherends and adhesive in cryogenic environment is one of the main reasons of the fracture and failure of adhesive joining structures. Therefore, the adhesive layer requires reinforcing materials which can reduce the CTEs to enhance the reliability of the adhesive joints. In this work, electro spun meta-aramid nanofiber mats which have high specific strength and low CTE were used to reinforce the epoxy adhesive. Microwave treatment was introduced to improve the adhesion strength through the enhancement of the mechanical strength of the nanofiber mat. Mechanical strength of microwave treated nanofiber mat was measured by tensile test with respect to the microwave irradiation time. The surface morphology and fiber orientation of the nanofiber mats were determined by a scanning electron microscopy (SEM). The residual solvent in the microwave treated nanofiber mats was checked via thermogravimetric analysis (TGA). Plasma treatment was conducted to functionalize the nanofiber mats to improve interfacial strength between meta-aramid nanofiber mats and epoxy adhesive. The characteristics of the plasma treated nanofiber mats were investigated using X-ray photoelectron spectroscopy (XPS). Single lap tests were performed to estimate the effect of the reinforcing materials on the adhesion strength. As a result, post-treated meta-aramid nanofiber mats were effectively reduced CTE of adhesive layer and increased adhesion strength.

1. Introduction

Adhesive joining structures have been widely used in cryogenic environments such as liquefied natural gas (LNG) ships and sealing parts of cryogenic containment system. The strength of the adhesive joints at the cryogenic temperatures is influenced by the property variation of adhesive at extremely low temperature and thermal residual stress generated from the large temperature difference (ΔT) from the adhesive bonding process to the operating temperature [1]. Thermal residual stresses have an important role in failure of the adhesive joint [2]. Therefore, the adhesive layer requires reinforcing materials that has low CTEs to relieve the mismatch of thermal expansion with adherends for the reliability of cryogenic structure. In addition, mechanical properties of adhesive layer are also important role in adhesion strength. Panta Jojibabu et al. showed the effect of carbon nanoparticle reinforcement in epoxy adhesive to enhance the lap shear strength [3]. Soohyun Nam et al. reinforced polyurethane (PU) adhesive with chopped glass fiber and investigated that effects of fiber length and volume fraction on fracture toughness at cryogenic environments [4]. However typical reinforcements such as carbon nano particles, clay and chopped fibers have a limit to increase their weight and volume fraction due to aggregation. The aggregation of particles and chopped fibers can cause the stress concentration in the adhesive layer, which reduces the adhesion strength significantly.

Electrospun nanofibers have several outstanding characteristics such as high surface to volume ratio, flexibility, high specific strength and modulus, and high porosity. Nanofibers can significantly increase the interaction between the fibers and the matrix materials due to its high specific area,

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

leading to better reinforcing effect than conventional fibers [5]. Moreover, the high percentage of porosity and irregular pores between the fibers can lead to an interpenetrated structure when dispersed in the matrix, which also enhances the mechanical strength due to the interlocking mechanism [6]. When a micro-crack is initiated in a matrix under contact wear and/or other stresses, the nanofibers remain intact across the crack planes and support the applied load. Therefore, crack opening is resisted by the nanofiber mats and the matrix is reinforced [7]. A few researchers have successfully fabricated nanocomposites reinforced with electrospun nanofibers. Jie Cai et al. fabricated composite film with eletrospun cellulose nanofibers and they showed the enhancement of tensile strength and modulus [8]. Michel M. Bregshoef et al. investigated the effect of electrospun nylon-4,6 fiber reinforcement on the enhancement of mechanical strength and transparency simultaneously [9].

Aramid fibers can be used to reduce the CTE and increase the mechanical strength of adhesive used in adhesively joining structures because they have high strength, good fracture toughness, excellent thermal resistance, and low density compared to inorganic fibers such as glass fibers and carbon fibers [10]. Additionally, CTE (15.0×10^{-6}/℃) of commercial meta-aramid fibers is lower than those of typical adhesives ($50\sim100\times10^{-6}$/℃) [11]. In this work, electrospun meta-aramid nanofiber mats were used to reduce the CTE and reinforce the strength of the epoxy adhesive. Microwave treatment was introduced to improve the tensile strength of the eletrospun nanofiber mats. Plasma treatments were conducted to improve the interfacial strength between meta-aramid nanofber mats and the epoxy adhesive. The effect of the nanofiber mats on the reduction of thermal residual stress and increase of adhesion strength was investigated by single-lap joint tests.

