EFFECT OF RESIDUAL SOLVENT AND CaCl$_2$ ON MECHANICAL PROPERTIES OF ELECTROSPUN META ARAMID NANOFIBER/EPOXY ADHESIVES

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1 Introduction

Epoxy resin has been widely used as adhesive materials due to their excellent adhesion strength and good chemical/corrosion resistance. Epoxy adhesives become quite brittle at cryogenic temperature, although some of them are ductile at the room temperature. Furthermore, the adhesives generate large thermal residual stress at the cryogenic temperature due to their high CTEs [1]. Therefore, both the mechanical and thermal properties of adhesives should be improved to increase the fracture toughness and durability of adhesive joints at cryogenic environment. Many studies have been paid to enhance the properties of adhesives by reinforcing with particles or fibers [2-4]. Aramid fibers are one of the strong candidates for reinforcing epoxy adhesives due to their relatively low CTE and high fracture toughness. But the aramid fibers exhibit poor adhesion characteristics which are affected by its chemically inert and insufficient functional groups [5-6].

Electrospinning is relatively simple method to fabricate the nanofibers offering a high specific surface area and high porosity with diameter ranging from nano to micro scale. This method also makes it possible to form unique morphologies or attach functional groups on the fiber surface by solution modification such as polymer blending and sol-gel method. However, there is a limit for the electrospun nanofibers to be applied in structures such as aircrafts and automobiles due to their lower mechanical strength than textile fibers made from same polymers [7].

Electrospinning utilizes high electrostatic forces for fiber production. The typical electrospinning apparatus consists of three major components: a high-voltage power supply, a spinneret (a metallic needle), and a grounded collector. When the electric field is applied, the polymer becomes charged. The electrified jet of polymer solution begins to stretch and whip around forming a long and thin thread. The liquid solution is continuously elongated and the solvent is evaporated during the whipping stage leaving an almost dry polymer fiber behind [8]. In this later stage, the rapid solidification of stretched chains induced the retardation of crystallization [9]. Thus, the mechanical property of electrospin nanofiber became lower. Recently, many studies have been paid to improve the strength of electrospin nanofiber. Huang et. al [10] found that the mechanical property of highly aligned PBDAPDA PI nanofiber mats increased by 4~6 times with heat treatment under high-temperature (300 ~ 430°C). Chen et. al also investigated that the tensile strength and elongation at break of the PI composite film reinforced with 2 wt% CNT/PI nanofibers were increased by 138% and 104%, respectively [11]. The residual solvent and salt after electrospinning also affect to the mechanical properties of the nanofibers. Li et. al demonstrated that metal halides, such as NaCl, LiCl, and CaCl$_2$, remaining in Nylon 6 decreased the fracture toughness, tensile strength,
modulus due to plasticization by ionic salts [12]. Furthermore, the residual solvents are also known to plasticize the polymers matrix [13].

Meta aramid, poly (m-phenyleneisophthalamide), as aromatic polyamide consists of a relatively rigid benzene ring and amide group. It was strongly hydrogen bonded with inter and intra molecular. When the meta aramid was fabricated by electrospinning, the residual solvent and by-product salts such as CaCl₂, LiCl were generated to the electrospun nanofiber owing to difficulty of removal during the process. The presence of by-product salts and residual solvent in the nanofiber is also known to deteriorate its mechanical strength. However, few reports have been studied on the influence of the residual or by-product salt on mechanical/ thermal property of the nanofiber.

Microwave technology is based on the efficient heating of materials by “microwave dielectric heating” effects in a short time. This effect is dependent on the ability of a specific material (solvent or reagent) to absorb microwave energy and convert it into heat. The electric component of an electromagnetic field causes heating by two main mechanisms: dipolar polarization and ionic conduction. Irradiation of the sample at microwave frequencies results in the dipoles or ions aligning in the applied electric field and, in the process, energy are lost in the form of heat through molecular friction and dielectric loss [14]. Recently, microwave has attracted a considerable amount of attention in many applications including the synthetic chemistry, solvent extraction [15].

