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50-Hz plasma treatment of glass fibre reinforced polyester at atmospheric pressure enhanced by ultrasonic irradiation

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Glass fibre reinforced polyester (GFRP) plates are treated using a 50-Hz dielectric barrier discharge at peak-to-peak voltage of 30 kV in helium at atmospheric pressure with and without ultrasonic irradiation to study adhesion improvement. The ultrasonic waves at the fundamental frequency of around 30 kHz with the sound pressure level of approximately 155 dB were introduced vertically to the GFRP surface through a cylindrical waveguide. The polar component of the surface energy was almost unchanged after the plasma treatment without ultrasonic irradiation, but drastically increased approximately from 20 mJ m^{-2} up to 80 mJ m^{-2} with ultrasonic irradiation. The plasma treatment with ultrasonic irradiation also introduced oxygen and nitrogen containing functional groups at the GFRP surface. These changes would improve the adhesion properties of the GFRP plates.

1. Introduction

Glass-fibre-reinforced polyester (GFRP) materials exhibit high strength-to-weight ratios and corrosion resistance, and are therefore used for a variety of applications particularly in civil engineering. For such applications GFRPs are often joined with similar or dissimilar materials using adhesives. However, they usually have smooth surfaces composed mainly of the polyester matrix materials with low surface energies. Therefore, the adhesive joint usually requires careful surface preparation. Plasma treatment, especially at atmospheric pressure is attractive for this application due to its environmental compatibility and high treatment efficiency without affecting the textural characteristics of the bulk material [1]. Among atmospheric pressure plasmas, a dielectric barrier discharge (DBD) serves this purpose. It is reported that the adhesion strength of the surface after 2-s DBD treatment was comparable to or higher than that achieved by the conventional abrasion method [2].

The efficiency of plasma processing can be further enhanced by external energy input [3]. Among possible techniques, ultrasonic irradiation by a high-power gas jet ultrasound generator is attractive because of its simple setup and high efficiency of the generated acoustic energy transferring into a plasma [4-7]. It is further reported that simultaneous ultrasonic irradiation during the DBD treatment can enhance oxidation at the GFRP surfaces [5]. In the present work, GFRP plates are treated with the 50-Hz DBD with and without ultrasonic irradiation for the purpose of adhesion improvement. Optical emission spectroscopy (OES) is used for plasma diagnostics. The treated surfaces are characterized using contact angle measurement, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (TOF-SIMS) and atomic force microscopy (AFM).

2. Experimental Setup

2-mm thick GFRP plates were used as specimens They contain 35 – 40 wt % glass fibres, and the surfaces are mostly covered with polyester matrix. The DBD was generated between two parallel-plate electrodes (50 mm × 50 mm, gap: 3 mm) driven at a frequency of 50 Hz with a step-up transformer. A 100-kΩ resistor was connected between the transformer and the powered electrode in order to avoid excess pulse current when a plasma was generated. The voltage and current were measured with a high voltage probe and a current-viewing resistor, respectively. The peak-to-peak voltage was set to 30 kV. The average electrical power applied in the DBD was calculated numerically. The power measured in this way was less than 0.5 W. The powered bottom aluminium electrode is covered with an alumina plate (100 mm × 100 mm × 3 mm), while the ground aluminium electrode has a 42 mm diameter perforated hole covered with a stainless steel mesh. A 40 mm inner diameter poly(methyl

methacrylate) waveguide is attached above the ground electrode for the introduction of ultrasound. A high-power gas-jet air-operated ultrasonic generator (30 kHz) is placed near the top of the waveguide. The sound pressure level is approximately 155 dB at the discharge. The acoustic field in the DBD setup is probed using the capacitive microphone and the signal is processed by means of the Portable Pulse Analyzer.The DBD and ambient air are separated using a thin polyethylene membrane clamped between the outer-wall of the waveguide and the upper part of the powered electrode. Helium gas was fed into the DBD at a flow rate of 3 L min^{-1}. Each GFRP plate was exposed to the DBD for 0, 10, 30, 60, 180 or 300 s.

The OES measurements were performed without a GFRP plate using an optical fibre and a 0.75 m spectrometer (grating 3600 grooves/mm) and a charge-coupled device (CCD) camera. The spectral resolution is 20 pm.

