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Chemical modification of PET surface and subsequent graft copolymerization with poly(N-isopropylacrylamide)

Parisa Golshaei, Olgun Güven*

Hacettepe University, Department of Chemistry, Beytepe, 06800 Ankara, Turkey

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ABSTRACT

Thermo-sensitivity has been introduced onto poly(ethylene terephthalate) (PET) surfaces by graft copolymerization of N-isopropylacrylamide (NiPAAm). The PET surface was first photo-oxidized in the presence of H_2O_2, to have enriched concentration of −COOH groups which were later reacted with allylamine (AlAm) to introduce vinyl end groups at the surface. These groups were used as active sites for thermally initiated graft copolymerization of NiPAAm. The influence of solvent, monomer concentration and time on grafting has been investigated. Spectroscopic analysis confirmed the presence of (AlAm) linked to treated surfaces as well as poly (NiPAAm) grown from them. The thickness of grafted layer can be adjusted between 10 and 18 μm via grafting degree by controlling of grafting reaction parameters. Imaging in water environment revealed the reversible modification of surface morphology below and above the lower critical solution temperature (LCST) of PNiPAAm. The grafted surfaces were analyzed by colorimetric assay, ATR-FTIR, Raman, and XPS spectroscopies and Thermogravimetric analysis (TGA), and Differential scanning calorimetry (DSC).

1. Introduction

The performance of polymeric materials in traditional and new applications does not depend only on their bulk, but also on their surface properties and interface behavior. The surface of many polymeric materials is inert and hydrophobic when not chemically treated. Applications requiring adhesion, biocompatibility, wettability, adsorption, permeability, and other properties depend on the surface properties of the material significantly [1,2].

The synthetic polymers have been widely used for biomedical applications such as hemodialysis membranes, blood-contacting devices, heart valves, artificial blood vessels, stents and biosensors [3]. Clearly, the surface structure and properties play a great role in the in vivo biological performance of polymeric materials and devices [4], because many biological reactions are triggered by chemical structure, topography, and molecular flexibility of the materials near the surface, such as protein adsorption, inflammation, blood coagulation, complement activation and biodegradation [5].

One of the engineering polymers that is widely used due to its excellent properties such as mechanical strength, permeability to gases, transparency, and chemical resistance is poly(ethylene terephthalate) (PET) [6]. While biocompatible polyesters such as PET are popular materials for the manufacture of tissue engineering scaffolds, their surface properties are not particularly suitable for direct tissue growth. The functional surface of PET film is very important in specific applications such as conductive film, biocompatible materials, and packaging film [7]. A common way to promote surface activation is through grafting with a polymer of desired properties.

Various methods such as chemical grafting, plasma grafting, photo-induced grafting, UV, ozone or electron-beam irradiation, etc., have been employed to graft hydrophilic and/or biologic materials to polymer surfaces to improve their biocompatibility [8–11]. Among these treatment methods for the surface modification of polymers, radiation-induced graft copolymerization is an important method to improve their dyeability, antistatic properties, moisture regain, or impart antibacterial properties to the surfaces [12].

Poly(N-isopropylacrylamide) (PNiPAAm), a typical thermo-sensitive polymer has been well investigated in biomedical applications such as drug delivery [13], cell culture for tissue engineering [14], bioseparation [15], enzyme immobilization [16], and cell adhesion onto substrate surface owing to its tunable hydrophilicity response to temperature. PNiPAAm is a well known thermo-responsive polymer with a lower critical solution temperature (LCST) of about 32 °C in aqueous solution [17].

The objective of this study is to develop temperature-sensitive surface by grafting PNiPAAm on the surface of PET film by conventional polymerization. In order to activate the surface of PET, polar carboxyl groups were generated at the surface of PET film through alkaline

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* Corresponding author.
E-mail address: guven@hacettepe.edu.tr (O. Güven).

