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# The mechanical interlocking and wetting at the interface between argon plasma treated UHMPE fiber and vinylester resin

S. I. MOON, J. JANG*
*Department of Chemical Technology, Seoul National University, Shinlimdong, San 56-1, Kwanakgu, Seoul, Korea 151-742*
*E-mail: jsjang@plaza.snu.ac.kr*

The ultra high modulus polyethylene (UHMPE) fiber was treated with argon plasma in order to improve the interfacial adhesion of UHMPE fiber/vinylester composites. Argon plasma treatment of the UHMPE fiber introduces micro-pittings and roughness onto the UHMPE fiber surface. These micro-pittings and surface roughness increase the interfacial adhesion of the UHMPE fiber/vinylester composites through the mechanical interlocking between the UHMPE fiber and vinylester resin. Argon plasma treatment also changes the UHMPE fiber surface into chemically more inert state in comparison with the control UHMPE fiber surface. These chemical changes decrease the efficiency of the mechanical interlocking as the inert surface makes the wetting of the UHMPE fiber by the vinylester resin difficult. In this study, the mechanical interlocking through the micro-pittings is known to play a key role in improving the interfacial adhesion of UHMPE fiber/vinylester composites by the argon plasma treatment. However, the complete wetting of the UHMPE fiber by the vinylester resin is known to be an important requirement for the effective mechanical interlocking between the UHMPE fiber and vinylester resin.

## 1. Introduction

The UHMPE fiber made from ultra-high molecular weight polyethylene by gel spinning method has excellent tensile modulus and tensile strength. Especially, due to low density the UHMPE fiber has most excellent specific tensile properties of all commercial reinforcing fibers [1–4]. Another outstanding property of the UHMPE fiber is its impact energy absorption capability. These excellent tensile properties combined with impact energy absorption capability make the UHMPE fiber applicable for many composite materials [4–11].

However, UHMPE fiber has inert surface and shows poor interfacial adhesion in composite materials. Therefore, the surface modification of UHMPE fiber has been an important research subject [12–23]. Of various surface treatment methods, low temperature gas plasma treatment (especially using oxygen) has been known to be effective for improving the interfacial adhesion of the UHMPE fiber composites [13–23].

Oxygen plasma treatment introduces oxygen containing chemical functional groups and micro-pittings on the UHMPE fiber surface. The chemical functional groups enhance the wetting of the UHMPE fiber surface by matrix resin and improve the interfacial adhesion between the UHMPE fiber and matrix resin. The micro-pittings induce mechanical interlocking between the UHMPE fiber and matrix resin and improve the interfacial adhesion. In order to investigate the relative importance of these two factors, many researches have been performed [14–17]. However, single consistent conclusion is difficult to be obtained because the plasma treatment results of UHMPE fiber are dependent on many parameters such as UHMPE fiber type, plasma reactor type, plasma treatment conditions and so on.

In this paper, in order to investigate the relative importance of chemical changes and micro-pittings on the UHMPE fiber surface in improving the interfacial adhesion, the UHMPE fiber was treated using argon plasma as a function of plasma treatment time. Argon is a inert gas and was thought to introduce micro-pittings without much chemical modifications. In addition, the argon plasma treatment of UHMPE fiber is compared with the oxygen plasma treatment in order to study the effect of carrier gas.

## 2. Experimental

### 2.1. Material

UHMPE fiber used in this experiment was Spectra 900 plain fabric. XSR-10 vinylester resin from Sewon Chemical Co. (Korea) was used as matrix resin. This

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* Author to whom all correspondence should be addressed.

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matrix resin is a kind of vinylester resin modified with carboxyl terminated acrylonitrile butadiene (CTBN) rubber. Benzoyl peroxide (BPO) was used as a curing agent and diallyl phthalate (DAP) was used as a crosslinking agent. Acetone was used as initiator solvent and viscosity reducer.

## 2.2. Argon plasma treatment

Plasma treatment apparatus manufactured by Korea Vacuum Co. (Korea) was used for the surface treatment of the UHMPE fiber. This plasma treatment apparatus is a parallel electrode type with a 13.56 MHz radio frequency (rf) generator. The powered electrode on which the sample is placed has the diameter of 35 cm and the distance between the two electrodes is 8 cm. The flow rate of argon was fixed at 9 sccm and the plasma output power was adjusted to 100 W.