2. Experimental

2.1. Electrospinning of meta-aramid nanofibers

Meta-aramid was synthesized using an equal molar ratio of m-phenylene diamine (P23954, Sigma–Aldrich, USA) and 1,3-isophthaloyl chloride (I19403, Sigma–Aldrich, USA) in DMAc (Samchun Inc., Korea) [12]. The average molecular weight of the polymer was 381,000g/mol (DMAc, GPC). A pristine meta-aramid solution was dissolved in DMAc at 80℃ for 6 hour to prepare solutions at 14wt.% and kept in 50℃ oven for 24 hour. An electrospinning process was performed at voltage of 15kV with a distance of 10cm between the collector and the tip of the syringe. The fabricated nanofiber mats were dried for 24 hour in 50℃ oven.

2.2. Post treatment process of meta-aramid nanofiber mats

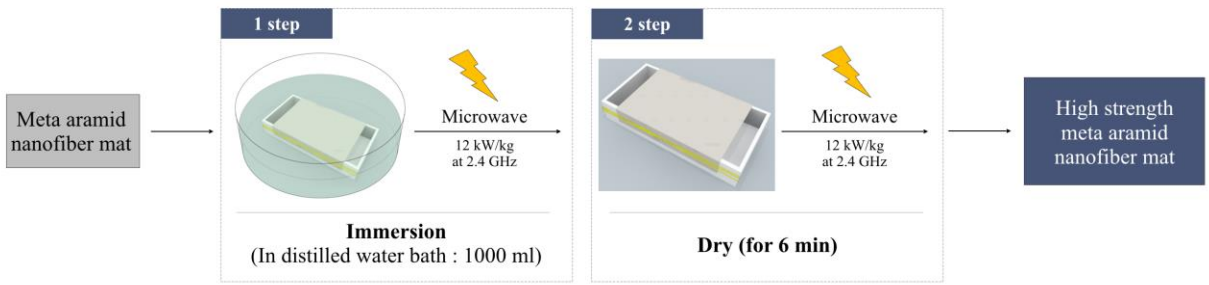

Figure 1. Schematic diagram of microwave treatment process

Microwave treatment was performed to obtaining high strength nanofiber mat, based on our previous work [13]. Microwave treatment of nanofiber mat is novel method to obtain high strength nanofiber mat in a very short time. In this work, microwave treatment was performed in the water bath for effectively removing residual solvent and by-product salt ($CaCl_2$) through the mass transfer in meta-aramid nanofiber. The microwave treatment was consisted of two-step process as shown in

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

Figure 1. In the step 1: Nanofiber mat was fixed only two part on rectangular shaped ceramic mold to produce the high aligned nanofiber. Tension was applied on longitudinal direction of fixed nanofiber mat during microwave irradiation. Microwave with an effective intensity per unit mass of 12kW/kg at 2.4GHz was irradiated on nanofiber mat during 3 min, 6 min, 9 min and 12 min. (MW_03, MW_06, MW_09 and MW_12, respectively) In the step 2 (Dry): take out the mold in the water bath and microwave was irradiated on nanofiber mat during 6 min to remove the residual water.

Plasma treatments were conducted by using a dielectric barrier discharge (DBD) plasma surface treatment system under atmospheric pressure to increase the interfacial strength between the meta-aramid nanofiber mats and the epoxy adhesive. The capacitively coupled atmospheric pressure plasma system had two parallel electrodes, the grounded electrode coated with a dielectric material (Al_2O_3) and the powered electrode and a base plate coated with the same dielectric material. The area of the electrodes and the width of the gap between them were 170 × 50 mm^2 and 1 mm, respectively [14]. The distance between electrodes and base plate were fixed at 3 mm. Plasma equipment was operated at 13.56MHz (a radio frequently) and 50,70W. The treatment time was 3-9 sec (P50W_3sec, P50W_6sec, P50W_9sec, P70W_3sec, P70W_6sec and P70W_9sec, respectively).

