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In situ monitoring the change of mechanical response induced by the diffusion of saline water in glassy cellulose acetate

Hadise Rahmani Seraji, Mohammad Karimi*, Leili Mahmoudi

Department of Textile Engineering, Amirkabir University of Technology (Tehran Polytechnic), Tehran 15914, Iran

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ABSTRACT

Dynamic mechanical analysis (DMA) in submersion mode has been used as an in situ and new technique to study the diffusion behavior of water and different salt solutions that are usually used as draw solutions in forward osmosis (FO) process, in glassy cellulose acetate (CA). The dramatic decay of elastic modulus (E') as a mechanical response upon water uptake against time at constant temperature (27 °C) and constant frequency (1 Hz) has been employed to calculate the diffusion coefficient of water and different salt solutions in CA near its glass transition temperature (T_g) based on the diffusion-controlled stress-relaxation theory. Fourier transform infrared-attenuated total reflectance (FTIR-ATR) spectroscopy has been used as an in situ conventional method to evaluate diffusion coefficients based on the simple Fickian model. Diffusion coefficients that have been obtained from both methods show appropriate order though no correlation has been found between two methods. From the results of two methods it may be concluded that DMA submersion mode measurements provide a robust and useful in situ method not only to elucidate at least qualitatively the type of sorption behavior of penetrant in a polymer solid but also to evaluate the diffusion coefficient if it combined properly with an adequate theory.

1. Introduction

Packaging, drug delivery, and membrane filtration are just few examples to show the importance of small molecules diffusion into polymers [1,2]. The transport of low molecular weight substances in polymers strongly depends on their structures and morphologies [3,4]. Two kinds of process may occur when a small molecule diffuses into a polymer network; one is the small molecule penetration between the interspace of polymer chains, and the other is scission of crosslinking points which are sensitive to the penetrant substance [5–7]. The former process may expand the intermolecular spacing and thus make polymer chains' configurational rearrangement easy that can be called plasticizing effect of the diffusing substance. The latter one occurs only in the case in which the polymer contains crosslinks that specifically react with the penetrant molecule. In general, both processes that mentioned above act to make the polymer network structure loosen [5–7]. This structural loosening or softening can simultaneously be followed by observing of the mechanical properties of the polymer film that include an increase in strain or film elongation, a decrease in E', a decrease in tensile strength, a decay of stress produced as a function of time which named diffusion-controlled stress relaxation and lowering of the T_g that is perhaps one of the most important physicochemical changes induced by the inclusion of plasticizers [8–10].

Small molecule like water with -135 °C T_g can act as a powerful plasticizer [4,11] specifically for polymers that intercrosslinked mainly with hydrogen bonds - one of the most typical water-sensitive bonds - though it can also act as an antiplasticizer in polymers [12–14]. For example, in the case of water as a penetrant, it can act as an antiplasticizer by forming stable bridges through hydrogen bonds [11]. When water diffuses into a hydrophilic polymer like Amilan, polyvinyl alcohol and CA, it is generally softened as a result of either a plasticizing effect of the penetrant or the scission of water-sensitive hydrogen bonds [5,15].

CA is considered as an environmentally-friendly polymer because of its origin [16]. Its molecular chains are intercrosslinked mainly with hydrogen bonds. There are mainly four different markets for its world consumption including filter tow for cigarettes, textile fibers, polarizing protection film in liquid crystal displays and coating, plastics and membranes [17]. CA membranes are widely used in water desalination processes like vast popular forward osmosis (FO) process [18–21]. Numerous investigations in this process have focused on the selection of a most suitable or optimal draw solution as a key component for successful development of FO technologies. It is conceivable that CA membranes, acting as water transport media, result in higher water flux as they are plasticized. Though the presence of salt ions such as Mg^{2+} in desalination process using membrane (like FO) changes in molecular

* Corresponding author.
E-mail address: mkarimi@aut.ac.ir (M. Karimi).

