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Chemically modified natural rubber latex - poly(vinyl alcohol) blend membranes for organic dye release

Janisha Jayadevan [a], Rosamma Alex [b], Unnikrishnan Gopalakrishnapanicker [a,*]

[a] Polymer Science & Technology Laboratory, Department of Chemistry, National Institute of Technology Calicut, NITC Campus (P.O), Kozhikode, Kerala 673601, India
[b] Joint Director (Rt), Rubber Research Institute of India, Kottayam, Kerala, India

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ABSTRACT

Novel blend membranes were prepared from chemically modified natural rubber latex (NRL) and poly(vinyl alcohol) (PVA) for release application. Chemical modification of NRL was done by grafting (dimethylaminoethyl methacrylate) (DMAEMA) onto NR particles by using a redox initiator system viz; cumene hydroperoxide/tetraethylenepentamine (CHP/TEPA), followed by dialysis for purification. The grafting was confirmed by dynamic light scattering (DLS), fourier transform infrared (FT-IR) spectroscopy and nuclear magnetic resonance spectroscopy (NMR). The grafted NRL was subsequently blended with PVA to make uniform membranes by solvent casting at 60 ± 2 °C. The blend membranes were characterised by FT-IR spectroscopy, X-ray diffractometry (XRD) and thermogravimetry (TGA). Moisture uptake, swelling and water contact angle experiments showed an increased hydrophilicity when the PVA content in the blend membranes was increased. Scanning electron microscopic investigations indicated the formation of pores in the membranes after a leaching cycle. The potential of the membrane for the use in the release application was tested with model organic dyes rhodamine B, methyl orange and fluorescein. Results from the release study indicate that the membranes can be used for the release of cationic dyes.

1. Introduction

Natural rubber latex (NRL) is a biomacromolecular system having *cis*-polyisoprene particles dispersed in aqueous medium [1]. It is a slight yellow milky liquid that undergoes coagulation by acids and electrolytes at room temperature [2,3]. Average size of the polymer particles in NRL is 0.02–3 μm. The particles are covered by a layer of proteins and lipids. These proteins and lipids are negatively charged, which provides colloidal stability to the NRL [4]. However, the colloidal stability is very sensitive to pH changes. This limits its use as a core material in latex form for many applications. The products from NRL such as tubings, surgical gloves and catheters find extensive applications in the biomedical field [5–8]. The advantages of these products are their elasticity, flexibility and resistance against splitting [9]. However, the products from NRL show some disadvantages such as low resistance to thermal degradation, poor resistance to ozone and organic solvents and biological incompatibility to the human body [10].

In view of the above, many efforts are being implemented to modify the features of NRL. There are three main approaches to improve the properties of NRL which includes a change in its chemical microstructure, addition of compatible chemical reagents into it or blending it with other suitable polymers [11–15]. It has been reported that the properties of NRL can be efficiently altered through graft copolymerisation [16–19]. Grafting of a second polymer onto NRL using redox initiators is a preferred method for modifying NR both in solution [20] and latex form [21–23]. Such grafting may lead to a core-shell structure; with a hydrophobic core and hydrophilic shell [19]. The core-shell type composite polymer emulsions possess structured latex particles with fine-tunable properties [24,25]. The key feature in this type of structured composite emulsions is the regulation of the structure of the latex particles without changing the basic composition [26]. This type of chemical modification results an enhanced colloidal stability at a lower pH range, since the resultant hydrophilic shell can act as an electrosteric stabiliser. The enhanced colloidal stability makes latex resistant to any mechanical and chemical disturbances and improves its processability [27].

Polyvinyl alcohol (PVA) is a water soluble synthetic polymer. It is a macromolecule of great interest because of its desirable characteristics such as hydrophilicity, good film forming ability, resistance to oxidation and excellent mechanical properties [28]. It has also been employed for different pharmaceutical and biomedical applications [29,30]. PVA has by now been identified as an excellent partner for many macromolecular systems [31–33].

There are different reports on the utilization of NRL and PVA individually or along with other polymers for drug/dye delivery applications

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* Corresponding author.
E-mail address: unnig@nitc.ac.in (U. Gopalakrishnapanicker).

