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# Films of recycled polyethylene terephthalate, obtained by electrospraying, for paper and textile impregnation

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The possibility of applying the electrospray method for recycling the polyethylene terephthalate (PET) waste has been studied. Besides, the successful deposition of PET films on paper and textile materials with purpose to obtain waterproof coatings has been demonstrated. The surface morphology of uncoated and coated materials has been observed by Scanning electron microscopy (SEM).The results from a comparative study of water permeability of non-impregnated and impregnated with PET both kinds of materials show that theimpregnatedones do not absorb water droplets. Thus, the potential of electrospraying as an effective method for PET wasterecycling and possible production of protective clothing and impervious paper has been revealed.

Keywords: recycled PET, electrospraying, paper and textile impregnation

## INTRODUCTION

Environmental pollution can be defined as an introduction of contaminants in the Nature, which is one of the global problems of contemporary society[1]. Anthropogenic activity of producing resistant organic materials is a major factor in the contamination. For example, 15 million tons of plastics have been produced in 2013 only in EU, which is 19% of the European waste stream [2]. Not surprisingly, Earth protectionand the "Idea of green life and technology" are the main topicsof many international events and high-level meetings, where it has been resolved that the plasticsare among the substantial environmental pollutants. That is why the reducing the plastic waste is announced as a major aim of the Member States during the Conference of the Parties(COP21) to the United Nations Framework Convention on Climate Change (UFNCCC), held in Paris.

Polyethylene terephthalate (PET) is one of the most used plastics for food and liquid packaging and other applications. PET is no degradable material, chemically resistant to the environmental conditions. Only around 22.5% of used PET bottles have been recycled in 2013 [2], thus defined PET as a significant waste of the human activity. Hence, the development of effective methods for PET recycling along with finding its new applications is of great importance for the ecology.

Potential methods for PET recycling are electrospinning and electrospraying, which are often considered as 'sister' technologies [3]. At present, the electrospinning is a popular technique for production of fibers [4-6] while the obtaining of PET waterproof coatings by electrospraying is unconventional and low studied recycling process yet. Generally, the electrospraying is a electrohydrodynamic process where a polymer solution is sprayed by the application of high potential electric field in order to obtain liquid droplet [3]. The construction and working principle of the apparatus are described in our previous paper [7]. Design of experimental set-up is shown in Fig.1. The apparatus could work in two regimes - electrospinning and electrospraying. The realization of one or another process is determined by solvents and solutions properties as well as the experimental conditions [3, 8-11] (Fig.2). The electrostatic potential, working distance, orifice diameter, speed of solution pumping, etc., influence PET morphology and define the production of fibers or films.

It has been shown [4, 9, 10] that for the electrospinning process PET could be dissolved in solvents like trifluoroacetic acid (TFA) [12] or tetrahydrofuran (THF) [13]. The concentration of PET in the solution has to be below5 g/cm$^3$, as reported in [12, 13]. Two-component chemical systems consisting of TFA and dichloromethane

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(DCM) in different ratios, as follows: 7:3 [4] and 1:1 [9, 14] have also been used. Mixture of trichloroacetic acid (TCA) and DCM in 1:1 volume ratio could also dissolve PET [15]. The concentration of PET in the solution should be between 10 and 20 g/cm$^3$ [4, 8, 9, 15].