## 2.3. Prepreg manufacturing

Resin bath was made by mixing the XSR-10 resin : DAP : BPO : acetone in the weight ratio of 100 : 20 : 1.2 : 15. The argon plasma treated UHMPE fiber fabric was impregnated into this resin bath and dried for 1 day at room temperature.

## 2.4. Composite manufacturing

The UHMPE fiber/vinylester composites were manufactured by open leaky mold method using a laboratory hot press. The curing temperature was 100 °C and the curing pressure of 4.1 MPa (≈600 psi) was applied after the initial 10 min. The total curing time was 2 h. The thickness of the samples was fixed at 2.7 (±0.1) mm.

## 2.5. Interfacial adhesion measurement

The interfacial adhesion of the UHMPE fiber/vinylester composites was measured as interlaminar shear strength (ILSS) by three point short beam method according to ASTM 2344 test method. The samples were cut in the size of 10 × 18 mm using a water jet cutter. The used span length was 12 mm and the crosshead speed was fixed at 2 mm/min. A LLOYD LR-10K universal testing machine was used for the ILSS measurement.

## 2.6. Surface analysis

The chemical change of argon plasma treated UHMPE fiber was investigated using diffuse reflectance FT-IR (DRIFT) spectroscopy. A Bomem MB-100 spectrometer with a deuterated triglycine sulfate (DTGS) detector was used. Dry nitrogen was purged to remove the interference of atmospheric $H_2O$ and $CO_2$. The resolution was fixed at 4 $cm^{-1}$ and total 200 scans were coadded.

The morphological changes of argon plasma treated UHMPE fiber surface were observed using scanning electron microscope (SEM). A Jeol JSM 840A microscope was used and gold coating was applied to the samples to give electronic conductivity.

## 3. Result and discussion

Argon is an inert gas and argon plasma treatment of polymer surface has been investigated in order to improve the printability, adhesion, and various properties of polymer surface. In this study, UHMPE fiber was treated with argon plasma in order to improve the interfacial adhesion of UHMPE fiber/vinylester resin [24].

Fig. 1 shows the variation of the interlaminar shear strengths in UHMPE fiber/vinylester composites with argon plasma treatment time. Argon plasma treatment of the UHMPE fiber improves the interfacial adhesion of UHMPE fiber/vinylester composite and maximum interlaminar shear strengths showed up at 3 min plasma treatment in this experimental condition.

Although argon is a chemically inert gas, energetic argon plasma can modify the UHMPE fiber surface in several ways. Firstly, argon plasma etches the UHMPE fiber surface by the collision of energetic particle such as argon ion to the UHMPE fiber. Plasma etching of UHMPE fiber is known to introduce micro-pittings on the UHMPE fiber surface [14–17]. Secondly, argon radicals or argon ions chemically modify the UHMPE fiber surface and functional groups can be introduced. As argon is a chemically inert gas, crosslinking through the combination reaction would take place if there is no contact with other gases. However, the argon plasma treated UHMPE fiber sample is contacted with air after the plasma treatment and the oxygen containing functional groups can be introduced through the reaction between the entrapped radical and oxygen [24].

The morphological changes of the UHMPE fiber surface by the argon plasma treatment were investigated using SEM and the SEM photographs of the argon plasma treated UHMPE fiber are represented in Fig. 2. Fig. 2a is the SEM photograph of control UHMPE fiber surface and small pittings can be seen although untreated fiber is expected to show clean and smooth surface. From this figure, the UHMPE fiber is thought to have been surface-treated by the manufacturer. These