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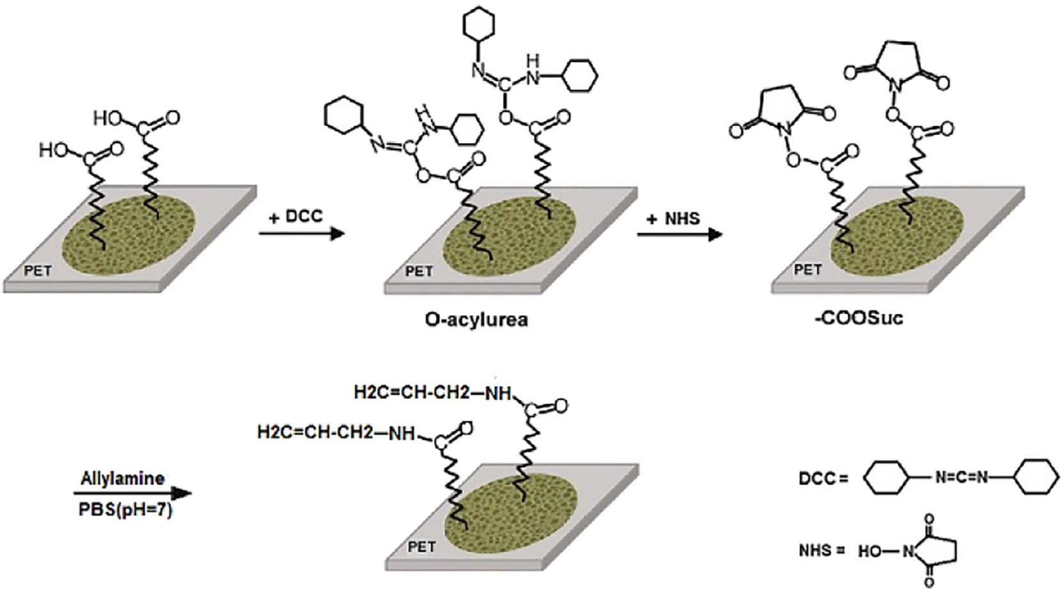
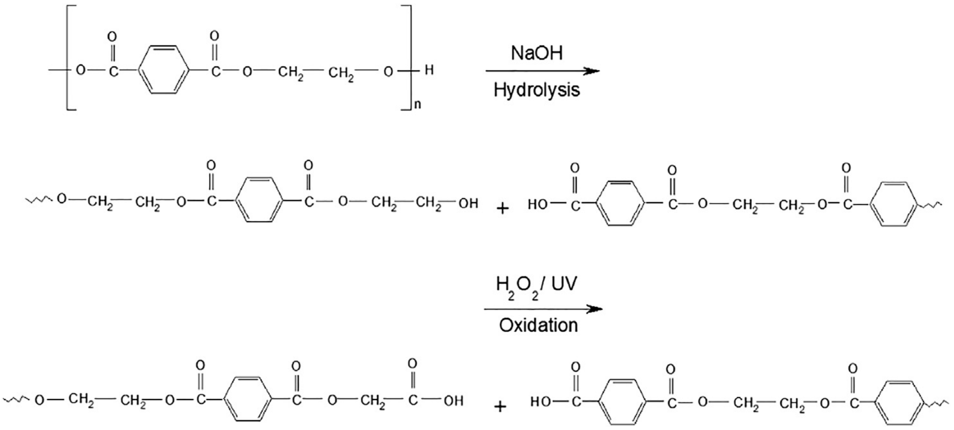


Fig. 1. Covalent immobilization of AlAm on modified PET surface to introduce vinyl end groups.



Scheme 1. Reactions proposed for primary functionalization of PET film surface.

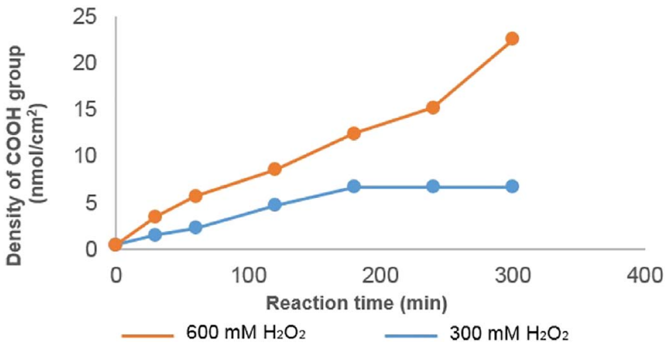


Fig. 2. [COOH] density on the oxidized surface of PET film treated under different oxidizing conditions.

hydrolysis and oxidation. Carboxylic acid groups were reacted with allylamine to introduce vinyl end groups at PET surface. Poly(N-isopropylacrylamide), was grafted on the surface of poly(ethylene terephthalate) films via these vinyl end groups by thermally initiated graft polymerization. The surface composition and structure of modified PET films were characterized by Fourier transform infrared spectroscopy (FTIR/ATR), Raman, X-ray photoelectron spectroscopy (XPS). The surface was analyzed with contact angle measurements, thermal gravimetric analysis (TGA), differential scanning calorimetry (DSC). To evaluate the amount of carboxyl and —N groups on the modified surface, PET was dyed with an acid dye which binds the —COOH and —N groups.

2. Materials and methods

2.1. Materials

Poly(ethylene terephthalate) (PET) film with 210 μm thickness was obtained from Toray Plastics Europe Lumirror, UK. The surfaces of the films were cleaned by extractions with acetone and methanol before use.

N-isopropylacrylamide (NiPAAm, 97%), Allylamine (99%), Benzoyl peroxide (BPO), Hydrogen peroxide (H_2O_2), *N,N*-dimethylformamide (DMF), N,N´-dicyclohexylcarbodiimide (DCC), N-hydroxysuccinimide (NHS), Toluidine Blue O (TBO) and Acid Orange II (AO) were purchased from Sigma & Aldrich Chemical Co. Ltd. These were high quality products and used as received, except NiPAAm that was purified by recrystallization from hexane. Water purified with a Milli-Q system (Millipore) was used for all experiments.

2.2. Primary functionalization of PET films

2.2.1. Oxidative hydrolysis (carboxylation) of PET films

Films to be hydrolyzed were immersed in aqueous sodium hydroxide (2 M NaOH) solution and allowed to react at 70 °C for the desired