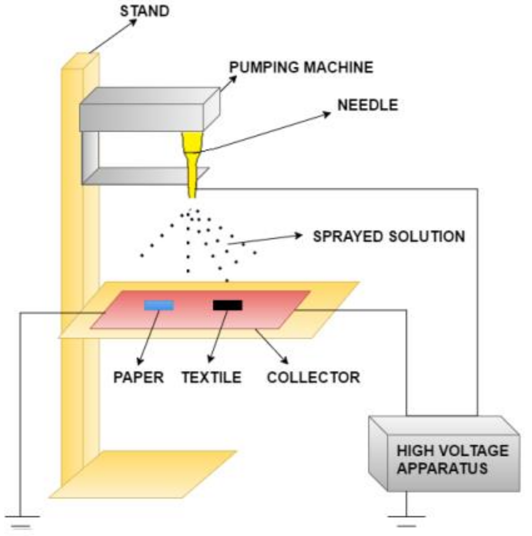


**Fig. 1.** Design of electrospinning/electrospraying apparatus.

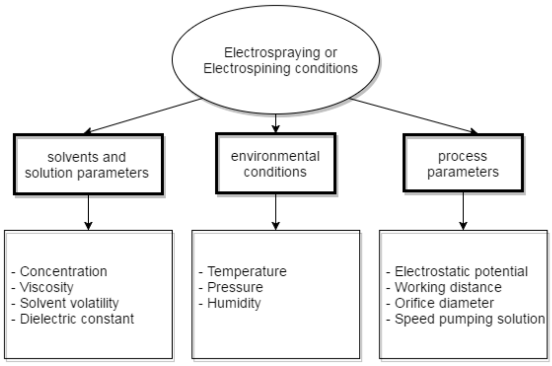


**Fig. 2.** The electrospraying or electrospinning conditions.

In our experiments we have chosen two-component chemical system consisting of TCA and DCM in 1:1 volume ratio. Up to now, TCA has not been used for electrospraying process to recycle PET waste; regardless it possesses similar to TFA solvent volatility. Moreover, it is environmentally less aggressive, with lower viscosity than TFA, which is favorable for electrospraying process. The lower price of TCA has also been a factor for our purpose.

The aim of the present work is to study the potentiality of electrospraying process for PET waste recycling, using TCA and DCM as solvents, and deposition of thin films on textile and paper surfaces with a view of possible production of waterproof clothing and impervious paper.

## EXPERIMENTAL

### *Reagents and Materials*

The PET waste material was collected from used mineral water bottles (Gorna Bania, Devin, Bankia). Trichloroacetic acid (TCA - ACS, 99% Sigma-Aldrich Chemie GmbH Germany) and dichloromethane (DCM, - ACS, 100% Valerus Ltd Bulgaria) were used as solvents. All chemical materials were utilized as received. Syringes and medical needles (with diameter 0.6mm) were used in the electrospraying process. The sharp end of the needles was preliminarily cut off for homogenization of the electric field. Small paper (blue copy-paper) and textile (black jeans) pieces (2x2 cm$^2$) have been prepared from relevant materials.

### *Preparation of polymer solution for electrospraying*

All waste bottles were cleaned with pure ethanol, prior to be dried. After that the bottles were cut to small pieces, each of them about 1x1cm$^2$. 20 wt. % PET solution has been prepared by dissolution of the waste in a mixture of TCA/DCM in 1:1 ratio (vol. %). Then the solutionwas homogenized by magnetic stirrer for 10 min at room temperature.

### *Electrospraying process*

A successful synthesis of PET electrosprayed films was done under electric field strength: E=1 kV/cm (20 kV applied voltage at 20 cm distance between collector and needle). The pumping speed of the solution was fixed at 0.013 cm$^3$/ min. Paper and textile pieces were positioned on the Al collector of apparatus before starting the process, which was held at environmental conditions.

### *Characterization of impregnated PET films*

The surface morphology of textile and paper pieces, non- impregnated and impregnated with electrosprayed PET films, was observed by digitalized scanning electron microscope (SEM Philips 515)at accelerating voltage 25 kV. The samples were metallized with gold coating films before SEM analysis.

Water permeability was studied by observation of the shape and size of the droplets, pipetted on the non- impregnated and impregnated materials and whether they passed or not through the samples.

For qualitative evaluation a universal wetting indicator, which gives a visible change of the color, was put under the paper and textile (non- and impregnated). The behavior of water droplets on the PET films was recorded by optical digital camera (Olympus TG-610).

## RESULTS AND DISCUSSION

### *Surface morphology of non-impregnated and impregnated textile and paper*

SEM micrographs of untreated textile and paper samples are presented in Fig. 3a and Fig. 4a, respectively, while the surface morphology of PET films, deposited on textile and paper is shown in Fig. 3b and Fig. 4b. The typical fibrous morphology of textile and paper is well seen. Usually, when the materials are hydrophilic, this type of microstructure defines high water permeability, due to the presence of voids between the fibers. The surfaces of impregnated textile (Fig.3b) and paper (Fig.4b) look smoother, because the deposited polymer films have evenly encased the fibers of the both types of materials, despite their complicated texture. This is an important prerequisite for reducing of water permeability of textile and paper. A comparison of the morphology between uncovered and impregnated materials allows concluding that the electrospraying process has been successfully applied at the experimental conditions chosen and the surface of textile and paper samples have been evenly coated by the recycled PET films.