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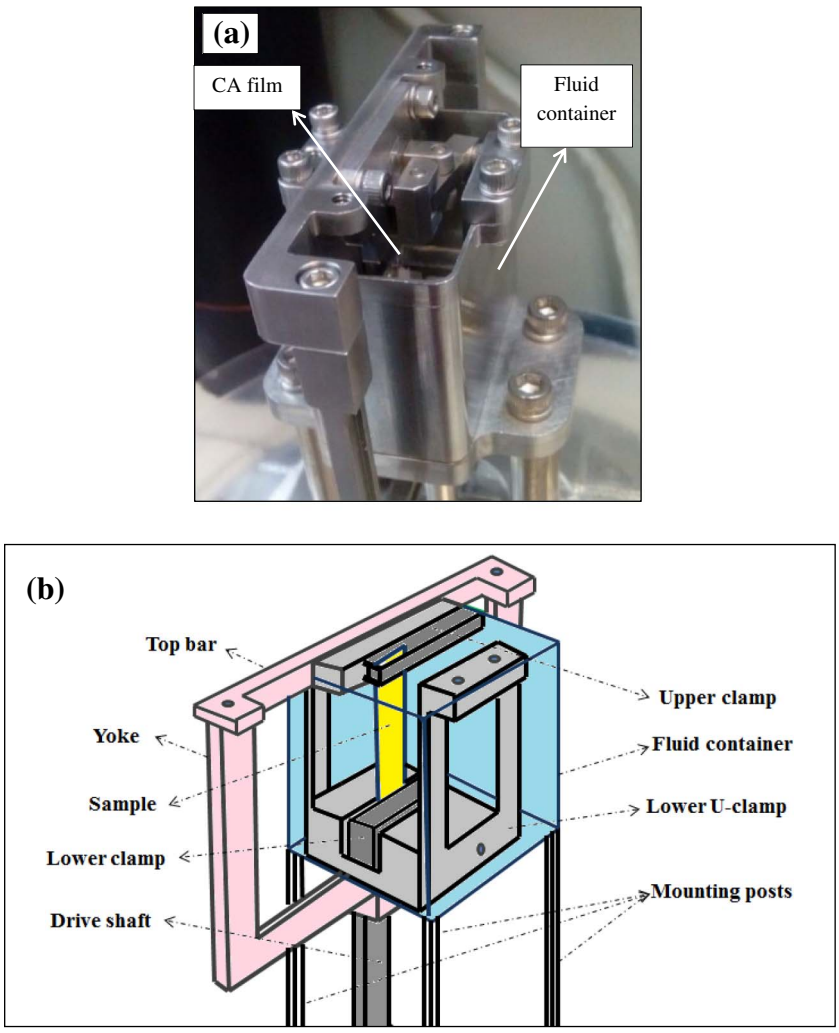

Fig. 1. Image of the DMA submersion tension clamp that has been used in this study (a), the flow scheme of the DMA test system (b).

motions of polymers and as a result water flux. The water flux of CA membranes depends not only on the amount of ions accumulated inside the membrane but also on the kind of ions. Addition of salt ions in water may cause glassy polymers become stiffer owing to reduced rates of segmental motions [14]. If this anti-plasticization response is happened, it can be accompanied by a decrease in water flux in FO process [12,13]. On the other hand, salt ions can change the hydrogen bond network of water in aqueous salt solutions. In other words, the hydrogen bond configurations of water molecules in the ionic hydration shells are distinctly different from those in pure water [22] and it can influence on water flux in FO process. Therefore, the state of CA in presence of salt solutions is a challenging problem and pursuing the molecular motions of CA may help to explain questions like why in FO process, against expectation, aqueous solution of $MgCl_2$ (as a draw solution) creates lower water flux than aqueous solution of NaCl at the same osmotic pressure.

To sum up, for applications take place in a wet environment like FO process it is obligatory to know the impact of solution environment (water and salt solution in case of FO process) on the mechanical properties of a given polymer. Consequently, in this study, it has been comprehensively surveyed the dramatic change of mechanical behavior of CA *dense* film near its T_g upon submersion in deionized water and in most common draw salt solutions that are used in FO process by DMA in immersion mode. It is a useful and robust method for measuring the mechanical properties of a polymer film in a liquid media and in recent years, intensive research has focused on the transition of mechanical response of materials, according to their final usage, in different environments by this technique [9,23–26]. More specifically, the effects of different monovalent and divalent solutes on the change of E' (the elastic modulus of cellulose acetate) have been explored to pursue their interactions with CA. These results can be helpful to better understanding of water and salt ion diffusion into polymer network near its T_g and further to give valuable details about either the molecular rearrangement due to the plasticizing effect of water or scission of water-sensitive hydrogen interchain-bondings in CA. Therefore, clarifying some aspects of this phenomenon is intended in the current work that is rarely considered in the previous literature. Finally, with the help of simple Fickian model the diffusion coefficient of water and different salt solutions by DMA data [5] as well as conventional and well known FTIR-ATR absorbance method [27–29] have been calculated and compared with each other. In addition, for further clarification of the subject matter, the dehydration steps and sorption of water as well as salt solutions in the CA film have been measured with the help of thermogravimetric analysis (TGA) and conventional gravimetric method, respectively.

2. Experimental section

2.1. Materials

CA with degree of substitution (DS) 2.45 was purchased from Sigma-Aldrich. Acetone, deionized water for chromatography, sodium chloride (NaCl), sodium bromide (NaBr), potassium chloride (KCl), potassium bromide (KBr), magnesium chloride ($MgCl_2$) and calcium