Applied Surface Science 258 (2012) 4636–4641

Contents lists available at SciVerse ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Microwave plasma induced grafting of oleic acid on cotton fabric surfaces

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ARTICLE INFO

Article history:
Received 21 October 2011
Received in revised form
30 December 2011
Accepted 31 December 2011
Available online 13 January 2012

Keywords:
Plasma
Cotton fabric
Surface functionalization
Hydrophobic
Contact angle
FTIR
Fatty acids
Oleic acid

ABSTRACT

Cotton fabric surface was successfully functionalized with microwave plasma (2.45 GHz, 500 W) to impart water repellency. The hydrophobic agent used was oleic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$), a fatty acid derived from various plant seed oils. Non-polymerizing gas (Argon) was used to create the plasma. The exposure of the cellulose to Ar-plasma generated radicals, which were subsequently used to initiate co-polymerization reactions with oleic acid. The FTIR spectra showed the presence of additional vibrations located at 2918, 2849, and 1707 cm^{-1} in the functionalized samples. Dynamic contact angle measurements were performed to assess the hydrophobic properties of the functionalized cotton fabric. The grafted cotton fabric showed excellent water repellency. In addition, the use of plant-derived monomers and biopolymers provides a different approach to use renewable resources to create functionalized biopolymeric substrates.

1. Introduction

Recently, there has been an increased commercial interest in producing water repellent surfaces. Several materials such as, nonwovens, textiles, polymer films, and paper products are hydrophilic. This interaction with water could lead to the reduction of the mechanical properties of the product or loss of its functionality. However, water repellency can be imparted to these products, leading to the protection of their mechanical properties and adding a new functionality. Surfaces with a static contact angle higher than 150° and low contact angle hysteresis are defined as super hydrophobic surfaces. Some examples of hydrophobicity in nature are the lotus leaves and roses petals. These materials have a hierarchical structure which imparts roughness to the surface. The combination of roughness and surface chemical composition give them the superhydrophobic property [1–3].

In order to impart water repellency to a hydrophilic material, a hydrophobic monomer must be covalently grafted to the hydrophilic surface. These monomers usually are derived from petroleum sources. It is desirable to impart water repellency to surfaces using monomers derived from renewable resources. Oils and fats derived from animals and plants provide good renewable resources for hydrophobic monomers [4]. Natural oils and fats are predominantly composed of triglycerides of carboxylic acids of long chain lengths. Once these carboxylic acids are extracted from the triglycerides molecules, they are called fatty acids. Thus, fatty acids are carboxylic acids with a long un-branched aliphatic chain and some of them have unsaturated carbons. The principal method to obtain fatty acids from triglycerides is by the trans-esterification reaction of oils with methanol. The reaction produces fatty acids along with glycerol [5].

Traditional methods for imparting hydrophobic properties are carried with wet chemistry. The disadvantage of this method is that it produces large amounts of toxic effluents. Liquid processes have many disadvantages when compared to gas phase processes. These disadvantages include the disposal of the used solvents, diffusion limited transport and poor control of reactants among others [6]. It is desirable to graft the monomer without producing toxic effluents in a dry process. Plasma technology presents a solution to this problem, since it is a dry and clean technology and it has matured enough to be used on industrial scale. Plasma is defined as a medium composed of radicals, metastable molecules, photons and charged particles such as ions and electrons. In general plasmas are generated by exposing a gas to radiofrequency or microwave electrical discharges. Microwave creates a plasma with higher density than radiofrequency. Plasma technology is becoming more attractive for surface modification of substrates. The advantage of using plasma is that there is no need to use toxic radicals as initiators or crosslinkers and the amount of toxic effluents is minimized. Furthermore, plasma is a cold process, thus, there is no thermal degradation of the substrate. In addition, plasma does not penetrate more than

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doi:10.1016/j.apsusc.2011.12.130

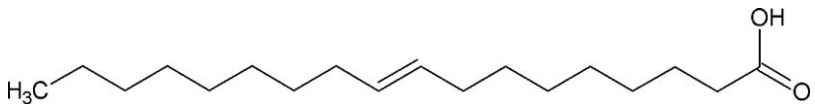

Fig. 1. Chemical structure of oleic acid.

100 nm from the surface. Therefore, the cotton fabric retains most of the desirable physical properties [7].

Hydrophobization of surfaces using oils or fatty acids has been reported. Dankovich and Hsieh used a direct reaction of cellulose with the triglycerides of plant oils. The process used the transesterification reaction of the triglycerides with the hydroxyl groups of cotton, thus, chemically grafting the fatty acid chain to the cellulose macromolecules. The treatment included a heating process that could cause damage to some polymeric surfaces [8]. Peroval et al. grafted unsaturated oils from fish and plants to arabinoxylan based films with the aid of electron beam and oxygen plasma. By measuring the contact angle, they observed an increase in hydrophobicity for some of the treated samples [9]. Gaiolas et al. grafted two natural products, myrcene and limonene, to cellulose fibers with the aid of cold plasma. They obtained contact angles above 100° for both substances [10]. Banerjee et al. increased the oil absorption capacity of the sawdust by grafting fatty acids to the surface. The increased oil absorption capacity was an indication of the surface becoming more hydrophobic [11]. Popescu et al. used radiofrequency plasma to graft fatty acids to cellulosic fibers [12,13]. Furthermore, Li and Zhu increased the dispersion capacity of organic solvents of SiO_2 nanoparticles by grafting oleic acid on their surfaces [14]. In the past, our group successfully functionalized cotton fabric with microwave plasma to impart water repellency. Vinyl laurate was used as the hydrophobic monomer [7,15]. Although the cotton fabric grafted with vinyl laurate showed excellent hydrophobicity and laundry durability, the drawbacks of vinyl laurate are that this monomer is derived from petroleum and it has an additional reaction step to produce the vinyl group when compared with its fatty acid and lauric acid.