In this study, the effect of residual solvent and CaCl₂ as by-product on the mechanical strength of the meta aramid nanofibers was investigated by using microwave. To reduce the impurity of the nanofiber, the specimen was treated by each condition of the “moist” and “wet”. FE-SEM was used to observe the surface morphology of the electrospun nanofiber mats with respect to the treatment time. The change of crystallinity and thermal properties was investigated using X-ray diffraction (XRD) and TGA measurements. The tensile test was performed to observe the influence of degree of residual solvent and CaCl₂ salt (by-product) removed by microwave on mechanical properties of the nanofiber. And the mechanical properties of the meta aramid nanofiber/epoxy composites with respect to treatment condition by a tensile test.

2 Experimental details

2.1 Materials

Meta-aramid was polymerized according to a well-known procedure 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) [16]. During the reaction, HCl was formed as a by-product and was neutralized with Ca(OH)₂. The neutralization process produced CaCl₂ salt (by-product) in the polymer solution. The average molecular weight of the polymer was 381,464 g/mol (DMAC, GPC). The synthesized polymer and CaCl₂ (by-product) were used for electrospinning without further purification. The presence of the salt may increase the solubility of the polymer and the conductivity of the solution, which enhance the ease and stability of the electrospinning process [17].

![image](image_url)

Fig.1 Schematic diagram of electrospinning method

2.2 Electrospinning

Meta-aramid was dissolved in DMAC to make 14 wt% solution. After the solution was inserted into the pipet, the meta aramid nanofiber was fabricated by electrospinning method as shown in
In this study, the removal of residual solvent and CaCl$_2$ in the meta aramid nanofiber was performed under microwave irradiation using an effective intensity per unit mass of 12 kW/kg at 2.4 GHz. The heating mechanism of the solvent under microwave irradiation conditions depends on its dielectric properties. The ability of a material to convert electromagnetic energy into heat at a given frequency and temperature is determined by the loss factor tanδ [14]. Generally, the loss factor of polymers is relatively lower than others (e.g. water). In this study, two kinds of treatment conditions with respect to moist contents were facilitated to enhance the loss factor of a dielectric material. As moist conditions, the moisture was initially absorbed into the nanofibers by spraying water. Then, the moist nanofiber was heated by microwave for 6, 12, and 18 min to remove the residual solvent. To determine the proper treatment time, the weight loss of the nanofibers was measured. As the wet conditions, the sample was soaked in 500 ml distilled water bath to remove the CaCl$_2$ from the surfaces or inner part in the nanofibers and then irradiated for 5, 10, and 15 min by using microwave. The time variables for the microwave treatment were set based on the time for the water temperature to reach a boil. After recovering the specimens from the water bath, the specimens were heated again using microwave to remove the water from the nanofiber for 6 min. The temperature of the water bath was measured by using a thermocouple.

2.4 Characterization

Field emission scanning electron microscopy (S-7400, Hitachi Co., Japan) whose acceleration voltage is 15 kV was used to observe the surface morphology of the electrospun nanofiber mats with respect to the microwave treatment time. And the average diameter of the nanofiber also measured by SEM for at least 30 ~ 40 specimens. The presence of CaCl$_2$ was also investigated to check the component by SEM-EDX. The thermal behaviors of the nanofibers with respect to the treatment condition was examined by using thermogravimetric analysis (TGA 6, PerkinElmer, USA) under nitrogen flow from 40 to 700°C at a heating rate of 10°C/min. The crystallinity characteristic of the nanofibers was determined by X-ray diffraction (X’pert Powder, PANalytical, Netherland) using Cu Kα$_1$ radiation (λ=1.54 Å) at a voltage of 40 kV and a current of 40 mA and recorded Bragg angles (2θ) range from 5° to 80°.

Mechanical properties of the nanofiber mats and the nanofiber toughened epoxy films were measured with a universal material testing machine (Model 5567, INSTRON, USA) at a crosshead speed of 1 mm/min. The nanofiber toughened epoxy adhesive (Resin: AW106, Hardener: HV953U, Araldite, Huntsman, UK) film was fabricated using the mold space of thickness 0.2 mm. All the specimens were cured in a dry oven at 80°C for 2 hours. The fiber volume fraction of the epoxy adhesives was approximately 20% calculated by a photomicrographic technique using SEM. These specimens were prepared in the form of standard dog-bone shapes according to ASTM standard D 638 by die-cutting the film. The samples were tested along the fiber alignment direction and the average tensile strength obtained from each samples was compared with respect to the treatment condition for the nanofibers. The thickness of the specimens was measured using a digital micrometer (Mitutoyo Absolute, Japan).
3 Result and discussion

Fig. 3 showed the surface morphologies of the meta aramid nanofibers with respect to the irradiation time by microwave. The surface roughness was increased and the bonding between adjacent fibers was also generated as the irradiation time increased. Fig. 4 presented that the average diameters of fibers increased until the critical points and after that, it decreased in spite of time increases.