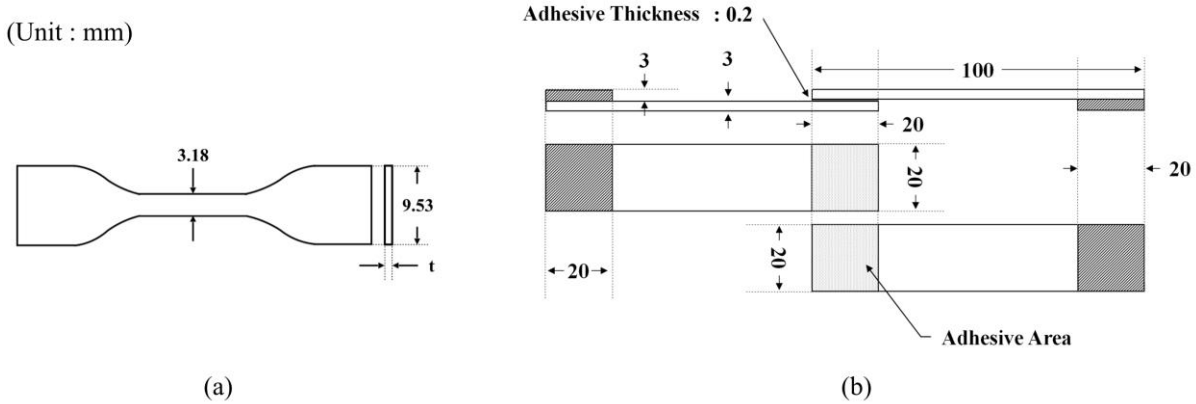

Figure 2. Specimen configuration; (a) tensile test specimens for nanofiber mats, (b) single lap joint

2.3. Tensile test of meta-aramid nanofiber mats

In order to investigate the mechanical strength of post treated meta-aramid nanofiber mats, tensile tests were performed according to ASTM D638. Figure 2 shows the detailed specimen dimensions. The gauge length, width and thickness of specimens were 15 mm, 3.18 mm, and 0.001~0.002 mm, respectively. Tensile tests were performed using INSTRON 5969 material testing system (INSTRON, USA) with 5N load cell and crosshead speed of 1.0 mm/min. Each specimens measured for 7 times were averaged.

2.4. Characterization of post treated nanofiber mats

SEM (JSM-5900, Jeol, Japan) with an acceleration voltage of 15 kV was utilized to investigate the surface morphology and fiber alignment of microwave treated meta-aramid nanofiber mats with respect to the microwave treatment time.

The residual solvent in nanofiber mat was measured by TGA (Pyris 1 TGA, PerkineElmer, USA). During the TGA analysis, the 2.0mg specimens were heated up to 800 ℃ from 25℃ at heating rate of 10 ℃/min under a nitrogen environment.

The surface modifications of plasma treated meta-aramid nanofiber mats were investigated using XPS (K Alpha+, Thermo Scientific, U.K.). Survey scans were taken in the range 0-1300eV and narrow scan were obtained of C1s and O1s peaks with respect to the plasma treatment conditions. In addition, O/C ratio was calculated by XPS scanning results.