In this study, a microwave plasma treatment was used to impart hydrophobic properties to hydrophilic cotton fabrics (which is composed of 99% cellulose, after scouring and bleaching). The hydrophobic agent used was oleic acid ($CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$), a monounsaturated fatty acid derived from various plant seed oils and animal fats. The amount of grafted fatty acid was determined by gravimetric method and Fourier Transform infrared spectroscopy. The hydrophobicity of the samples was measured by dynamic contact angle of water.

2. Experimental

2.1. Materials

The fabric used in this project was 100% cotton fabric scoured, desized, and bleached. For contact angle measurements, distilled water was deionized in a Milli-Q plus system from Millipore (Billerica, MA) to reach final resistivity of 18.2 MΩ cm. Oleic acid ($C_{18}H_{34}O_2$, Fig. 1) and ethanol were reagent grade and obtained from Fisher Scientific. Argon gas for the microwave plasma was a commercial grade.

2.2. Plasma surface modification

Cotton samples were first rinsed with water to remove any foreign matter and dried. Then, fabric substrates were pretreated in Ar microwave plasma (PLASMAtech, KY) with a generator of 2.45 GHz and a chamber of 1000 cubic inches. Samples were plasma treated for 240 s at 500 W, 60 ml/min Ar flow rate and a pressure of 25 Pa. This process created free radicals on the cellulose surface and cleaned the substrate. Activated samples were immediately immersed in ethanolic solutions of oleic acid with different molar concentrations (0, 0.033, 0.066, 0.1, 0.2, 0.3 and 0.4 mol/l). Afterwards, the samples were air-dried and placed gain in the plasma chamber for an Ar-plasma treatment for 240 s with the same conditions as described previously. Three specimens were treated independently from each concentration. Samples were rinsed in ethanol several times to remove the excess of non-grafted oleic acid and air-dried. Then, samples were conditioned at standard conditions (65% RH ± 2% and 70 °F ± 1 °F) for at least 48 h before any testing.

2.3. Weight measurements

Samples were conditioned at 65% RH ± 2% and 70 °F ± 1 °F before and after plasma treatment to perform gravimetric analysis (Standard conditions for textile testing according to ASTM method D1776-98). The amount of oleic acid grafted on cellulose macromolecules was determined by a modified calculation based on the AATCC Test method 20A-2000 for nonfibrous content on samples. The amount of oleic acid grafted to the fabric is expressed as percent of weight increase (% add-on = $((m - m_0)/m_0) \times 100$, where m_0 is the initial weight of the conditioned fabric, and m is the weight of the treated fabric after rinsing, drying, and conditioning).

2.4. Fourier transform infrared spectroscopy

Fourier transform infrared (FTIR) spectra of the samples were recorded using Spectrum-One equipped with a universal attenuated total reflectance (UATR) accessory (PerkinElmer, MA). The UATR-FTIR has a ZnSe-diamond crystal composite that allows the FTIR spectra collection without any special sample preparation and the analysis of the surface composition of materials. This particular UATR accessory allows the infrared beam to have a penetration depth of around 1.66 μm at 1000 cm^{-1} [16,17]. The UATR accessory has a "pressure arm", which is used to apply a constant pressure to the samples positioned on top of the crystal to ensure good contact between the crystal and the sample. FTIR spectra were collected at a spectra resolution of 4 cm^{-1}, with 32 co-added scans over the range from 4000 to 650 cm^{-1}. The spectra were baseline corrected and normalized to the highest absorption peak. The FTIR analysis was carried out in a laboratory conditioned at 65% RH ± 2% and 70 °F ± 1 °F. All samples were conditioned at least 48 h prior to testing. Ten spectra were collected from each sample for a total of 30 spectra for each concentration (3 replications × 10 spectra).

2.5. Dynamic water contact angle measurements

In order to assess the hydrophobic properties of the samples, dynamic contact angle measurements were performed using water as the test liquid. Contact angle measurements were acquired with a FTA1000 instrument (First Ten Angstroms, VA). A 30 gauge needle was used to place a drop between 6 and 8 μL on the fabric surface. Pictures of the water drops on the fabric surface were taken every 2 s for 2 min. Laplace–Young fit method was used to calculate the contact angles. One measurement of contact angle was done per sample for a total of 3 measurements for each concentration. The data were analyzed using Statistica software from StatSoft.