AFM imaging (10 μm × 10 μm) was performed on an N8 NEOS (Bruker Nano GmbH, Herzogenrath, Germany) operating in an intermittent contact mode and using SSS-NCLR cantilevers (NANOSENSORS™, Neuchatel, Switzerland) for the GFRP plates before and after the plasma treatments for 60 s. Images were recorded at a scan speed of 0.5 lines min^{-1}.

Contact angles were measured with deionized water and glycerol in air at room temperature both before and after the treatments for evaluation of the surface energy. The polar component of the solid surface energy of the GFRP plates was determined by the two-liquid geometric method [8].

XPS data were collected using a double anode (Mg/Al) source, and for the present measurements the Mg K□ line with an energy of 1253.6 eV was used, with a lateral resolution of 2 mm to study the changes in elemental compositions and the functional groups on the GFRP surfaces before and after the treatments for 60 s. Atomic concentrations of all elements were calculated by determining the relevant integral peak intensities subtracting a Shirley-type background. In addition, a high-resolution analysis was performed on the carbon 1s (C1s) peak (pass energy 40 eV) acquired over 3 scans. The binding energies were referred to the hydrocarbon component (C-C, C-H) at 285 eV. The spectra were deconvoluted through curve fitting, taking purely Gaussian components with linear background subtraction.

TOF-SIMS analyses were performed using a TOF-SIMS IV (ION-TOF GmbH, Münster, Germany). TOF-SIMS were acquired using 25 ns pulses of 25 keV Bi^+ that were bunched to form ion packets with a nominal temporal extent of < 0.9 ns at a repetition rate of 10 kHz, yielding a target current of 1 pA. These primary ion conditions were used to acquire 500 μm × 500 μm ion images of the sample surfaces with a lateral resolution of ~2 μm.

3. Results and Discussion

The current wave form at 50 Hz generally looks rather spiky due to the significant difference between the current pulse width and a period of the sinusoidal voltage waveform. The current pulse width of the DBD was approximately 1 μs. Ultrasonic irradiation decreases the current pulse width strongly, while it increases the height of the current several times. This result corresponds to the fact that the current waveform of the helium DBD driven at 40 kHz changed from glow to filamentary with ultrasonic irradiation [5,7].

OES was measured to identify excited species and estimate the gas temperature via the rotational temperature of N_2 in the DBD. Traces of nitrogen in the discharge originate from the surrounding air since the discharge was not completely gas tight. OES of the DBD with and without ultrasonic irradiation includes N_2 and N_2^+ bands. Ultrasonic irradiation reduced the optical emission intensity, but led to no detectable difference in the relative profile between the rotational spectra recorded with and without ultrasonic radiation. The best fit was found for a rotational temperature of 300 K for the DBD with and without ultrasonic irradiation (Fig. 1). It is therefore indicated that heating of the gas by ultrasonic irradiation was negligible.

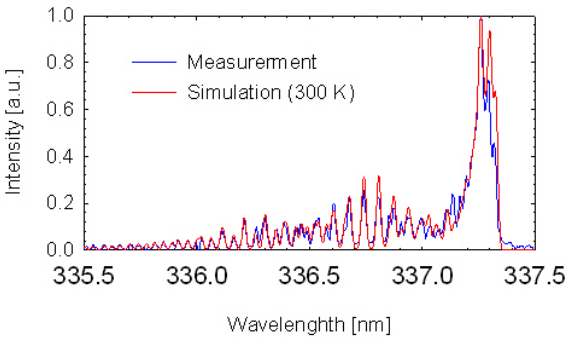

Figure 1. Measurement and simulation for the 0-0 transition of the 2nd positive system of nitrogen in the OES of the helium DBD with ultrasonic irradiation. The best fit was found for a rotational temperature of 300 K. The measured spectral resolution (FWHM) is 20 pm.

Surface roughening is often useful for adhesion improvement because of the increased surface area

and mechanical interaction with the adhesive. Six, three and seven AFM images were obtained on the untreated specimen, the plasma treated specimen, and the plasma treated specimen with ultrasonic irradiation, respectively. The surface roughness values (S_a) were extracted from the AFM images. No significant difference in surface roughness is observed for the specimens before and after the treatments. It is possibly because the energy applied to the plasma was too low for the efficient surface roughening.