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

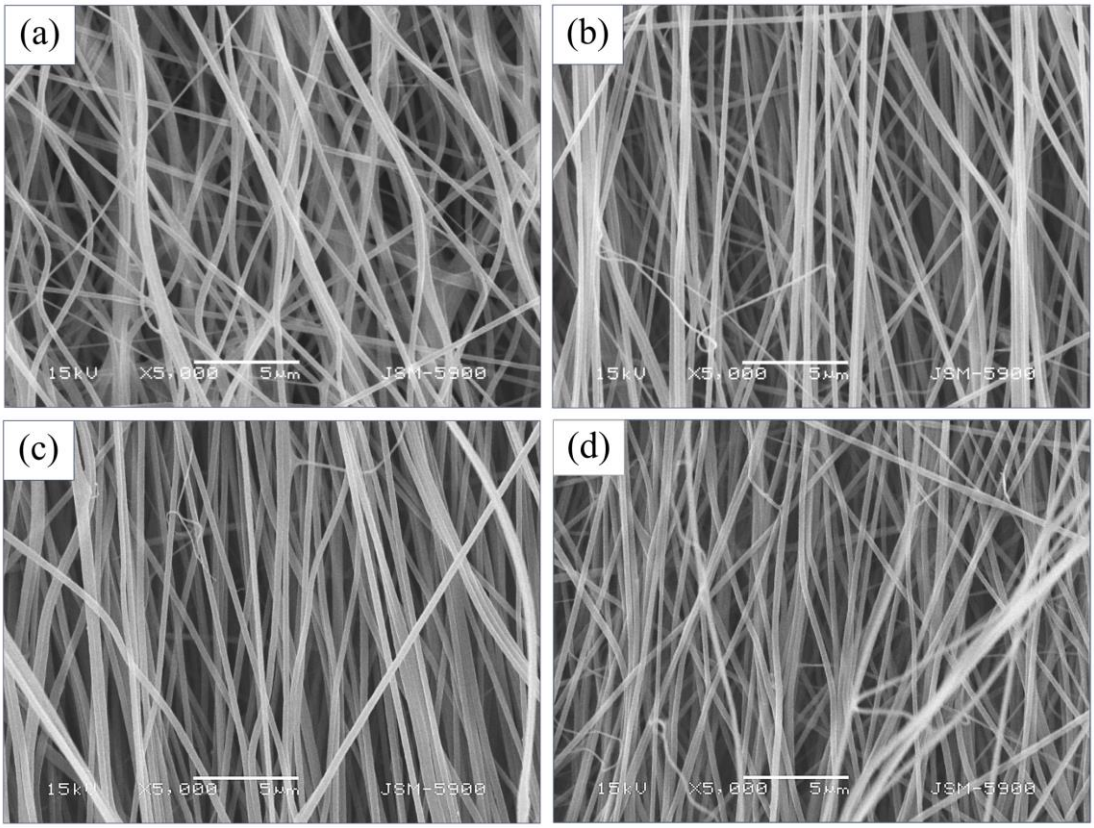

Figure 3. Morphology of nanofiber mats; (a) untreated, (b) MW_03, (c) MW_06, (d) MW_09

2.5. Single lap joint test

Single lap joint was fabricated to investigate reinforcing effect of post treated meta-aramid nanofiber mat based on ASTM D1002. The geometry and dimensions of the single lap joint is detailed in Figure 2. A S35C carbon steel was selected as an adherend and the low viscosity epoxy resin of DP-460 (3M, USA) as an adhesive. The thickness of adhesive layer was maintained at 0.2mm by using a space mold. Steel adherends were abraded by using #80 sand paper. Surface treated adherend was cleaned by acetone to remove abrasive particles and contaminants on the adhesion area.

Meta-aramid nanofiber mats which had an average thickness of 0.02~0.025 mm were carefully cut into pieces with dimension of 20mm x 20mm. The nanofiber mats were carefully placed in the specimens, after wihich the epoxy adhesive was applied to the specimens to impregnate the nanofiber mats. All the joint specimens were cured at 60 ℃ for 2 hour in the hot press. After curing, adhesive fillets of the joint were completely removed.

Single lap joint tests at the room temperature were conducted using a computer-controlled material testing machine (4206, INSTRON, USA) based on ASTM D1002. The tests were conducted with a loading speed of 1.0 mm/min. Each cases measured for 5 specimens were averaged.

3. Result and discussion

3.1. Charcterization of post-treated meta-aramid nanofiber mats

Figure 3. shows the surface morphology of meta-aramid nanofiber mats with respected to microwave treatment time. After the microwave treatment, meta-aramid nanofiber was effectively aligned to longitudinal directions because the drawing effects was occurred by elevated temperature when the microwave was irradiated on nanofiber mats. In the cases of microwave treatment time up to 6min, diameter of nanofiber was decreased and some nanofibers were broken caused by excessive

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

longitudinal tension as the microwave treatment time increased.

