Mechanical experiments as a tool for study of swelling-deswelling and structural properties of porous polymers

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HIGHLIGHTS

- Tensile stress measurements for characterization of polymer structure are applied.
- The relation of the porosity and the stress produced during swelling is discussed.
- "Skin" effect during deswelling is confirmed.
- Stability of mesopore structure of polymer depends on swelling degree.
- Loss of solvent during deswelling of porous polymer is of stepped character.

GRAPHICAL ABSTRACT
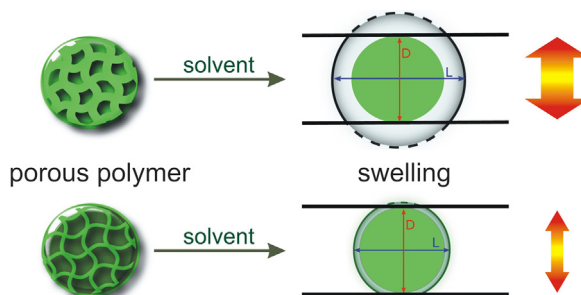
ABSTRACT

The expansion and structural parameters for a series of crosslinked porous polymers are discussed during their swelling. In the study, commercial Amberlite XAD2, XAD4 XAD16 and XAD7HP resins of varying porosity and polarity were used as model polymers. Videomicroscopy LM is combined with in-situ strain-stress measurements during the process of wetting the polymer with ethanol. The force exerted by the expansion of the spherical polymer particle due to swelling reflects the structural properties of the polymer and is related to the total porosity of a given type of polymer matrix. The pore structure of the samples was characterized by liquid nitrogen adsorption and their swelling degree was assessed by light microscopy. The deswelling curves, represented by strain-stress curves, are stepped for polymers of lower porosity; the first step represents the evacuation of the solvent from the pores. This process is regulated by the external pore openings in a particle; the second, elongated step on the deswelling curve represents the evaporation of the solvent from the polymer network.

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1. Introduction

In the last few years, numerous experimental and theoretical efforts have been devoted to the study of polymer swelling. Novel systematic studies are focused on modulating the structure and permeability of polymeric materials, with a view to enabling the high absorption of the solvent and optimizing the kinetics of swelling. Considerable attention is given to hydrogels, which have a number of potential applications in chemical sensors (Guenther et al., 2007), environmental protection (Yan et al., 2009), bioengineering (Zhang et al., 2017; Lui and Ip, 2016) and medicine (Sharpe et al., 2014; Sivakumar and Rao, 2002). Various efforts have already been undertaken to improve the deswelling and reswelling of these polymers. The studies in question focused on modifying the polymer matrix structure with the use of e-beam irradiation or microwave radiation (Zhao et al., 2008; Lugo-Medina et al., 2007) or introducing additional elements to the

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network (Can et al., 2007; Takeno et al., 2017; Utech and Boccaccini, 2016). It is expected that pores created during synthesis and within the range of mesopore size are also important as far as the swelling kinetic is concerned. To the perspective of preparing polymer particles with open external pores seems promising as it may help avoid creating an external membrane characterized by limited permeability, which appears in the case of PNIPAAm (Zhang et al., 2002). The addition of silica particles into polymer or clay minerals, apart from improving the permeability of the solvent, influences favorably the mechanical toughness of the polymer material (Takeno et al., 2017; Wang and Li, 2015). In order to achieve it, precise measurements of swelling kinetic are indispensable; in most of referenced papers, such measurements were performed with the use of the gravimetric method. The swelling process for polymers containing pores is more complicated than for a monolithic polymer. In a porous polymer, gas and liquid media diffuse and, consequently, swelling is more rapid (Zaleski et al., 2017). The diffusion of solvent molecules into pore system results in high permeability of polymer bulk material and swelling starts the moment the material is immersed, which is a result of the total exposition of the internal surface to solvent molecules. Thus, in this case, it may be assumed that the adsorption of the solvent on internal pore surface, which may be considered as a transition stage, and which shall be followed by penetration of the solvent into the bulk polymer. Porosity is the factor regulating transportation within particle. It is should be mentioned that the internal surface of porous polymers reaches as many as hundreds square meters per gram of the polymer specimen and constitutes, in some sense, a membrane through which the solvent molecules have to pass.