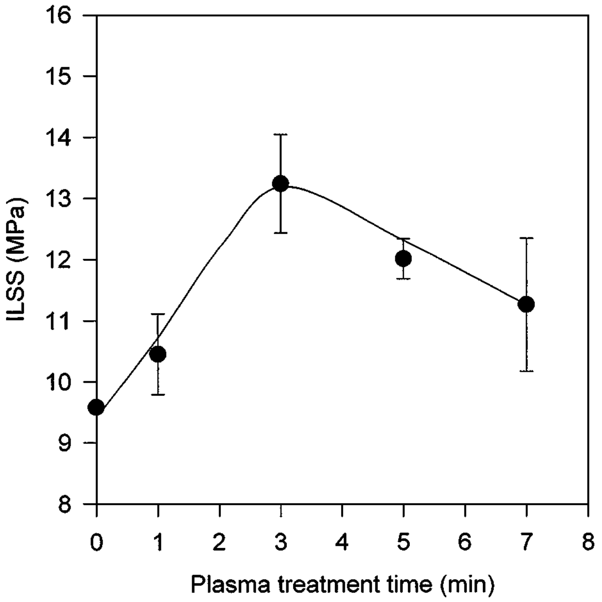

*Figure 1* The changes of interlaminar shear strengths of UHMPE fiber/vinylester composites with the argon plasma treatment time of the UHMPE fiber.

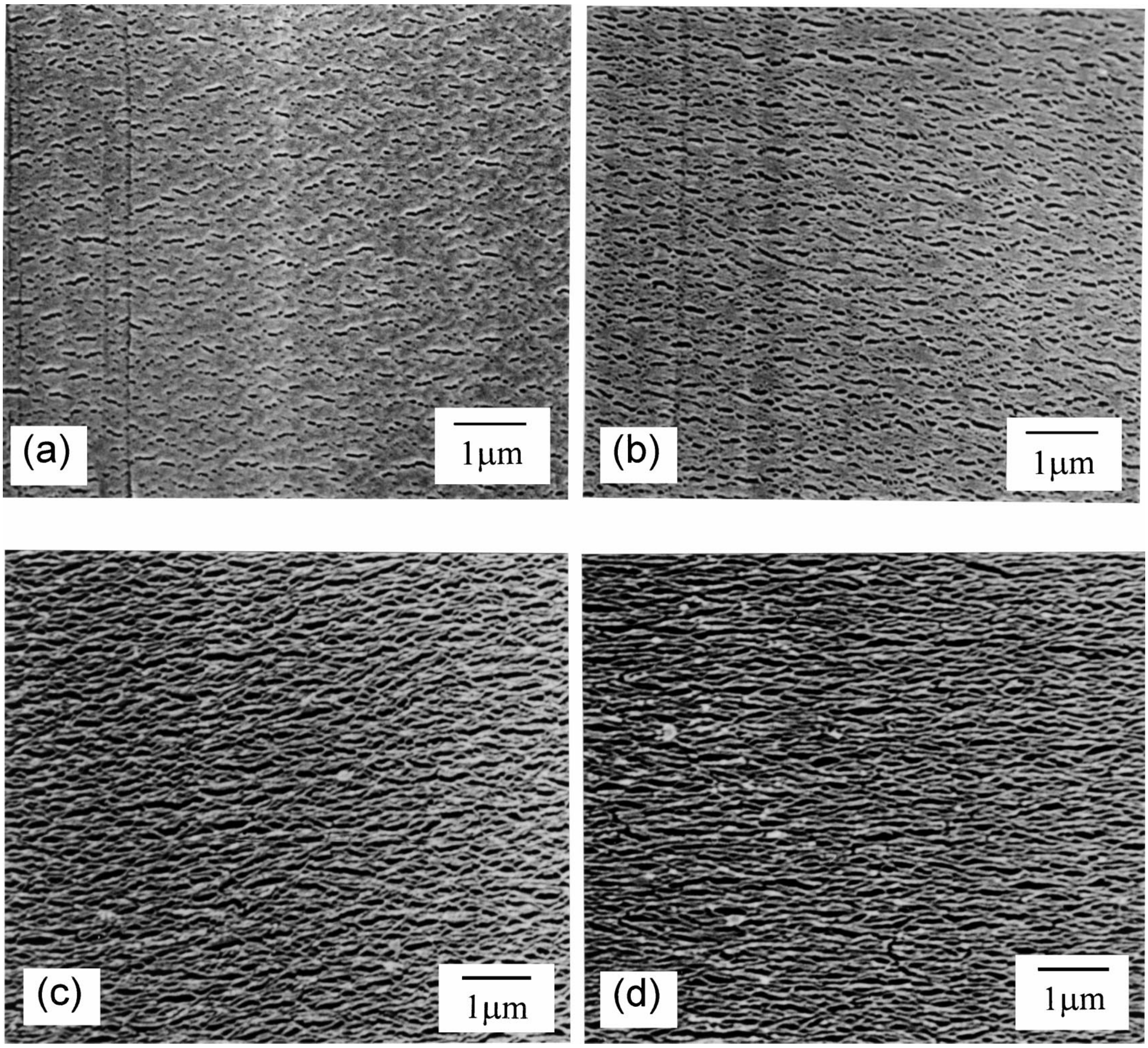

*Figure 2* The SEM photographs of argon plasma treated UHMPE fiber surface: (a) control; (b) 1; (c) 3; and (d) 5 min treatment.

pittings may be introduced during the fiber manufacturing process. However, the exact origin of these pittings could not be known.