In moist condition of the microwave, the moisture heated the nanofiber up to its boiling point. The salt contents made the nanofiber to be reached the higher temperature due to its ability of absorbing microwave energy [18]. The plastic deformation occurred as the temperature reaches above the Tg of fibers. While the water molecule and residual solvent was evaporated under a high temperature, the pressure gradient was generated in the nanofibers and then, the vapor was diffused from inside into outside of the fiber. In this process, if the amount of the vapor which moved to the surface inner layer is greater than the amount of the expulsion toward the outside of the fiber, the portion of the vapor will be remained in surface inner layer. Furthermore, the vapor (water, residual solvent) remained in the surface inner layer is converted from the vapor to the liquid due to the temperature difference between the inside of the fiber and the outside of the fiber. As a result, the surface layer of the fiber was melted to form the skin adjacent fiber on the portion of the surface due to the liquefied remaining solvent [19,20]. However, the amount escaping from the inside to the outside was limited due to the surface skin indicating closed system. At a critical point, the amount of moisture was gradually decreased and the pressure also reduced by decrease of vaporization [21]. It indicates that the average diameter of the nanofiber will be decreased as the treatment time passed by the critical point.

Fig. 5 shows the images of the nanofiber surface with respect to microwave treatment time under the wet condition. We observed that the surface roughness and diameters of the nanofibers were increased (W05) by treatment condition under its boiling temperature. On the other hand, above the boiling point, the surface roughness and diameter was decreased (W10). But, after 15 min, the diameter and surface roughness might be
slightly increased due to swelling of the fiber. Wet condition is composed of 2 steps; (1) the microwave irradiation, (2) the dry process by microwave. In this condition, the water bath was boiled at 9 min for 500 ml of water. In this process, the removals of the residual solvent and CaCl$_2$ in the nanofibers are easier than moist condition due to the generation of mass transfer (diffusion) in water bath. Besides, the water bath treatment bath facilitates the crystallization and the rearrangement in the nanofiber. In the second step, the nanofiber mats dried by microwave (6 min). Since there were few salt and residual solvent unlike the moist condition, the fusion had not occurred.

The SEM-EDX was performed to observe the presence of CaCl$_2$ after the microwave treatment as shown in table 1. After electrospinning, the contents of CaCl$_2$ were remained on meta aramid nanofiber. After the moist condition treatment, the contents of CaCl$_2$ was decreased by 15~40%. It caused by the degradation of salts in the highly elevated temperature [18]. On the other hand, in case of wet condition, the contents of CaCl$_2$ were significantly reduced within 2% for 5 min.

Furthermore, the contents of CaCl$_2$ were almost removed by treatments for 15 min. It indicates that the microwave treatment with water bath was very effective on the removals of CaCl$_2$.

Fig. 6 shows the XRD results of the nanofibers with respect to the microwave treatment. The broad peak at 24° showed the amorphous region of electrospun meta aramid mats. Generally, it is difficult to fabricate the highly crystallized nanofiber due to the rapid solidification during electrospinning [9]. However, in case of wet condition, the sharp two peak of α-phase crystalline was shown at 14.8°, 16.7°, 22.5°. The crystallinity was also significantly increased. As a result, the wet condition of microwave was favorable to the rearrangement of the molecular chain and crystallization. The dry process of wet condition also made the structure of the nanofibers become a dense [22].

