



NEW METHOD OF HYDROPHOBIZATION OF POLYETHYLENE TEREPHTHALATE FABRIC FOR BLOOD VESSEL PROSTHESIS

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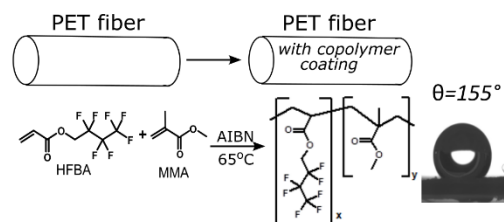
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Abstract

The radical block copolymerization of 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA) with methyl methacrylate (MMA) at 65 °C under normal atmospheric conditions on the surface of polyethylene terephthalate (PET) tissue (Dacron), used for the production of vascular prostheses, was carried out. It was found that the copolymerization of HFBA and MMA in 10:1 ratio results in a superhydrophobic coating with a contact angle $\theta = 155^\circ$. The examination of the surface using scanning electron microscopy confirmed the presence of a highly structured fluoropolymer coating on a micro and nanoscale.

Key words: polyethylene terephthalate, 2,2,3,3,4,4,4-heptafluorobutyl acrylate, vascular prostheses, superhydrophobicity, radical copolymerization.



Introduction

Polyethylene terephthalate (PET) and polytetrafluoroethylene (PTFE) are currently used clinically for vascular prostheses [1]. However, a coating of only polyethylene terephthalate (PET) or polytetrafluoroethylene (PTFE) will not give the surface pronounced superhydrophobicity, which is important in terms of preventing thrombosis [2]. Even for a clean, smooth PTFE coating, the contact angle is only 120° [3]. In this context, many researchers have associated the latest advances with the development of a structure similar to that found on lotus leaves [4]. Despite the complexity and sophistication of these techniques, the contact angles for water on the resulting coatings range between 120 – 150° .

The purpose of our work was to search for a new, easily implemented method of hydrophobicity of PET fabric, by the copolymerization of methyl methacrylate (MMA) and 2,2,3,3,4,4,4-heptafluorobutyl acrylate (HFBA). The nontriviality of this approach is that the hydrophobization is carried out by block copolymerization of MMA and HFBA on the surface of PET fabric in a normal atmosphere with O_2 .

Results and discussion

From the analysis of SEM micrographs of the surface of PET tissue treated with monomers, it was found that a liquid mixture of MMA/HFBA monomers had penetrated between the PET fibers and had copolymerized (Figs. 1a–d) [5]. During the copolymerization of MMA and HFBA monomers on the surface of PET fabric at 1:1 and 1:2 ratios, the weight gain of the samples was 343% and 150%, and the contact angle with water

was 110° and 120° (Table 1). Upon an increase of the molar fraction of HFBA to 1:5, the contact angle θ increased to 135° , while an increase in the mass of the tissue was only 11% at the MMA/HFBA ratio of 1:10 (Fig. 2, Table 1). The PET fabric treated as described above becomes superhydrophobic with a $\theta = 155^\circ$ (Fig. 2, Table 1).

Despite this, the analysis by energy-dispersive X-ray spectroscopy (EDS-SEM) indicated the presence of a significant amount of fluorine on the surface of the sample ($v \sim 8$ wt %). The macroscopic image demonstrates that the dimensions of the hemispherical structures on the surface of the PET tissue vary from 500 nanometers to 10 micrometers (Figs. 1a,b).

Thus, the superhydrophobicity of the PET tissue treated using this method can be attributed to a decrease in the surface energy due to the presence of polyfluoroalkyl side-chain groups

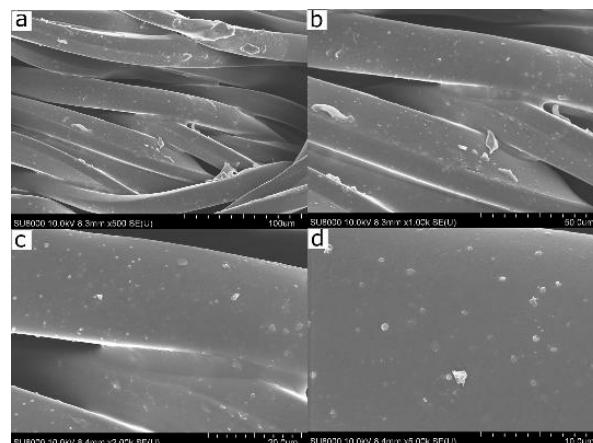
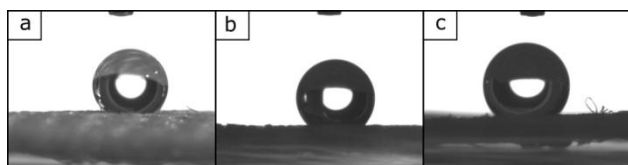