Fig. 2b–d represent the SEM photographs of the UHMPE fiber surface after the argon plasma treatment for 1, 3, and 5 min in turn. The introduction of extensive micro-pittings and surface roughness by the argon plasma treatment can be seen from the figure. One minute argon plasma treatment of the UHMPE fiber increases the size of micro-pittings and makes the UHMPE fiber surface a little rough. Three minute argon plasma treatment increases the micro-pittings and surface roughness of the UHMPE fiber surface greatly (Fig. 2c). There is no large change in SEM photographs after 3 min argon plasma treatment of the UHMPE fiber comparing the Fig. 2c with the Fig. 2d.

These micro-pittings improve the interfacial adhesion of the UHMPE fiber/vinylester composites through the mechanical interlocking between the UHMPE fiber and impregnated vinylester resin. It has been known that this mechanical interlocking plays a very important role in improving the interfacial adhesion of plasma treated UHMPE fiber composites [10, 14–16]. However, in order for these micro-pittings to be effective in the interfacial adhesion of UHMPE fiber composites, the contact between the UHMPE fiber surface and matrix resin is required [17]. If the contact between the UHMPE fiber and vinylester resin is not complete, the interfacial voids may act as weak points in the interfacial adhesion of the UHMPE fiber composites.

In order to investigate the chemical changes of the UHMPE fiber by the argon plasma treatment, DRIFT spectroscopy was used. It is well known that the DRIFT spectroscopy is useful to investigate the surface of particle or fiber samples [25–27]. Fig. 3 represents the DRIFT spectrum of the control UHMPE fiber in the spectral region from 2000 to 600 $\text{cm}^{-1}$. The peaks at 1473 and 1464 $\text{cm}^{-1}$ are due to $CH_2$ bending mode and the peaks at 730 and 720 $\text{cm}^{-1}$ are due to $CH_2$ rocking mode. Some of other small peaks are attributed to the crystalline phase and some peaks are due to combination mode [28]. At 1740 $\text{cm}^{-1}$, there is a small peak and is thought to be from carbonyl group. Considering from this DRIFT spectrum and SEM photograph in Fig. 2a, the UHMPE fiber is thought to have been surface-treated by the manufacturer.

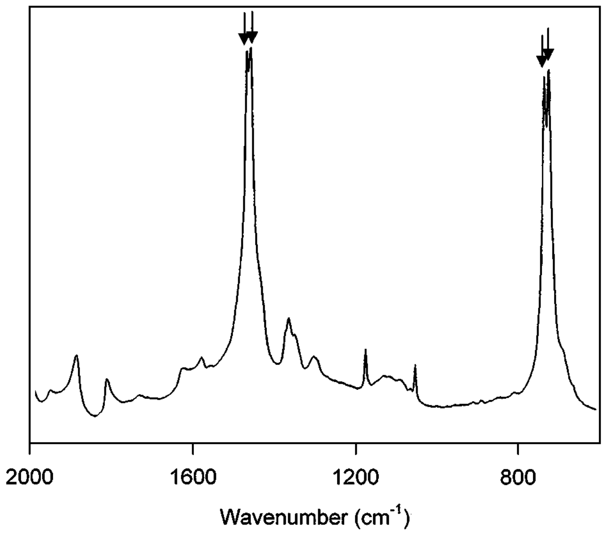

*Figure 3* The DRIFT spectrum of control UHMPE fiber.

The chemical changes of the UHMPE fiber by the argon plasma treatment can be investigated by observing the changes of peaks due to carbonyl, C−O single bond and C=C double bond. In this study, the changes of the integrated peak intensities from carbonyl, C−O single bond and C=C double bond were investigated. The peak due to carbonyl stretching is assigned to 1740 cm$^{-1}$, the peak from C=C stretching to 1632 cm$^{-1}$, and the peak due to C−O stretching is near 1100 cm$^{-1}$. The peak at 1894 cm$^{-1}$ is due to the crystalline combination mode and can be used as an internal standard peak because of following reason.

