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Rapid surface treatment of polyamide 12 by microwave plasma jet

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ABSTRACT

Polyamide 12 (PA 12) films were plasma treated using a microwave surface wave jet at atmospheric pressure. The parameters were the treatment time and the gas composition (argon or argon with admixtures). Moreover, the influence of power modulation was studied. It was found that significant change in wettability is achieved very rapidly, after only 25 ms of treatment. Plasma-induced surface changes are discussed using AFM, ATR-FTIR and XPS results. It is concluded that the increase in wettability is caused by both chemical and morphological changes.

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1. Introduction

Microwave discharges at the atmospheric pressure, especially surface wave sustained discharges, have flexible operating conditions resulting in a wide range of processing applications, such as thin film deposition, gas decontamination, plasma sterilisation, light sources and lasers, particle production, material processing, etc. [1–4].

Polyamide 12 (PA 12) is a thermoplastic material that is rigid, hard wearing, and resistant to oils, solvents, and alkalis. A known problem with polyamide and many other polymers are their poor hydrophilic properties, which affect their wettability, printability, adhesion, etc. In polyamide it is related to the availability of the hydrogen bonds among the molecules with amide groups. This can be overcome by increasing the surface energy by an appropriate surface modification method. One of the promising methods is plasma surface modification [5,6].

Plasma treatment is widely used nowadays as an effective tool for physical and chemical modification of polymer surfaces, while not affecting the bulk material [7–11]. Under the bombardment of active species (charged particles, excited particles, radicals, UV radiation, etc.) generated by the plasma, the polymer surface can be modified either by removing surface contamination [12–14], introducing new chemical functional groups [15–17] or depositing a thin coating [18,19]. Plasma surface modifications are often used to improve surface adhesion, hydrophilicity and roughness as required for the enhanced wetting, dyeing and printing [20–22]. Traditionally, most plasma systems operated at low pressure, requiring rather expensive and complicated vacuum equipment [23]. This can be avoided by using dielectric barrier discharge (DBD) systems or plasma jets working at the atmospheric pressure [5,6,10]. Using the microwave discharges can be advantageous over DC, low frequency or RF plasmas as they generally have higher power density, which can positively influence both homogeneous and heterogeneous plasma–chemical reactions. The net effect could then be a potentially faster plasma treatment.

This paper aims to find and to report the treatment conditions (gas admixture, treatment time, continuous wave versus amplitude modulation), for which the plasma jet treatment would induce sufficient hydrophilisation of the polyamide 12 surface without damaging it.

The interest in such enhanced hydrophilisation came from an application – polyamide sheet gluing. With this application in mind we also tried to achieve shorter treatment time compared to the established techniques.

Important issue that was considered as well, was the ageing effect of treated samples. The modification of polyamide surface by plasma treatment was investigated by means of contact angle measurement, atomic force microscopy (AFM), attenuated total reflectance Fourier transform infra-red spectroscopy (ATR-FTIR) and X-ray photoelectron spectroscopy (XPS).

2. Experimental set-up

2.1. Plasma system

The surface treatment was carried out using an atmospheric pressure microwave electrode-less jet – surfatron (commercial

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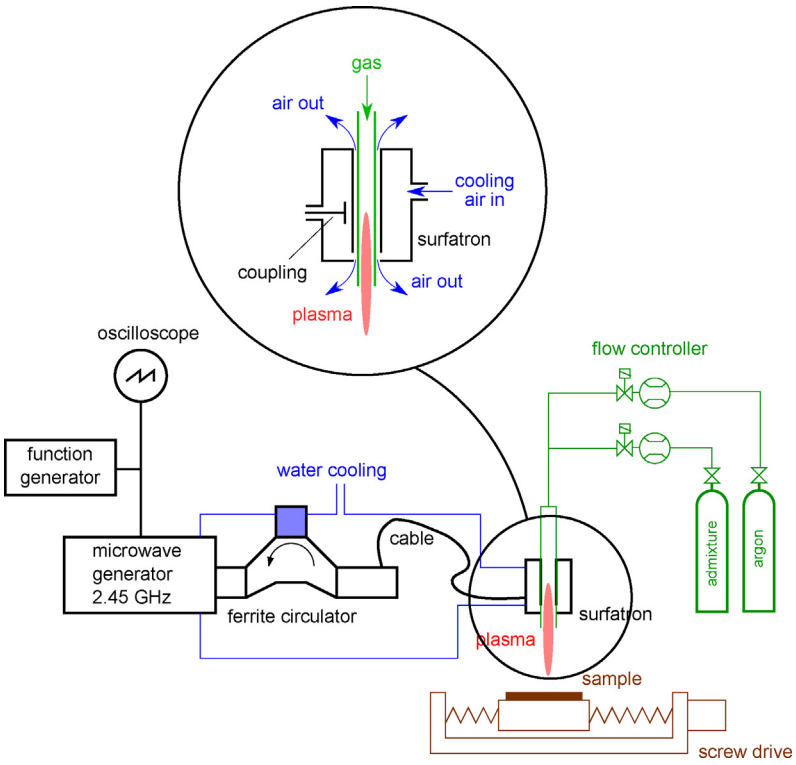

