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# Effects of the atmospheric plasma treatments on surface and mechanical properties of flax fiber and adhesion between fiber–matrix for composite materials

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ABSTRACT

In this study, flax fibers were treated by argon and air atmospheric pressure plasma systems under various plasma powers to improve interfacial adhesion between the flax fiber and high density polyethylene (HDPE) and unsaturated polyester. The interfacial adhesion of argon treated flax fiber for HDPE matrix is superior than those of air treated and untreated flax fiber. However for the adhesion between flax fiber and polyester matrix, air treatment is more efficient than argon treatment. Besides, greater plasma power causes greater interfacial adhesion, which was proved by pull out tests. The surface characteristics of flax fibers were examined using Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and Scanning electron microscopy (SEM), and roughness tests. X-ray photoelectron spectroscopy analysis (XPS) indicated that the air plasma-treated fiber had higher oxygen concentration and higher oxygen/carbon ratio than the untreated fiber and argon plasma treated fiber. Changes in the surface chemical composition and functional groups, and increases in surface roughness were obtained. After both plasma treatments, it was clearly seen that a new functional group (O—C=O) generates on the flax fiber surface.



## 1. Introduction

In recent years, natural fiber reinforced polymeric composite materials have replaced many of the synthetic fibers (glass, carbon, aramid, etc.) reinforced composite materials in various applications. Natural fibers such as jute, flax, hemp, ramie, coir, and banana can be attractive as engineering materials due to low cost, nontoxic, reduced tool wear (nonabrasive to processing equipment), very high strength-to-weight ratio, lightweight, renewable and biodegradability compared to synthetic fibers [1–5]. The extent of environmental pollution caused is less compared to synthetic fibers [6].

The performance and properties of natural fiber reinforced polymeric composite materials depend on the properties of the individual components (fibers and matrix) and their interfacial adhesion. To provide appropriate interfacial interactions their surface properties must be modified accordingly [7]. Chemical (alkali treatment [8–10], silane treatment [11,12], acetylation treatment [1,2,13–15], etc.) and physical (plasma treatments [16–18], corona treatment [19] and electron beam irradiation [20]) modifications of the fiber surface have been done to improve the compatibility between natural fiber surfaces and polymer matrices. Although the chemical treatments of fiber surfaces have been somewhat successful in improving the interfacial bonding, there are problems related to the high cost of the treatment and the disposal of the chemicals after treatment [2]. In recent years, increasing concern about environmental pollution problems has limited wide industrial application of chemical surface treatments [2,17,21]. In contrast to other treatments, the plasma techniques are considered as dry and clean processes. The pre-treatment and finishing of textiles by atmospheric plasma technologies becomes more and more popular as a surface modification technique [22]. It offers numerous advantages over the conventional chemical processes. Plasma surface modification does not require the use of water and chemicals, resulting in a more economical and ecological process. The enormous advantage of plasma processes concerns the drastic reduction in pollutants [23].

Plasma modification of the surface results in surface cleaning, which promotes adhesion and action of coupling agents. It may

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also cause ablation or etching of material, which results in a rougher surface, promoting physical adhesion. Besides, modification of the surface chemical structure and introduction of free radicals are possible as well [2,18,24]. Atmospheric plasma technique allows surface modification of fibers without affecting the bulk properties. In addition, no solvent is used, and the duration times of treatment are short [2,25].

By controlling the plasma variables, such as the nature of gas, discharge power and exposure time, a great variety of surface properties can be improved, mainly wettability [26–29], roughness [1] and adhesion [15,18,30]. Plasma may cause two type of interactions with the surface, one of which is chain scission on the surface which leading to surface etching, cleaning or activation. This type of interaction appears when non-polymerizing gases like helium, argon, oxygen, air and nitrogen are used. Plasma induced polymerization or grafting on the textile surface, the second type of interaction, can be conducted by using various polymerizing gases and precursor like fluorocarbons, HMDS, $C_2H_4$ or vapors (monomers) (e.g., acetone, methanol, allyamine, and acrylic acid) [31,32]. Usually inert gas like helium, or argon is used for both etching and grafting on the surface during the plasma treatment [31].

The goal of our research was to improve the surface properties of flax fibers by atmospheric air and argon plasma treatments for a better adhesion between flax fiber and polymer matrixes such as high density polyethylene (HDPE) and unsaturated polyester. Plasma powers (100, 200 and 300 W) were changed while maintaining a constant exposure time during air and argon atmospheric plasma treatments. The functional groups and the elemental composition on the surface were determined by Fourier transform infrared spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS) analyses, respectively. The effects of plasma treatment on fiber properties were determined by surface roughness, fabric tensile test and pull-out tests. Scanning electron microscopy (SEM) was used to investigate the surface morphologies after plasma treatments of flax fiber.