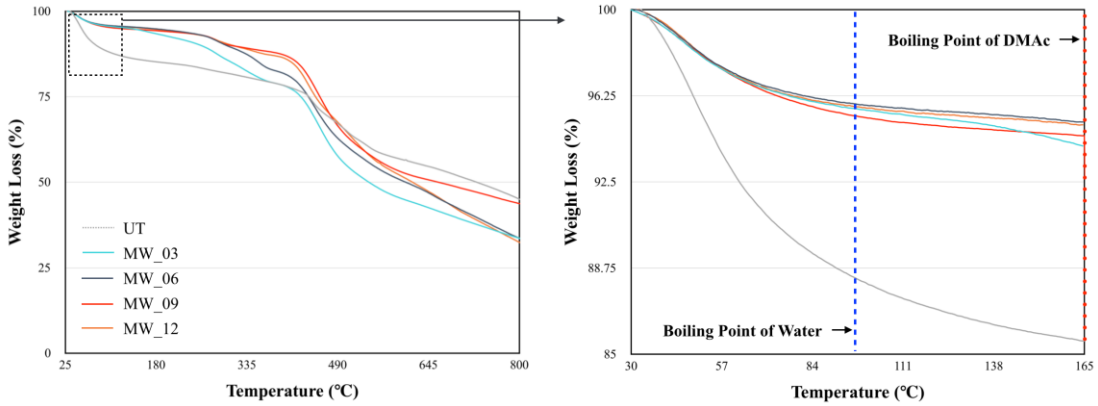

Figure 4. TGA measurement results with respect to microwave treatment time

Treatment conditions	Weight loss at 100℃ (Water)	Weight loss at 165℃ (DMAc)
UT	11.9	2.54
MW_03	4.37	1.58
MW_06	4.16	0.73
MW_09	4.70	0.78
MW_12	4.28	0.74

Table 1. TGA measurement results with respect to microwave treatment time

At the TGA analysis result shown in Figure 4, residual water and solvent contents were dramatically decreased after the microwave treatment. A summary of measured data are shown in Table 1. The reduction of residual solvent and water was caused by mass transfer (diffusion) due to the concentration differences between the nanofiber and surrounding water [15-16].

The formation of functional group via plasma treatment on the meta-aramid nanofiber mat was confirmed by XPS analysis. Scanning results are shown in Figure 5 and the summary of the recorded data is given in Table 2. In both cases of 50W and 70W, O/C ratio was decreased as plasma treatment time increased. When the treatment time was 3 second, the specimen showed the highest O/C ratio value. After 3 second for the treatment time, O/C ratio decreased due to degradation of meta-aramid nanofiber mats.

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

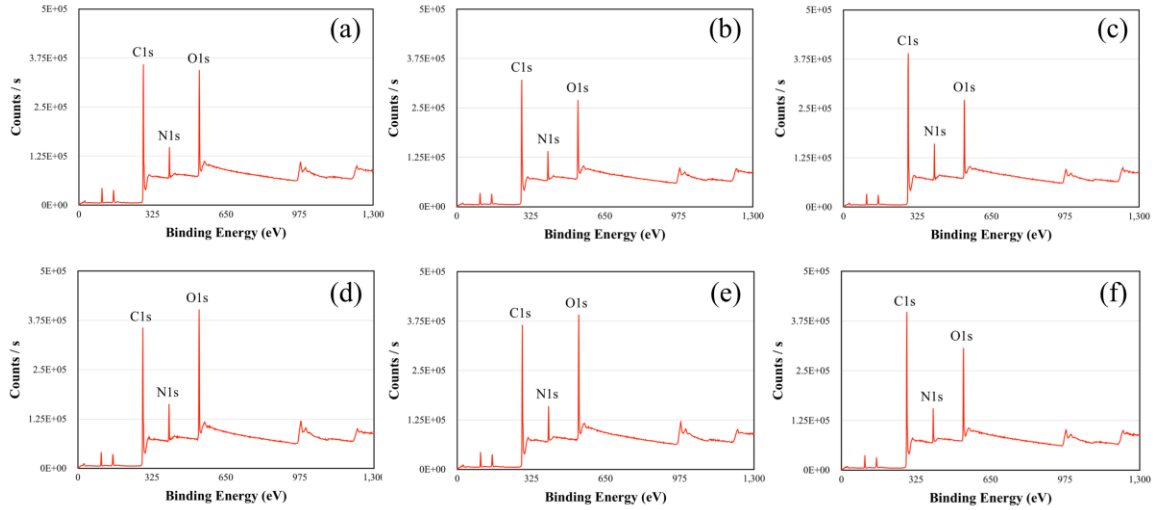

Figure 5. Result of XPS analysis. (a) P50W_3sec, (b) P50W_6sec, (c) P50W_9sec, (d) P70W_3sec,

Treatment conditions	Atomic % of C	Atomic % of O	O/C Ratio
UT	71.18	14.31	0.2
P50W_3sec	66.05	19.75	0.3
P50W_6sec	68.64	17.62	0.26
P50W_9sec	71.08	15.57	0.22
P70W_3sec	63.2	22.83	0.36
P70W_6sec	63.94	22.04	0.34
P70W_9sec	69.85	17.25	0.25

Table 2. Summary of XPS results.

