

POLYESTER FABRIC MODIFIED WITH ATMOSPHERIC DIELECTRIC BARRIER DISCHARGE SUPPLIED WITH VOLTAGE OF DIFFERENT FREQUENCIES

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Final characteristics of polymers are the compromise between wanted surface and bulk properties. Important change of the polymer use-value can be caused by modification of characteristics of its upper structural units (i.e. in region under the surface deep some tens of nanometers). These changes – and modification – can be performed i. a. by treatment with the “cold” plasma and moreover with low costs and minimum environmental impact. Modification of polymer surface characteristics may proceed during functionalization, when plasma particles react with polymer surface molecules and new chemical functional groups are formed on polymer surface. These chemical reactions can be influenced with composition of atmosphere in the plasma reactor, e.g. application of oxygen plasma leads to polymer surface energy and wettability increase. To evaluate the efficiency of this process, we studied connection of the ADBD supply energy/voltage frequency and changes of the polymer surface chemical composition. ADBD was operated in the filamentary regime. Experiments proved that growing supply voltage frequency that produced also reactor input energy increase allowed both substantial reduction of treatment time and more effective modification.

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1. INTRODUCTION

Polymer surface properties like wettability and adhesion can be modified without changing polymer bulk properties by use of methods employing low temperature (“cold”) plasma treatment. For survey of these methods see e.g. [1].

Probably the easiest way to get the low temperature plasma at atmospheric pressure is the application of an atmospheric dielectric barrier discharge (ADBBD). ADBBDs have proven to be applicable to various purposes; in addition they are also scalable to very large systems.

The goal of in this paper described experiments is study of connection between the discharge supply energy/voltage frequency and changes of functional groups at polyester fabric surface caused by modification.

2. EXPERIMENTAL

For experiments polyester fabric was used. Tested fabric was cut in pieces 100×100 mm (fibre average sectional diameter about 300 μm, mesh size about 250×250 μm, textile thickness about 0.5 mm). Before modification all test samples were properly cleaned.

Experimental reactor (Fig. 1) consisted of two plane iron electrodes put into open cylindrical vessel (diameter 153 mm, height 146 mm). Both flat round electrodes were 45 mm in diameter and 10 mm thick. The barrier composed 83×83 mm and 3 mm thick glass table stuck to the higher placed electrode. Distance between electrodes was adjustable and during all experiments was held at 9 mm. All tests were performed with samples placed on the lower electrode connected to the ground during all experiments.

Tests were carried out in air at room conditions (pressure about 1.00791 bar (756 Torr), temperature about

20 °C and humidity about 30%. To hold the composition of the atmosphere (air) in reactor constant during the measurements, air from the reactor was continually exhausted with a compressor (air flow speed 0.04 m³s⁻¹). ADBBD was supplied either at [14.7 kV, 50 Hz, modification time 360 s, reactor input energy about 0.5 W] or [11.5 kV, 2.5 kHz, modification time 30 s, reactor input energy about 40 W]. Supply voltage values were chosen to be maximum permissible values in regard to supply voltage source characteristics and risk of ADBBD transition to spark or arc discharge. ADBBD was operated in the filamentary regime. Hydrophilicity was evaluated by means of the drop test [2].

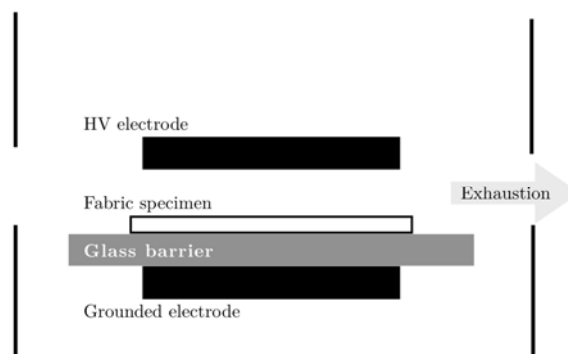


Fig. 1. Cross-section of the reactor

Chemical composition of the fabric surface was analyzed by X-ray photoelectron spectroscopy (XPS) performed with Omicron Nanotechnology system incorporating Al K_α radiation (hν = 1486.7 eV) and operating at 15 kV, 5.2 mA. The pressure in the chamber was maintained at 2×10⁻¹⁰ mbar. Spectra were acquired at the take-off angle of 85° relatively to the sample surface and all binding energies were given in reference to carbon line (C1s) at 285 eV.