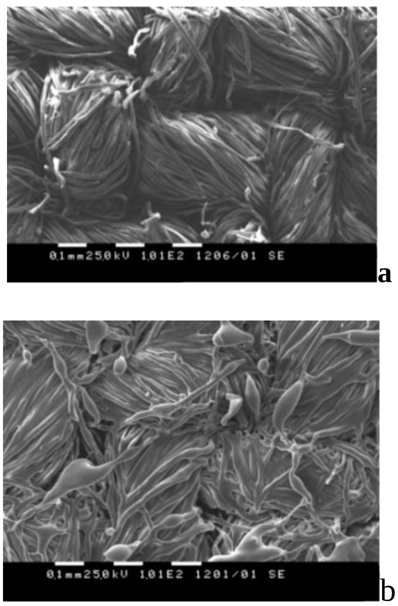


**Fig.3.** SEM micrographs of the surface morphology of non-impregnated (a) and PET impregnated textile (b).

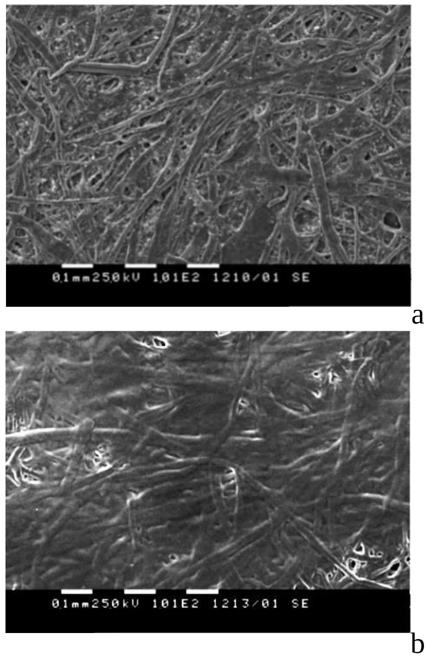


**Fig. 4.** SEM micrographs of the surface morphology of non-impregnated (a) and PET impregnated paper (b).

### *Water resistance of non-impregnated and impregnated materials*

The results of water resistance study of non-impregnated (a, b, c) and impregnated (d, e, f) textile (Figs. 5, 6) and paper (Figs.7, 8) are presented on Figs. 5 - 8. Two types of pictures – in front (Fig.5, 7) and top view (Fig.6, 8) of the samples, have been taken for better illustration of the droplet behavior on the surface of the materials. Selected images: at the beginning (0 s – a, d), in the middle (5 s – b, e) and at the end (10 s – c, f) of the study are included in the figures. It is clearly demonstrated that the water drop spread (Fig.5, 6 a, b, c) on the textile surface, its shape and size changed and the drop completely disappeared in 10 s. In the same time a change in the color intensity

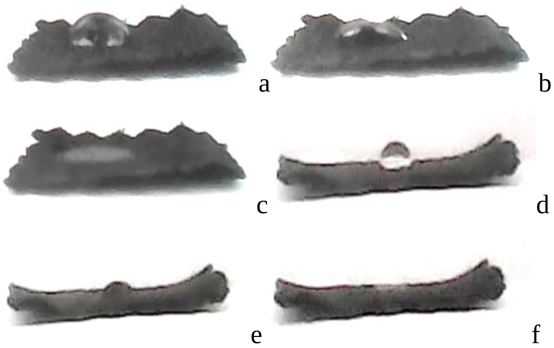


**Fig. 5.** Digital images of the front view of non-impregnated textile (a-c); PET impregnated textile (d-f); at the beginning of testing (a, d); in the middle (b, e); at the end(c, f).

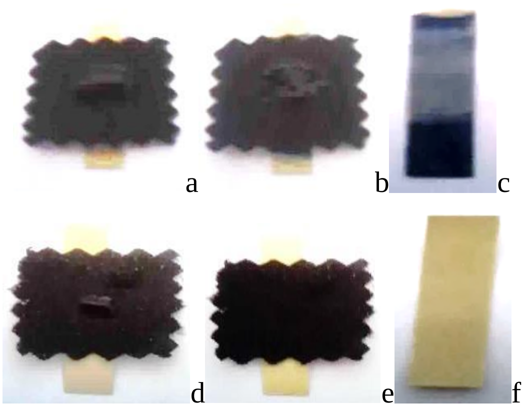


**Fig. 6.** Digital images of the top view of: non-impregnated textile (a-c); PET impregnated textile (d-f); at the beginning of testing (a, d); at the end(b, e); yellow indicator (c, f).