## 2. Experimental details

### 2.1. Materials

A woven flax fabric with an area weight of 217 g/m$^2$ was used in this study. The flax fabric was supplied by Mert İpek Limited, Turkey. High density polyethylene (HDPE) and polyester were used as resin in the pull-out test. HDPE (commercial name S 0452; specific gravity: 0.950–0.956 g/cm$^3$, melt flow index (MFI): 0.30–0.50 g/10 min) was supplied by PETKIM Petrokimya Holding A.Ş. of Turkey. Polipol unsaturated polyester 383-T (specific gravity: 1.11 g/cm$^3$, viscosity brookfield: 950 cP), which is isophthalic acid type resin, was used as resin in the pull-out test. Argon gas (Ar) (99.995% purity) was provided from Linde Gaz A.Ş. (Turkey).

### 2.2. Atmospheric plasma treatments

Uniform glow discharge plasma system operating under atmospheric condition was used. Detailed explanation of device was given in elsewhere [33]. This device can be operated with rectangular or cylindrical electrodes. In this study, four cylindrical electrode pairs with three power section were used. Each electrode pairs were placed 4 cm apart from each other. The samples ($10 \times 40$ cm$^2$) were placed between the electrodes and passed at various plasma powers (100–300 W) for 2 min. In all treatments, air (20.9% oxygen, 79.1% nitrogen, and relative humidity <3 ppm) and argon (99.995% purity) were used as process gas.

### 2.3. Characterization techniques

#### 2.3.1. Tensile testing

The tensile strength of flax fabric was measured using a Lloyd LLOYDX-LR5K according to standard ISO 13934-1 standard in warp direction [34].

#### 2.3.2. Attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR)

The effect of argon and air plasma treatment of flax fiber on the functional groups of flax fiber was investigated by attenuated total reflectance-Fourier transform infrared spectroscopy (ATR-FTIR) analysis. ATR-FTIR, a Perkin Elmer, model spectrum 2000, was used in this study. The spectrometer was used in the absorption mode with a resolution of 4 cm$^{-1}$ in the range of 4000–400 cm$^{-1}$.

#### 2.3.3. X-ray photoelectron spectroscopy (XPS) analysis

Surface characterization of flax and plasma-treated flax fibers were performed with a Specs ESCA instrument. Spectra were recorded by using a monochromatic Al Kα radiation source at a power of 200 W (10 kV, 10 mA), base pressure of $10^{-9}$–$10^{-10}$ torr in the sample chamber, and EA 200 hemispherical electrostatic energy analyzer. X-ray photoelectron spectroscopy (XPS) survey spectra were collected in constant analyzer energy (CAE) mode with pass energy of 96 eV for elemental quantification purposes. The concentrations of different chemical states of carbon in the C1s peak were obtained by fitting the curves with Gauss–Lorentz functions. The curve fitting of results was performed on smoothed data following a Shirley background correction.

#### 2.3.4. Friction coefficient

To measure the kinetic friction coefficient of the fabric surface, the Frictorq instrument was used as described by Lima et al. [35].

#### 2.3.5. Pull-out test

Fiber/matrix adhesion was characterized by obtaining interfacial shear strength via pull-out test [1]. Pull out tests for HDPE and polyester were carried out after embedding of the fibers in the HDPE matrix for 90 min at 180 °C and in polyester matrix for 180 min at room temperature.

Shimadzu AUTOGRAPH AG-IS Series universal testing machine at contact speed 0.1 mm/min were used. The debonding force $F_{max}$, the diameter $d$, and the embedded length of the fibers $l_e$ were determined and the interfacial shear strength $\tau_d$ (IFSS) was calculated from the following equation:

$$\tau_d = \frac{F_{max}}{d\,\pi\,l_e} \tag{1}$$

#### 2.3.6. Surface morphology

The surface morphologies of plasma treated and untreated flax fibers were examined using a FEI Quanta FEG 250 Scanning electron microscope (SEM) operated at 2.5 kV. The surfaces of the flax fibers were coated with gold by means of a plasma sputtering apparatus prior to SEM investigation. Then, the flax fibers were investigated at 10,000× magnification to observe the surface morphological changes caused by the plasma treatments.

## 3. Results and discussion

### 3.1. Tensile testing

In order to determine the extent to which plasma treatment of flax fiber affects the strengths of treated fibers, tensile strengths of flax fibers were determined using tensile test and presented in