3. RESULTS

Modification effectivity and aging

Modification effectivity (i.e. wettability changes) is expressed by means of the area of feathering time evolution (Fig. 2). Tests were performed after modification and on the 3rd, 7th and 20th day after treatment. Sorption of modified PES fabric had improved and hydrophilicity of all samples expressed by the area of feathering time evolution had increased. Use of supply voltage of higher frequency (2.5 kHz) reflected in important increase of reactor input energy and it had also manifested in rise of modification effectivity (about 100%) in comparison with the 50 Hz supply voltage.

Modification effect time stability and reduction (aging), i.e. stability of acquired surface changes is an important aspect for practical application of plasma methods. Aging process of DBD treated polyester fabric surface consists in its hydrophilicity reduction and recovery of textile hydrophobicity, both in times after treatment, due to transformation of created hydrophilous functional groups on the surface of fabric. Transformation is caused by chemical reactions of appropriate functional groups with air components. During aging backwards changes of dipoles orientation into their primary position might be also expected. Speed of these changes can be connected with characteristics of the surrounding, e.g. moisture content in air (higher moisture content in air is connected with faster reduction of the hydrophilicity degree).

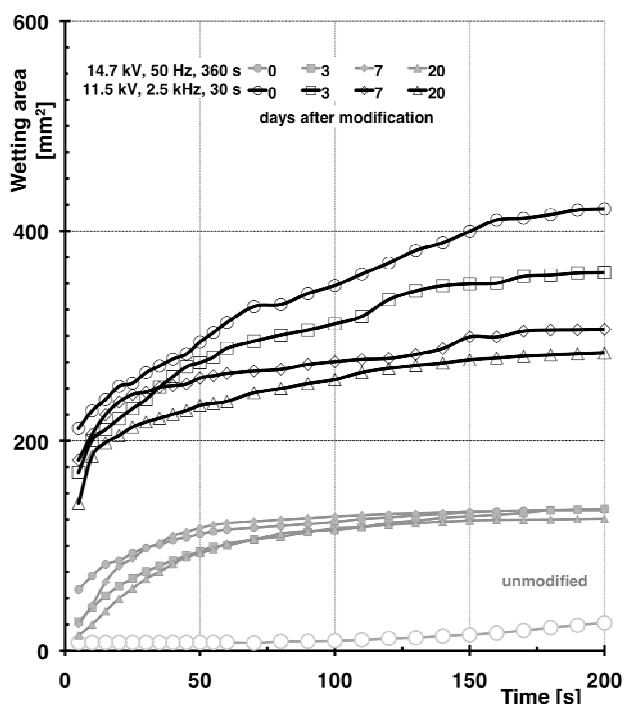


Fig. 2. Hydrophilicity of the fabric expressed by the area of feathering time evolution

We tested the modification effect time stability by measurements of hydrophilicity changes expressed by means of the wetting area time evolution in different times after modification (see Fig. 2). Modified fibres were stocked in darkness in air at atmospheric pressure and room temperature between tests. In case of 50 Hz voltage

supply frequency hydrophilicity remained almost stable in the first twenty days after treatment. In case of 2.5 kHz voltage supply the recovery of hydrophobicity started to proceed immediately; hydrophilicity reduction was about 25% after 6 days and about 40% after 20 days.

Chemical analysis

The decrease of water-absorption time can be attributed to increased roughness of the fiber surfaces due to plasma etching and introduction of more polar groups due to plasma chemical modification. To ascertain polyester fabric chemical changes caused by modification, we provided ESCA tests. Results of ESCA tests of untreated and treated fabric are summarized in Tables 1 and 2.

Table 1. Relative chemical composition and atomic ratios determined by ESCA tests

Sample	C [%]	O [%]	O/C
2.5 kHz; 11.5 kV; 30 s	64.98	33.63	0.517466
50 Hz; 14.7 kV; 360 s	65.02	34.02	0.523163
unmodified	75.01	24.15	0.321974

Table 2. Atomic percentage of the different chemical groups on polyester fabric

Sample	C-C, H	C-charged	C-O	C=O	C=O, OH
2.5kHz; 11,5 kV; 30 s	46.40	26.01	17.79	9.81	0
50 Hz; 14.7 kV; 360 s	66.48	11.19	14.74	7.59	0
unmodified	75.83	11.21	7.39	5.57	0

After modification the O/C value has increased 1.62 times in case of 50 Hz voltage supply and 1.61 times in case of 2.5 kHz voltage supply. These values are lower than those referred in [3], obtained by modification with the atmospheric pressure plasma jet (APPJ). It is obvious that rise of supply voltage frequency (and reactor input power) allows significant reduction of treatment time.

