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Preparation of thermosensitive membranes by radiation grafting of acrylic acid/*N*-isopropyl acrylamide binary mixture on PET fabric

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Abstract

Thermosensitive membranes were prepared by radiation-induced graft copolymerization of monomers on PET fabrics. A binary mixture of *N*-isopropyl acrylamide (NIPAAm) and acrylic acid (AA) was grafted on polyester fabric as a base material to introduce thermosensitive poly(*N*-isopropyl acrylamide) pendant chains having LCST slightly higher than 37 °C in the membrane. The influence of ferrous sulfate, radiation dose and monomer composition on the degree of grafting was studied. The structure of the grafted fabric was characterized by thermogravimetric analysis, differential scanning calorimetry and scanning electron microscopy. The thermosensitive nature of the fabric was monitored by swelling at different temperatures. The graft copolymerization of AA with NIPAAm enhanced the LCST of the resultant membrane to ~37 °C. The moisture vapor transmission rate (MVTR) and air permeability of the fabric decreased slightly, may be due to the slight blocking of the fabric pores. The immobilization of tetracycline hydrochloride as the model drug and its release characteristics at different temperatures were monitored.

Keywords: PET fabric; Radiation grafting; Acrylic acid; *N*-isopropyl acrylamide; Membranes

1. Introduction

Intelligent drug delivery systems have generated enormous medical and economic impact on human healthcare. They can precisely control drug release rates or target active ingredients to the specific organ tissue in a living organism. Constant blood level may be achieved and maintained for appropriate time periods without fluctuations, whilst unwanted side effects can be reduced or even eliminated, and the number of applications may be reduced. The emergence of new polymer materials with "*intelligent*" properties answering to specific requirements and the applications makes it possible to produce symptom-oriented responsive systems (Schild, 1992).

One conventional route of drug delivery is directly through the skin (Sershen and West, 2002). A transdermal drug delivery device is generally in the form of skin patches which may be of an active or a passive design and provides an alternative route for administering medication. This approach to drug delivery offers many advantages over traditional methods. As a substitute for the oral route, transdermal drug delivery enables the avoidance of gastrointestinal absorption with its associated pitfalls of enzymatic and pH-associated deactivation. This method also allows for the reduced pharmacological dosages due to the shortened metabolic pathway of the transdermal route versus the gastrointestinal pathway. The patch also permits constant dosing rather than the peaks and valleys in medication level associated with orally administered medications. Multi-day therapy with a single application, rapid notification of medication in the event of emergency as well as the capacity to terminate drug effects rapidly via patch removal, are all further advantages of this route.

The radiation grafting of specific monomers on polymer surfaces is a very interesting strategy for obtaining desired properties for specific uses because it may change the surface activity without causing serious modifications of the mechanical properties in a polymer (Bozzi and Chapiro, 1988; Anjum et al., 2006; Curti et al., 2005;

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Gubler et al., 2006; Choi and Nho, 2000; Chauhan et al., 1999). Graft polymerization may be achieved by any of the direct radiation and by the preirradiation methods (Gupta et al., 2006; Liu et al., 2007). Textiles show a lot of promises as biomaterials in medical technology where the prime requirement of surface modification is to make it biointeractive. Several attempts have been made to modify poly(ethylene terepthalate) by radiation-induced grafting of acrylic acid (AA) to get functionalized surface for tissue engineering (Gupta et al., 2002, 2007). The ionic bonding of collagen with carboxyl functional groups made the polymer surface bioreceptive.

Poly(*N*-isopropyl acrylamide) (PNIPAAm) has been extensively investigated for temperature-modulated drug delivery systems due to its thermosensitive properties, such as the lower critical solution temperature (LCST of 32 °C) (Hoffmann, 1987; Afrassiabi et al., 1987). Below LCST, the hydrophilic PNIPAAm chains interact with water. However, above LCST, the hydrophobic PNIPAAm chains collapse and such interactions do not occur anymore. In fact, the hydrophobic and collapsed PNIPAAm chains actively interact with biocomponents, such as cells and proteins or other hydrophobic components, while the hydrophilic hydrated and flexible PNIPAAm chains do not interact with them. It is this thermoresponsive nature of PNIPAAm which is exploited for its biomedical applications, such as drug release (Eickman et al., 2004; Minghong et al., 1999).