In both cases, i.e. a nonporous polymer or a porous one, the extent of swelling may be expressed by swelling degree defined as $SD\% = \frac{V_1 - V_0}{V_0} * 100\% = \frac{m_1 - m_0}{m_0} * 100\%$, where: m_0 and V_0 is the mass and volume of the dry material, while m_1 and V_1 is mass and volume of the swelled material, respectively. The amount of the solvent entrapped in the polymer is determined gravimetrically or volumetrically. In both methods, the precise determination of the mass or volume takes time and continuous measurements of both these parameters are difficult. Especially great care should be taken in the case of gravimetric experiment, when for a given time, it is necessary to dry the particles of the liquid solvent which does not take part in swelling. Regardless of the method applied, time dependence of swelling is similar and presents characteristic curve with rapid rise of mass or volume at the beginning of swelling and, finally, saturation at equilibrium, exhibiting a flat segment on the curve. In most cases, stable state is reached after tens of minutes. However, the time of equilibration depends on polymer-solvent interactions, temperature and particle dimensions. Usually, any inflection points are observed on swelling-time curves.

A similar shape of the swelling curve is observed for porous polymers although the uptake of solvent is of dual character. As it was mentioned earlier, a part of the solvent takes part in pore filling and part of solvent diffuses into polymer "body," penetrating the interchain space. This part of the solvent represents pure swelling. In gravimetric or volumetric measurements, the resulting effect of mass or volume increase is observed. The change of particle mass determined gravimetrically is the sum of these two parts of the solvent; it is not possible to measure the share of both parts. In volumetric measurements, the change of particle volume is the result of swelling of pore walls only. The condensed solvent alone inside pores is not measurable as the particle volume increases. Thus, both parts of the solvent entrapped within the particle are again indistinguishable.

Both the abovementioned swelling presentations do not provide sufficient information on swelling mechanism. Porous cross-linked polymers obtained by microemulsion synthesis possess usually specific internal structure composed of primary particles bonded to each other. Thus, polymer porosity is of a complex character. Solvent molecules are entrapped due to different forces in various fragments of the polymer skeleton. It should be emphasized that the dimensions of the pores within the bulk polymer are much lower than the dimensions of the pores created during microemulsion synthesis; the latter are larger and ranged as mesopores.

In the present paper, a different approach to polymer swelling characterization is proposed. Rather than registering mass or volume changes during swelling, the expansion force of spherically shaped polymer particles is recorded. Such a procedure makes it possible to measure the increase of the particle volume via the measurements of the mechanical expansion of the particle. Commercial, cross-linked polymers were chosen for the experiment. The porosity of the samples under study accelerate the swelling and deswelling processes. The presence of pores enables the polymer to absorbs a large amount of the solvent, but the distribution of the solvent within a particle is inhomogeneous. A part of the solvent is dispersed randomly within the polymer network while another part is located in the pore interior and held there due to capillary forces; this latter part constitutes a separate phase of the pure solvent.

All the polymers chosen for the study, Amberlite XAD2, XAD4 and XAD16, poses the same chemical character and chemical composition (styrene-divinylbenzene), as well as a different pore structure and total porosity. Additionally, for comparative purposes, Amberlite XAD7, a nonionic moderately polar acrylic polymer, was used.

2. Experimental

Amberlite XAD2, XAD4, XAD16 and XAD7HP polymers (Rohm & Haas Co) were purchased from Sigma Aldrich. Prior to the swelling experiment, polymers were rinsed with deionized water and dried at 80 °C under vacuum. Ethanol 99.8% was received from POCH (Poland). Swollen particles were obtained by immersing polymer particles (selected from the 0.5–0.6 mm fraction, dried and degassed at 80 °C) in the excess of solvent.

The swelling degree of all polymeric matrices in ethanol was determined by the volumetric method, with the use of an optical microscope (inverted materials microscope, MA200 M, Nikon Co. For measurements of volume changes before and after immersion with ethanol, 5 beads of 0.5–0.6 mm fraction were used, and the value of swelling degree was averaged.

The structural parameters of dry materials and samples before and after swelling in ethanol were derived from a conventional liquid nitrogen sorption experiment at 77 K with the use of an automated sorption analyzer, ASAP 2045, Micromeritics Inc. The specific surface area (S_{BET}) was calculated from the linear form of the BET equation in the relative pressure range from 0.05 to 0.25 (Brunauer et al., 1938). The pore size distribution (PSD) was calculated using the BJH standard method (Barrett et al., 1951). The total pore volume (V_p) was estimated from a single point adsorption at $p/p_0 = 0.989$.

The densities (d) of polymer skeleton for all samples were calculated on the basis of the weight and volume of particles with subtracted pore volume determined in the nitrogen experiment. The obtained numerical values of $d_{s,cal.}$ were compared to those given by manufacturer $d_{s,ref.}$.

Mechanical measurements were examined with the use of Zwick Roell Z2.5 Materials Testing Machine. Firstly mechanical stability of all types of polymer dry particles was measured by crushing single polymer sphere between two discs with tensil stress