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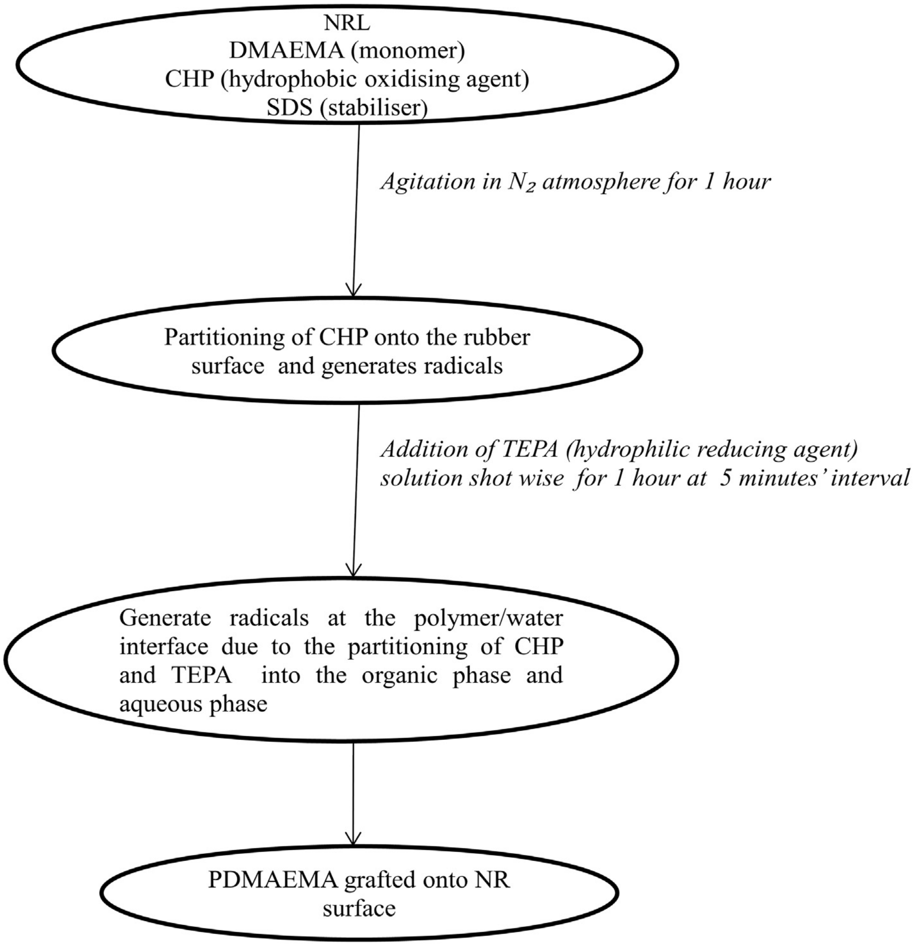

Scheme 1. Chemical modification of NRL.

[34–39]. A few articles report their combination with improved properties for similar applications [40]. However no reports are available on chemically modified NRL/PVA blends for dye/drug release applications.

The goal of the present work is to modify NRL physico-chemically, and to develop novel membranes for release applications. The study initially focuses on the chemical modification of NRL with dimethylaminoethyl methacrylate (DMAEMA) by using a redox initiator system (cummene hydroperoxide/tetraethylene pentamine) (CHP/TEPA). The modified NRL has then been physically blended with PVA to form high quality membranes. The grafting has been monitored by DLS, FT-IR and NMR. The blended systems have been characterised by using FTIR, XRD, TGA and SEM. Pore generation has been achieved for the membranes by a swelling-deswelling cycle. The efficiency of the membranes for controlled release has been confirmed by three model organic dyes rhodamine B, methyl orange and fluorescein.

2. Materials and methods

2.1. Materials

Natural rubber latex (34% DRC) used in this study was a commercial sample procured from a rubber plantation at Thekkumkutty, Calicut, Kerala, India. Dimethylaminoethyl methacrylate (DMAEMA) monomer and the tetraethylene pentamine (TEPA) co-initiator were purchased from Aldrich, Germany. Sodium dodecyl sulfate (SDS) and cumene hydroperoxide (CHP) were procured from Alfa Aesar, Briton. PVA used for blending was purchased from Aldrich, USA with a molecular weight in the range 89,000–98,000 g/mol. The dyes used for the release studies such as rhodamine B, methyl orange and fluorescein were purchased from Merck, India.

2.1.1. Preparation of chemically modified latex

The chemically modified latex was prepared by grafting a water soluble polymer poly dimethylaminoethyl methacrylate (PDMAEMA) onto the surface of hydrophobic NR particles by an in situ polymerization of dimethylaminoethyl methacrylate (DMAEMA) monomer. The process was initiated by the redox couple cumene hydroperoxide (CHP)/tetraethylenepentamine (TEPA). The grafting procedure for NRL is shown in (Scheme 1). The composition of the reagents used for the experiment is given in (Table 1).

In the grafting process, the mixture of NRL, DMAEMA, CHP and SDS was agitated initially for 1 h in N_2 atmosphere. TEPA solution was added shot wise for 1 h, at an interval of 5 min, to initiate polymerization. The system was cooled in an ice/water bath during the process and held at a low temperature for the first 8 h of reaction. After that gradual warming to room temperature, another 16 h were given for the completion of the reaction. Separation of the reaction products

Table 1
Reaction conditions for graft *co*-polymerization of DMAEMA on NRL surface.

Ingredients	Quantity (g)
Rubber latex	83.5
DMAEMA	2.5, 5, 10, 15, 20
CHP	0.1
TEPA	0.1
SDS	1