Fig. 1. Schematic drawing of the experimental set-up.

SAIREM Surfatron 80 with integrated matching) [24]. Fig. 1 shows the experimental set-up. The microwave generator (2.45 GHz) was operated both in continuous wave (CW) and amplitude modulated (AM) mode using a function generator. The sinusoidal AM envelope with 260 Hz frequency was chosen (min. 150 W, max. 350 W) to have the same mean power (250 W) as CW mode. The microwaves were fed from the magnetron to the surface wave launcher (surfatron) via a waveguide, ferrite circulator and coaxial cable. The matching was adjusted to maintain the reflected power below 10 W.

The surfatron design is a coaxial resonant cavity with a narrow gap around a discharge tube located in the centre of the surfatron. The surface wave discharge is produced by applying high frequency electric field intensified by this narrow slit to a gas flowing in the discharge tube. The discharge tube was made of fused silica, its inner diameter being 1.5 mm and outer diameter 4 mm. The end of the discharge tube was 2 cm distant from the launching gap. The flow of the working gas (argon) was maintained at 1.45 slm (standard litre per minute) by a flow controller. The admixtures such as O_2 or N_2 could be added into the main gas. The flow of O_2, N_2 was measured directly by flow controller.

Thermal management was carried out by water cooling of the generator, circulator and surfatron itself. Additionally, the discharge tube was cooled by compressed air, which was also blowing onto the sample, helping to cool and preserve the polyamide surface.

2.2. Surface treatment

During the surface treatment, the PA 12 samples were fixed on a planar substrate holder placed near the end of the discharge tube from which the plasma was blown out. By vertical positioning of the holder, the distance of the sample from the tube end could have been adjusted suitably. The holder was motorised and the variable horizontal speed of samples passing through the plasma determined the total exposure time. The treatment time ranged from 25 ms to 1 s.

During the plasma treatment, the ambient conditions were 23 °C temperature and 45–60% humidity.

2.3. Material analysis

Surface free energy of the samples was determined by a sessile drop technique, i.e. from a contact angle θ between the solid sample surface and the surface of measuring liquid droplet placed on it. The contact angles were measured directly from the images of the sessile drops (1.5 μl volume) taken with digital camera of Surface Energy Evaluation System [25].

For the calculation of the surface free energy the Owens–Wendt model [26], which divides the surface free energy γ into disperse γ^d and polar γ^p components, was used. The Owens–Wendt model leads to this equation:

$$2\sqrt{\gamma_s^d \gamma_l^d} + 2\sqrt{\gamma_s^p \gamma_l^p} = \gamma_l(1 + \cos\theta) \quad (1)$$

In this equation, the surface free energy components of a solid surface γ_s^d and γ_s^p are the two unknowns, which imply that for this model it is necessary to use at least two different measuring liquids, e.g. water (γ_l^d=21.8 mJ/m^2, γ_l^p=51.0 mJ/m^2) and glycerol (γ_l^d=34.0 mJ/m^2, γ_l^p=30.0 mJ/m^2). From the knowledge of their polar and disperse parts of the surface energy and two contact angles measured, the model gives us the values of surface free energy components of the polyamide. The total surface free energy is simply their sum.

The AFM images were taken by TM Microscopes' AutoProbe CP-Research device with the probe head operated in a contact mode. Maximal dynamic amplitude constant (DAC) lateral resolution was 0.25 Å, maximal DAC vertical resolution was 0.025 Å. Maximal lateral scan range is 90 μm and maximum vertical scan range is 7.5 μm. The AFM data were rendered to 3D pictures and analysed by the Gwyddion software [27].

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