The depth of plasma modification is very small and is known to be lesser than 1 $\mu$m [16, 24]. The diameter of the UHMPE fiber is much larger than the plasma modification depth and the penetration depth of IR ray in DRIFT spectroscopy is large than the plasma modification depth. Therefore, this crystalline peak at 1894 cm$^{-1}$ can be useful for the internal standard peak if the plasma treatment does not change the crystallinity of the UHMPE fiber greatly. The crystallinity of the UHMPE fiber does not change greatly by the plasma treatment considering from the heat of melting in differential scanning calorimeter.

Fig. 4 represents the changes of the integrated peak intensity from carbonyl stretching mode with the argon plasma treatment time. For the comparison, the changes of the integrated peak intensity by the oxygen plasma treatment are shown together. Oxygen plasma treatment of the UHMPE fiber increases the carbonyl groups with the plasma treatment time. However, argon plasma treatment of the UHMPE fiber does not change or decreases a little the carbonyl group with plasma treatment time. The variation of the integrated peak intensity due to C−O stretching mode with the argon plasma treatment time is shown in Fig. 5. In the case of C−O groups, oxygen plasma and argon plasma treatment decrease the C−O groups on the UHMPE fiber surface with the plasma treatment time. This phenomenon can be explained as follow.

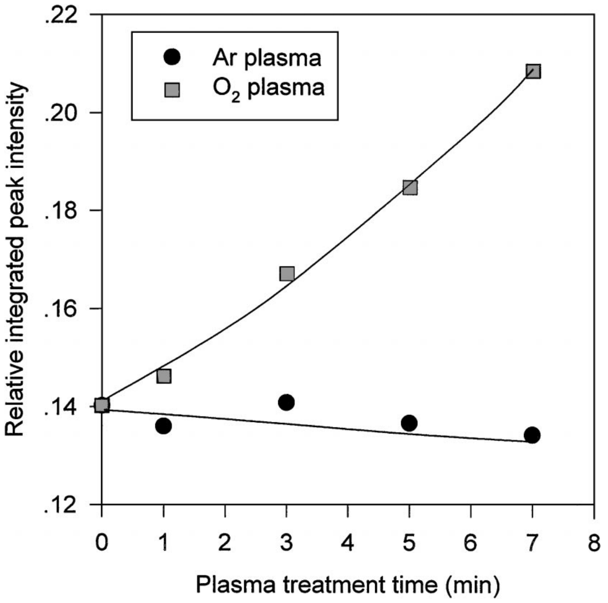

*Figure 4* The changes of relative integrated C=O stretching peak intensities with the argon plasma treatment time.

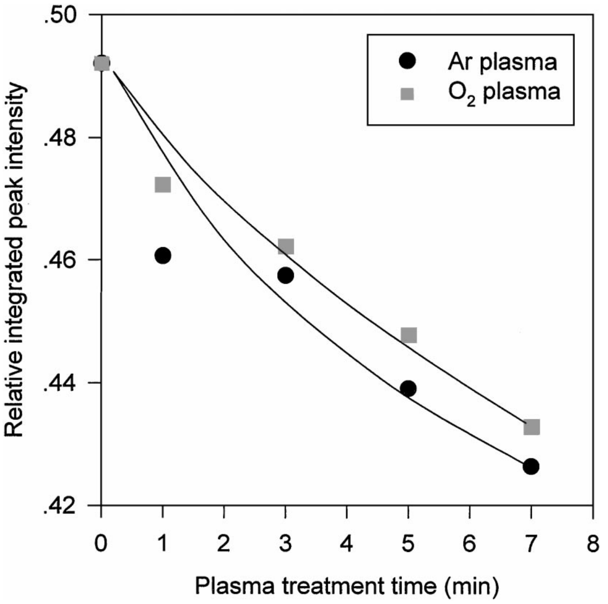

*Figure 5* The changes of relative integrated C−O stretching peak intensities with the argon plasma treatment time.