Thermal properties of polymers are highly affected by its structure, size, and crystallinity. Fig. 8 showed the thermal properties of nanofiber mats with respect to treatment condition. The untreated specimens including the by-product salts and residual solvent presented the weight loss of 7% at 100°C and then continuously degraded. In case of moist condition of microwave, the specimens showed a low thermal stability compared to that of untreated specimens, because its skinned surface (Fig.3) might be hinder the vaporization of the moist resulted in residue of moisture. On the other

Table. 1 The EDS results of the meta aramid nanofiber treated with each process

<table>
<thead>
<tr>
<th>Element</th>
<th>% Cl</th>
<th>% Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>No treated</td>
<td>21.28</td>
<td>11.69</td>
</tr>
<tr>
<td>S6</td>
<td>17.95</td>
<td>9.91</td>
</tr>
<tr>
<td>S12</td>
<td>18.11</td>
<td>9.67</td>
</tr>
<tr>
<td>S18</td>
<td>12.61</td>
<td>6.86</td>
</tr>
<tr>
<td>SA5</td>
<td>1.39</td>
<td>0.72</td>
</tr>
<tr>
<td>SA10</td>
<td>1.05</td>
<td>0.58</td>
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<tr>
<td>SA15</td>
<td>0.13</td>
<td>0.11</td>
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</tbody>
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Fig. 6 XRD results of the nanofiber treated with microwave at each condition.

Fig. 7 Thermal properties of the nanofiber treated with microwave at each condition.
hand, the specimens treated with the wet condition showed the high thermal stability compared to that of untreated specimens. The weight loss at 100°C was decreased as follows 3.8%, 1.9%, 0.7% as treatment time increased. As a result, the removal of impurity (residual solvent, salt) in nanofiber mats could significantly increase the thermal stability of the fibers.

Fig. 9 showed the result of tensile strength of the nanofiber mats with respect to treatment condition by microwave, respectively. The nanofiber mats treated in moist condition with 12 min was significantly increased by 2.3 times compared to that of untreated one. It indicates that the skinned structure of nanofibers with adjacent fiber is affect to its mechanical properties. In case of the wet condition, the specimens with 5 min presented the highest value improving 2.6 times in all specimens because treatment in water bath can make the impurity of the nanofiber to remove resulted in the high crystallinity related to mechanical strength. However, the mechanical strength of the specimens with long treated time decreased due to the expansion by swelling.

The tensile tests were conducted to obtain the strength of the meta-aramid nanofibers toughened epoxy composite films after the microwave. Fig. 10 shows the result of the tensile strength of meta aramid nanofiber toughened epoxy composite film. Among them, the tensile strengths of the specimens toughened with W05 and W10 were significantly enhanced by 38 ~ 55% compare to that of the neat epoxy. However, the tensile strengths of specimens toughened with M06, 12, 18 were slightly increased by 10 ~ 17% compared to that of the neat epoxy. Since the effective surface area of the nanofibers was decreased by forming the bonding between the adjacent fibers, the wettability might be decreased. From the results, the mechanical strength of the nanofiber toughened epoxy composites was affected by the strength of nanofiber and its geometric property. The microwave treatment with wet condition can improve the strength of the nanofiber with excellent wettability.

4 Conclusions

In this study, the effects of residual solvent and CaCl₂ salt (by-product) on the mechanical strength of the meta-aramid nanofibers were investigated by using microwave. The following conclusions were derived from the results.

1. The surface roughness and diameter of the meta-aramid nanofiber were increased as treatment time increases.

2. The wet condition of the microwave (W15) to the nanofiber is most effective on the removal of by-product CaCl₂ with the amount of from 33% to 0.2%. Furthermore, in case of moist condition, the salt also was reduced by 15 ~ 40% due to degradation by highly elevated temperature.
3. The thermal stability and crystallinity of the nanofiber were enhanced by wet condition of microwave. In case of wet condition, it is favorable to removal of impurity and re-arrangement of molecules in the nanofiber.

4. Tensile strength of the specimens can be dramatically increased up to 2.6 times by both moist and wet conditions inducing the change of surface geometry and enhancing of crystallinity.

5. The tensile strength of epoxy toughened with nanofiber at the wet condition (W15) was significantly increased by 54%. However, the specimens toughened with nanofiber treated in moist condition was slightly increased by 10~17% due to lack of the effective surface.

From the results, we concluded that the presence of the residual solvent and by product salts also significantly affect to the degradation of the mechanical strength of nanofiber. We also suggested that microwave treatment is very effective method to increase the mechanical property of the nanofiber by reducing impurity in a short time.

References