The wettability of the GFRP surface plays an important role for the adhesion improvement. However, helium DBD treatment without ultrasonic irradiation did not significantly improve the wetting as shown in Figure 2.

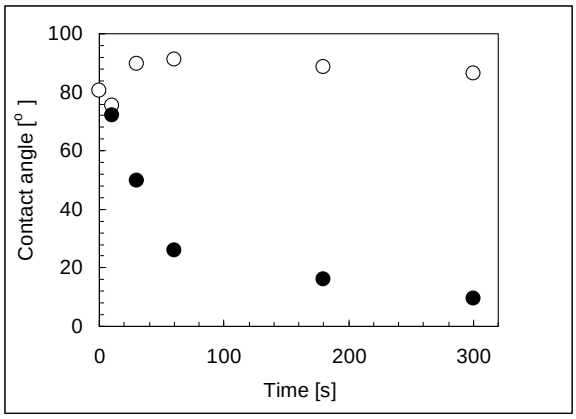

Figure 2. Water contact angle before and after plasma treatment with (filled circle) and without (open circle) ultrasonic irradiation.

This can again be attributed to the low energy input to the helium plasma. On the other hand, the water contact angle of the GFRP markedly decreased when ultrasound was introduced. The longer treatment further improved the wetting of the GFRP surfaces. Accordingly, the polar component of the surface energy of the GFRP was increased by the plasma treatment with ultrasonic irradiation. It is a significant contrast from the atmospheric pressure plasma treatment driven at approximately 40 kHz AC voltage, where only moderate improvement of wettability was observed with ultrasonic irradiation [5-7, 9].

XPS survey analysis was carried out in order to analyze the elemental composition of the GFRP surfaces before and after the 60-s treatments with and without ultrasonic irradiation. The O/C ratio remained almost unchanged after the plasma treatment without ultrasonic irradiation, while it slightly increased from 0.23 to 0.25 after the plasma treatment with ultrasonic irradiation. An increase in the O/C ratio indicates that oxygen-containing polar functional groups are introduced at the surfaces, improving the wettability. This result shows an agreement with that of the contact angle measurement. On the other hand no clear change was seen in the nitrogen content before/after the DBD treatment with/without ultrasonic irradiation.

TOF-SIMS ion images indicate that oxygen containing species were homogeneously distributed in all cases. The homogeneous distribution of nitrogen species was observed only on the specimen surface after the plasma treatment with ultrasonic irradiation. It is suggested that nitrogen from ambient air reacted with the sample surfaces during the plasma treatment with ultrasonic irradiation. XPS detects similar amounts of traces of nitrogen on all the surfaces, while TOF-SIMS detects more intense nitrogen species on the surfaces treated with ultrasonic irradiation. This difference can be explained from the fact that TOF-SIMS is more surface sensitive (~1 nm) compared to XPS (5–10 nm).

It is reported that ozone production is pronounced with ultrasonic irradiation when an atmospheric pressure O_2 DBD is driven at a lower frequency [10]. This might explain the reason why in the present work why the treatment efficiency of 50-Hz DBD was significantly improved by ultrasonic irradiation. However, further investigation is necessary for a deeper understanding of all the involved surface modification mechanisms.

4. Conclusion

A 50-Hz DBD plasma treatment can be an economical method for surface modification, but without ultrasonic irradiation it did not change the surface properties of the GFRP plates significantly under the present tested conditions. The surface roughness remained almost unchanged after the plasma treatments with and without ultrasonic irradiation. It is found that ultrasonic irradiation to the 50-Hz DBD enhanced the treatment efficiency markedly so that a certain amount of oxygen and nitrogen containing polar functional groups were introduced at the GFRP surfaces. This is in marked contrast to the 40-kHz DBD where the ultrasonic irradiation enhanced treatment efficiency only moderately [5-7]. The attachment of these functional groups on the surfaces will most likely contribute to the increase in the polar component of surface energy and thus improve the adhesion properties of the surfaces.

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