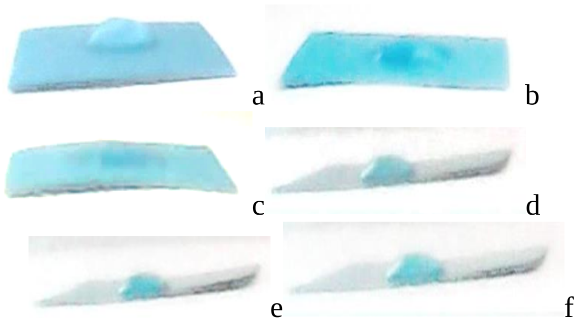


**Fig. 7.** Digital images of the front view of: non-impregnated paper (a-c); PET impregnated paper (d-f); at the beginning of testing (a, d); in the middle(b, e); at the end (c, f).

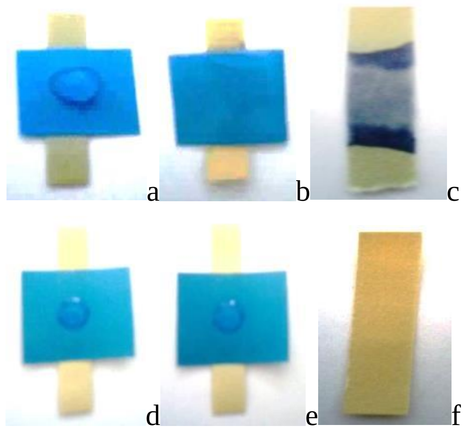


**Fig. 8.** Digital images of the top view of: non-impregnated textile (a-c), PET impregnated textile (d-f); at the beginning of testing (a, d);at the end (b, e); yellow indicator (c, f).

of the indicator was detected (Fig. 6c), which is a proof that the textile absorbs and leaks the water. Similarly, the drop on the surface of impregnated textile (Fig.5, 6d, e, f) changed its shape and size, but the color of indicator, disposed under the impregnated textile remained unchanged (Fig. 6f). All of this proves that the PET films have evenly covered the textile surface, thus assuring its waterproof property.

The water permeability survey of the non-impregnated (Fig.7, 8a, b, c) and the impregnated paper is illustrated in the corresponding figures (Fig. 7, 8d, e, f). The water drop spreads on the surface of untreated paper analogically to its behavior on the surface of non-impregnated textile. The indicator under the paper changes its color (Fig.8c), because of the water absorption as it was established in the case of non-impregnated textile. On the surface of impregnated paper the water drop retains its shape and size till the end of the observation (Fig.7, 8d, e, f). Besides, no change of the color intensity of the indicator was registered (Fig.8f). Obviously, this is due to the lack of water absorption in the impregnated waterproof paper.

## CONCLUSION

The results of the present study demonstrate the potential of the electrospray process as a promising method for recycling of polyethylene terephthalate (PET), which is one of the most significant wastes of the human activity. For the first time, a two-component chemical system, consisting of TCA and DCM in 1:1 volume ratio, was successfully applied as a solvent in the electrospray deposition of films from PET waste. The selected solvents and PET concentration in the solution provide the required viscosity and electrical conductivity for realizing the electrospraying process. By optimizing the spray process parameters (electric field strength 1 kV/cm and pumping speed –0.013 $cm^3$/min) thin PET films were successfully deposited on textile and paper samples. The estimation of the water permeability performed show that the impregnated with PET both kinds of materials do not absorb water droplets. Thus, the results obtained demonstrate the prospects for application of recycled PET films in the production of waterproof materials.

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# ФИЛМИ ОТ РЕЦИКЛИРАНПОЛИЕТИЛЕНТЕРАФТАЛАТ, ОТЛОЖЕНИ ВЪРХУ ХАРТИЯ И ТЕКСТИЛ ЧРЕЗ ЕЛЕКТРОРАЗПРЪСКВАНЕ

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(Резюме)

Изследвани са възможностите за приложение на метода на електроразпръскване за рециклиране на отпадъчен полиетилен терефталат (ПЕТ) (бутилки, опаковки за храни и др.). Демонстрирано е също така успешното отлагане на ПЕТ филми върху хартия и текстил с цел получаване на водоустойчиви материали. Повърхността на покритите и непокрити хартия и текстил е охарактеризирана чрез сканираща електронна микроскопия (СЕМ). Сравнителното изследване на водната пропускливост на покрити и непокрити повърхности показа, че покритите с ПЕТ материали не пропускат водните капки. На тази основа е заключено, че процесът на електроразпръскване има потенциал като обещаващ метод за рециклиране на отпадъчен ПЕТ, чийто продукт може да се използва за производството на защитни облекла и непропусклива хартия.