ESCA scans proved increase of number of methylene carbons singly bonded to oxygen. The carbon radicals, formed by the abstraction of hydrogen atoms from the polymer chains recombine with oxygen atoms generated by the electron impact dissociation [4]. This process results in formation of the oxygen-containing polar groups on the fabric surface.

4. SUMMARY

We studied connection of the atmospheric dielectric barrier discharge (ADB) supply energy/voltage frequency (50 Hz and 2.5 kHz respectively) and changes of the polymer surface chemical composition during functionalization, when plasma particles react with polymer surface molecules and new chemical functional groups are formed on polymer surface. ADBD was operated in air at room conditions in the filamentary regime. Effectivity of the modification process was determined with hydrophilicity measurements and ESCA scans.

Test indicated, that growing supply voltage frequency (and coexistent reactor input energy increase) allowed substantial reduction of treatment time. In case of 50 Hz voltage supply frequency hydrophilicity remained almost stable in the first twenty days after treatment. In case of 2.5 kHz voltage supply the recovery of hydrophobicity started to proceed immediately; about hydrophilicity reduction was about 25% after 6 days and 40% after 20 days.

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МОДИФИКАЦИЯ ПОЛИМЕРНОГО МАТЕРИАЛА АТМОСФЕРНЫМ ДИЭЛЕКТРИЧЕСКИМ БАРЬЕРНЫМ РАЗРЯДОМ РАЗЛИЧНОЙ ПИТАЮЩЕЙ ЧАСТОТЫ

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Конечные свойства полимеров являются компромиссом между желаемыми поверхностными и глубинными характеристиками. Существенное изменение потребительских свойств полимеров может быть вызвано модификацией характеристик его приповерхностных структурных слоев (т.е. на глубине нескольких десятков нанометров поверхностного слоя). Такая модификация может быть реализована с помощью облучения «холодной» плазмой без дополнительных затрат и минимального влияния на окружающую среду. Модификация поверхностных характеристик полимера может происходить во время обработки, когда компоненты плазмы взаимодействуют с молекулами поверхности полимера, при этом на поверхности полимера образуются новые химические группы. Эти химические реакции могут зависеть от состава газа в плазменном реакторе. Например, применение кислородной плазмы приводит к увеличению прочности поверхности полимера и ее смачиваемости. Чтобы оценить эффективность данного процесса, изучалась зависимость изменения химического состава поверхности полимера от параметров атмосферного диэлектрического газового разряда (ADBД). Эксперименты подтвердили, что увеличение питающей частоты разряда, а также входной энергии реактора приводит к существенному сокращению времени облучения и более эффективной модификации.

МОДИФІКАЦІЯ ПОЛІМЕРНОГО МАТЕРІАЛУ АТМОСФЕРНИМ ДІЕЛЕКТРИЧНИМ БАР'ЄРНИМ РОЗРЯДОМ РІЗНОЇ ЖИВИЛЬНОЇ ЧАСТОТИ

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Кінцеві властивості полімерів є компромісом між бажаними поверхневими і глибинними характеристиками. Істотна зміна споживчих властивостей полімерів може бути викликана модифікацією характеристик його приповерхневих структурних шарів (тобто на глибині декількох десятків нанометрів поверхневого шару). Така модифікація може бути реалізована за допомогою опромінення «холодною» плазмою без додаткових витрат і мінімального впливу на навколишнє середовище. Модифікація поверхневих характеристик полімеру може відбуватися під час обробки, коли компоненти плазми взаємодіють з молекулами поверхні полімеру, при цьому на поверхні полімеру утворюються нові хімічні групи. Ці хімічні реакції можуть залежати від складу газу в плазмовому реакторі. Наприклад, застосування кисневої плазми призводить до збільшення міцності поверхні полімеру і її змочуваності. Щоб оцінити ефективність даного процесу, вивчалася залежність зміни хімічного складу поверхні полімеру від параметрів атмосферного діелектричного газового розряду (ADBД). Експерименти підтвердили, що збільшення живильної частоти розряду, а також вхідної енергії реактора призводить до істотного скорочення часу опромінення і більш ефективної модифікації.