Figure 1. FE-SEM images of the surface of the PET-Poly(MMA/HFBA) (1:10) sample: (a) $\times 500$, scale—100 μm ; (b) $\times 1000$, scale—50 μm ; (c) $\times 2000$, scale—20 μm ; (d) $\times 5000$, scale—10 μm .

Table 1. Mass gains during the copolymerization on the fabric samples and contact angles of a water drop sitting on a hydrophobized fabric

Sample	Fabric mass gain, %	Contact angle, deg
PET-Poly(MMA)	70 ± 1	85 ± 5
PET-Poly(HFBA)	13.5 ± 0.5	140 ± 5
PET-Poly(MMA/HFBA) (1:1)	343 ± 1	110 ± 5
PET-Poly(MMA/HFBA) (1:2)	150 ± 1	120 ± 5
PET-Poly(MMA/HFBA) (1:5)	11.0 ± 0.5	135 ± 2
PET-Poly(MMA/HFBA) (1:10)	5.5 ± 0.5	155 ± 3

**Figure 2.** Images of water drops on the surface of the samples of PET fabric with synthesized copolymer: (a) Poly(MMA/HFBA) with 1:1 ratio, (b) Poly(MMA/HFBA) with 1:5 ratio, (c) Poly(MMA/HFBA) with 1:10 ratio.

in its copolymer coating. Additionally, the presence of numerous structured micro- and nanofeatures (Figs. 1c,d) contributes to the surface roughness [6].

Experimental section

This work was concerned with Dacron polyester fabric manufactured by PTGO SEVER (Russia), 99% methyl methacrylate (Merck), and 99% azobisisobutyronitrile (Chemical Line). 2,2,3,3,4,4,4-Heptafluorobutyl acrylate, described previously [5], was synthesized from acryloyl chloride (97%, Sigma-Aldrich) and 2,2,3,3,4,4,4-heptafluorobutyl alcohol (98%, PiM-Invest) in dichloromethane (99.8%, Merck) in the presence of Et₃N (99.5%, Panreac) using the method for synthesis of 1H,1H-perfluoroheptylacrylate [7]. The yield was 77%, the purity was 98%, Bp = 51–52 °C at 50 mm Hg, n_D^{20} = 1.3319.

The radical block copolymerization of MMA and HFBA was carried out on the PET fabric using different ratios of the monomers (see Table 1) in the presence of 2.5% AIBN at 65 °C under normal atmospheric conditions. The initiator was dissolved in a mixture of the monomers with different molar ratios (Table 1). A square-shaped sample of the initial tissue with an area of 1 cm² was then moistened with this mixture and placed in a 5 mL glass reactor. The reactor was closed and thermostatted at 65 °C for 8 h. After the copolymerization, the tissue samples were washed with chloroform and acetone. The final stage was to dry the sample for 5 min using a jet of hot air (70 °C).

The contact angle measurements were carried out under static conditions using the sessile drop method with a Contact Angle Measuring System (DSA 100, KRÜSS GmbH) device at room temperature in air for 20 min.

The observations of the surface of the samples were carried out using a Hitachi SU8000 field-emission scanning electron

microscope (FE-SEM), in secondary electron mode, at 10 kV acceleration voltage. The morphology of the samples was studied taking into account possible influence of metal coating on the surface [8]. The EDS-SEM studies were carried out using an Oxford Instruments X-max 80 EDS system at 10 kV accelerating voltage.

Conclusions

A new simple method for creating hydrophobic tissue-based PET material was developed. The process involved the radical block copolymerization of MMA and HFBA, which were mixed in 1:10 ratio, at 65 °C in a normal atmosphere directly on the fabric base which could be used to make prosthetic blood vessels. This afforded the material with superhydrophobic properties ($\theta = 155^\circ$). The resulting material could be used for the production of prosthetic blood vessels as well as blood transfusion and dialysis equipment.

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