3.2. Mechanical property test

Figure 6. (a) shows the tensile test results of microwave treated meta-aramid nanofiber mats. The tensile strength of MW_03 increased by 110% compared with that of untreated specimen. Over 3 min of microwave treatment time, tensile strength decreased due to high tension applied on the nanofiber mats.

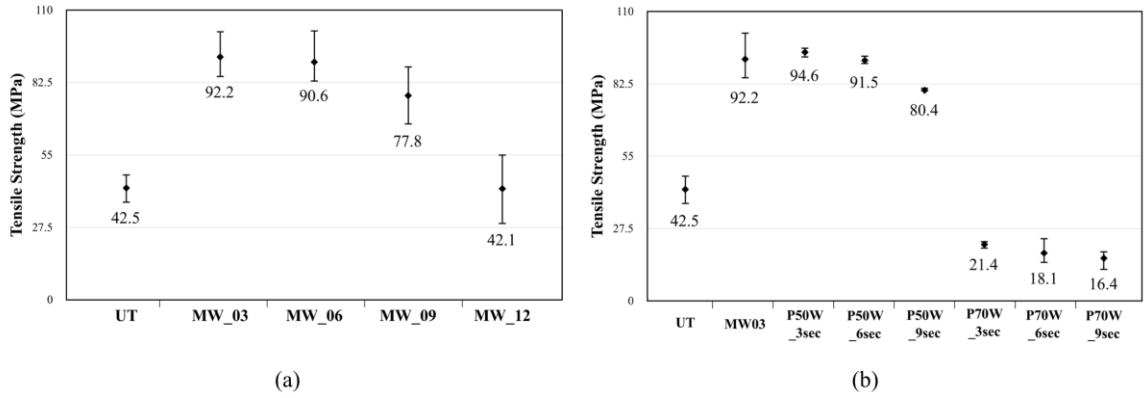

Figure 6. (a) Tensile test results of microwave treated nanofiber mats with respected to treatment time, (b) Tensile test results of plasma treated nanofiber mats with respected to plasma conditions.

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

Figure 6. (b) shows the influence of plasma treatment on the tensile strength of meta-aramid nanofiber mats. All specimen without UT were irradiated by microwave for 3 minute before the plasma treatment. P50W_3sec specimen shows the highest tensile strength and over 3 sec of the plasma treatment time caused the degradiation of the specimen. In the cases of specimen treated under 70W power, tensile strength dramatically decreased.

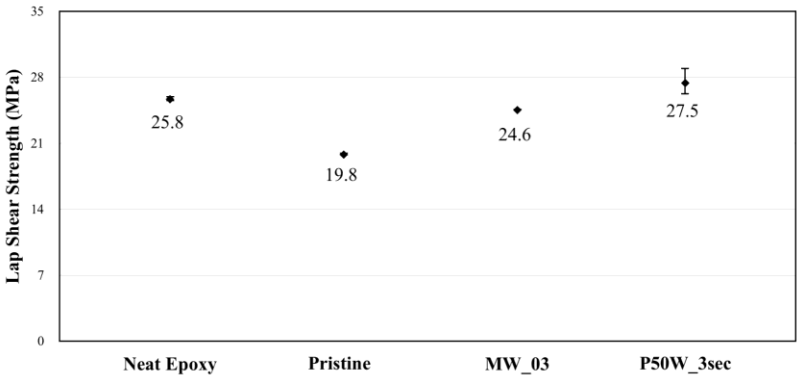

Figure 7. The result of single lap joint test

The single lap joint test results are shown in figure 7. Lap shear strength of the pristine meta-aramid mats reinforced specimen decreased because of significant amount of residual solvent in the nanofiber mats as shown in TGA results. The MW_03 specimen has almost similar strength with the neat epoxy specimen because of weak bonding between inert surface of meta-aramid nanofiber mats and the epoxy adhesive. On the other hand, lap shear strength of P50W_3sec was increased by 7% compared to that of the neat epoxy adhesive due to synergetic effect of improvement on mechanical strength of meta-aramid nanofiber mats and interfacial strength.

3. Conclusions

In this work, effects of post-treatment for meta-aramid nanofiber mats on the adhesion strength of epoxy adhesive joints were investigated. Base on the results, the following conclusions were obtained.

- Tensile strength of meta-aramid nanofiber mats increased by 116.9% after the microwave treatment.
- From the TGA analysis results, residual solvent was effectively removed through the microwave treatment.
- O/C ratio was increased about 50% when meta-aramid nanofiber mats were treated by the dielectric barrier discharge (DBD) plasma under atmospheric pressure.
- Lap shear strength increased by 7% when the post treated meta-aramid nanofiber mats (P50W_3sec) were reinforced in adhesive layer.