The grafting of PNIPAAm on different polymers has been carried out by several workers and temperature-responsive character of the grafted materials has been investigated (Jun et al., 2001; Kondo et al., 1998; Huang et al., 2003; Yoshida et al., 1992). However, efforts are being made to develop NIPAAm-based copolymers so that its LCST can be enhanced a bit higher than 37 °C which would make their use in the controlled drug delivery in human being (Jones, 1999). The binary mixtures of AA and NIPAAm have been grafted onto different polymers, such as polyethylene and cellulose (Kondo et al., 1998; Wen et al., 2001). Effect of the preirradiation dose as well as the temperature of the grafting reaction on the efficiency of the grafting process was investigated and the optimized values of dose and temperature were found to be 20 kGy and 50 °C, respectively (Palacios et al., 2003). The calculated monomer reactivity ratios by their graft copolymerization (r_1 and r_2) were found to be 0.35 and 0.01, respectively. The grafted polymers exhibited temperature-responsive character in the range of 17–30 °C. A novel method of preparation of easily stripped off temporary wound dressing material has been reported in the literature (Li et al., 1999). In this process, NIPAAm monomer is grafted on the nonwoven using gamma ray irradiation to activate the surface of the material. The LCST in thermoresponsive NIPAAm is still retained after the grafting reaction. This makes the dressing cloth stripped off easily and without hurting the tissue.

Our interest is to develop thermoresponsive textile patch based on polyester (PET) fabric that would provide transdermal delivery of a drug at a temperature higher than the body temperature. We have carried out the grafting of NIPAAm/AA on PET fabric using gamma radiation to develop a material which is temperature sensitive and releases the drug at a temperature just above the body temperature. A detailed study of the influence of grafting parameters and the characterization of the materials has been reported.

2. Experimental

2.1. Materials

Plain weave commercial grade PET fabric was used in this study. NIPAAm, AA and ferrous sulfate were supplied by Aldrich, CDH Biochem Ltd. and Merck India Ltd., Mumbai, respectively. AA was purified by distillation under reduced pressure. Distilled water was used for all experiments. Fabric samples of size 5 cm × 2.5 cm were washed in 1:10 methanol/water for 12 h to remove spin finish from the fabric. Subsequently, fabric was boiled in distilled water for 1 h and then dried in oven vacuum for 6 h to a constant weight.

2.2. Irradiation

A ^{60}Co gamma radiation source, supplied by Bhabha Atomic Research Centre, India, was used for the irradiation of the samples. The dose rate was 0.18 kGy/h. Irradiations were carried out in air under ambient conditions.

2.3. Graft copolymerization

Graft copolymerization of binary mixture of NIPAAm and AA was carried out by preirradiation grafting method. PET fabric was exposed to the gamma radiation operating at 0.18 kGy/h. The irradiated samples were placed in reaction tubes which contained aqueous solutions having constant monomer concentration of 40% (vol%) along with the Mohr's salt of 0.05–0.5% (wt%). Solutions were prepared with different AA/NIPAAm molar ratios. The tubes were deareated by bubbling nitrogen and sealed. Subsequently, tubes were placed in a thermostated water bath at 60 °C for 8 h. After the reaction, the samples were washed with water and methanol repeatedly at ~30 °C to extract homopolymer as well as unreacted monomer formed during the grafting reaction. The grafted samples were dried under vacuum to a constant weight. The degree of grafting was determined gravimetrically as per the following expression:

$$\text{Degree of grafting} = \frac{W_g - W_0}{W_0} \times 100, \quad (1)$$

where W_0 and W_g are the weight of the ungrafted and grafted fabrics, respectively.