The control UHMPE fiber used in this study shows large C−O stretching peak and small carbonyl stretching peak. The oxygen plasma treatment of the UHMPE fiber decreases the C−O groups and increases the carbonyl groups with the plasma treatment time. Therefore, the oxygen plasma treatment changes the surface of the UHMPE fiber into more highly oxidized state. However, the argon plasma treatment decreased the C−O groups and does not change or decreases a little carbonyl groups. Argon plasma treatment mainly etches the UHMPE fiber surface and the additional introduction of oxygen containing chemical functional groups does not occur almost.

Fig. 6 shows the changes of the C=C stretching peak with the plasma treatment time. Argon plasma treatment does not change the amount of C=C groups on the UHMPE fiber surface. Considering from these Figs 4–6, the argon plasma treatment of the UHMPE fiber etches the fiber surface and the amount of

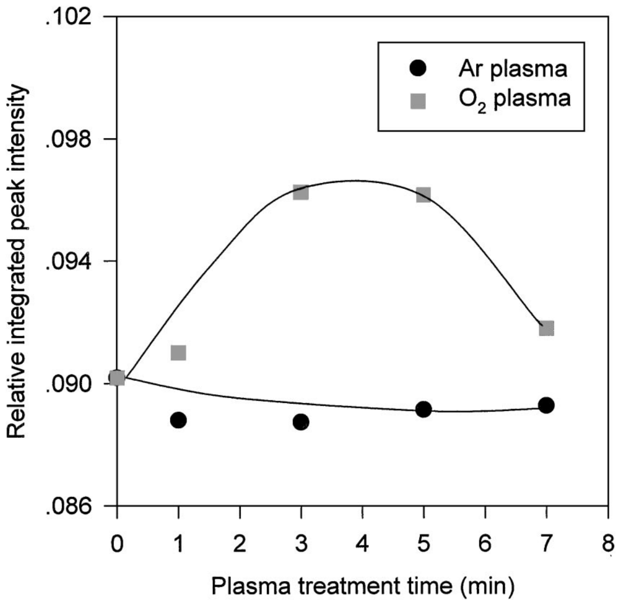

*Figure 6* The changes of relative integrated C=C stretching peak intensities with the argon plasma treatment time.

functional groups on the UHMPE fiber surface decreases with the plasma treatment time.

Considering the chemical and morphological changes of the UHMPE fiber by the argon plasma treatment together, the increase and decrease of the interfacial adhesion of the UHMPE fiber/vinylester composites represented in Fig. 1 can be explained as follows.

The initial argon plasma treatment of the UHMPE fiber increases the size of the micro-pittings and the surface roughness of the UHMPE fiber surface. This increased micro-pittings and surface roughness improve the interfacial adhesion of the UHMPE fiber/vinylester composites through the mechanical interlocking between the micropittings and vinylester resin. However, as the argon plasma treatment time becomes longer, the UHMPE fiber surface becomes more inert and oxygen containing functional groups are decreased. Therefore, UHMPE fiber wetting by the vinylester resin becomes poor as the argon plasma treatment time becomes longer and the mechanical interlocking between the UHMPE fiber and vinylester resin becomes less efficient. From these results, it can be known that the mechanical interlocking between the micropittings and impregnated vinylester resin is an important factor for the improving the interfacial adhesion of plasma treated UHMPE fiber/vinylester composites. The complete wetting of the UHMPE fiber by the matrix resin is known to be an important preliminary condition.

## 4. Conclusion

The interfacial adhesion of argon plasma treated UHMPE fiber/vinylester composites was investigated and the following conclusions can be obtained.

The argon plasma treatment of the UHMPE fiber introduces micro-pittings on the UHMPE fiber surface and these micro-pittings improve the interfacial adhesion of UHMPE fiber/vinylester composites through mechanical interlocking between the UHMPE fiber and vinylester resin.

This mechanical interlocking through the micro-pittings requires the interfacial wetting between the UHMPE fiber and vinylester resin as a preliminary condition. The argon plasma treatment of the UHMPE fiber modifies the UHMPE fiber surface chemically more inert state and these chemical modifications reduce the efficiency of mechanical interlocking between the UHMPE fiber and vinylester resin for long period argon plasma treatment.

It can be concluded that the mechanical interlocking and chemical modification should be considered as a combined cooperative factor in improving the interfacial adhesion of UHMPE fiber/vinylester composites instead of considering as separative factors.

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