From the result, it was found that post treated meta-aramid nanofiber mats are promising materials to enhance the adhesion strength of single lap joints at room temperature.

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

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea(NRF) funded by the Ministry of Science, ICT and Future Planning(NRF-2014R1A1A1A05003672); it was also supported by the Ministry of Education (MOE) and National Research Foundation of Korea (NRF) through the Human Resource Training Project for Regional Innovation (2015H1C1A1035930); and it was also financially supported by the Carbon valley construction program through the Ministry of Trade, Industry&Energy(MOTIE) and Korea Institute for Advancement of Technology(KIAT). (A000600040).

References

[1] K.H. Lee and D.G. Lee, Smart cure cycles for the adhesive joint of composite structures at cryogenic temperatures. *Composite Structures*, 86:37–44, 2008.

[2] K.C. Shin and J.J. Lee, Effects of thermal residual stresses on failure of co-cured lap joints with steel and carbon fiber-epoxy composite adherends under static and fatigue tensile loads, *Composites: Part A*, 37:476-478, 2005.

[3] P. Jojibabu, M. Jagannatham, P. Haridoss, G.D. Janaki Ram, A.P. Deshpande and S.R. Bakshi, Effect of different carbon nano-fillers on reheological properties and lap shear strength of epoxy adhesive joints, *Composites: Part A*, 82:53-64, 2016.

[4] S.H. Nam, Y.H. Yu, I.B. Choi, C.S. Bang and D.G. Lee, Fracture toughness improvement of polyurethane adhesive joint with chopped glass fibers at cryogenic temperatures, *Composite Structures*, 107:522-527, 2014.

[5] Z.M. Huang, Y.Z. Zhang, M. Kotaki and S. Ramakrishna, A review on polymer nanofibers by electrospinning and their applications in nanocompsoites, *Composites Science and Technology*, 62:2223-2253, 2003.

[6] M. Tian, Y. Gao, Y. Liu, Y. Liao, R. Xu, N.E. Hedin and H. Fong, Bis-GMA/TEGDMA dental composites reinforced with electrospun nylon 6 nanocomposite nanofibers containing highly aligned fibrillar silicate single crystals, *Polymer*, 48:2720-2728, 2007.

[7] B. Avinash, M. Yiu-Wing, W. Shing-Chung, A. Mojtaba and C. Pei, Electrospinning of polymer nanofibers: Effects on oriented morphology, structures and tensile properties, *Composites Science and Technology*, 70:703-718, 2010.

[8] C. Jie, C. Jingyao, Z. Qian, L. Miao, H. Jingren and X. Anhong, Well-aligned cellulose nanofiber-reinforced polyvinyl alcohol composite film: Mechanical land optical properties, *Carbohydrate Polymers*, 140:238-245, 2016.

[9] M.M. Bregshoef and G.J. Vancso, Transparent Nanocomposites with Ultrathin, Electrospun Nylon-4,6 Fiber Reinforcement, *Advanced Materials*, 11:1362-1365, 1999.

[10] K.L. Mittal, Contact angles, wettability and adhesion, *Vol. 6, Leiden: Brill NV*, 2009.

[11] A.J. Kinloch, Addhesion and adhesives, *London: Chapman and Hill*, 1987.

[12] King FW. Du Pont Company. United States patent US 3,079,219; 1960. .

[13] H.J Oh, S.H. Han and S.S. Kim, A Novel Method for a High-Strength Electrospun Meta-Aramid Nanofiber by Microwave Treatment, *Journal of polymer science, Part B: Polymer Physics*, 17:807-814, 2014.

[14] J.K. Kim and D.G. Lee, Adheison characteristics of plasma surface treated carbon/epoxy composite, *Journal of Adhesion Science and Technology*, 17:1017-1037, 2003.

[15] J. Chen, C. G. Wang, X. G. Dong, H. and Z. Liu, Study on the Coagulation Mechanism of Wet-Spinning PAN Fibers, *Journal of Polymer Research*, 13:515-519, 2006.

[16] R. N. Ibbett, and Y. L. Hsieh, Effect of Fiber Swelling on the Structure of Lyocell Fabrics, *Textile Research Journal*, 71:164-173, 2001.

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