Free volume changes in the swelling process of vegetable oil-based UV-cured polymers

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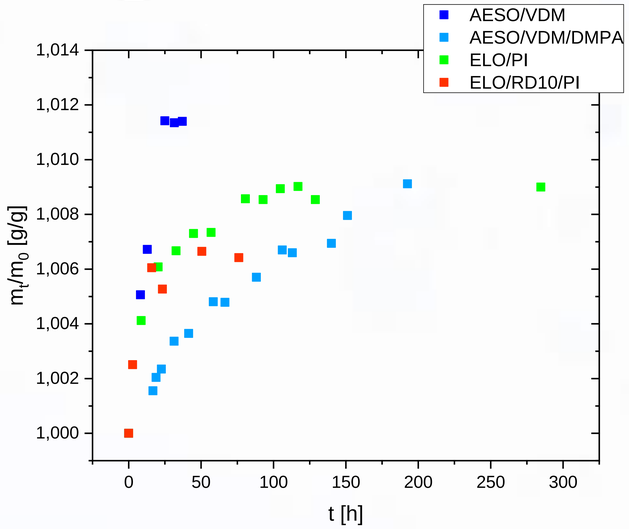

Fig. 1 Time dependence of reduced weight *m(t)/m0* at swelling experiment for investigated samples

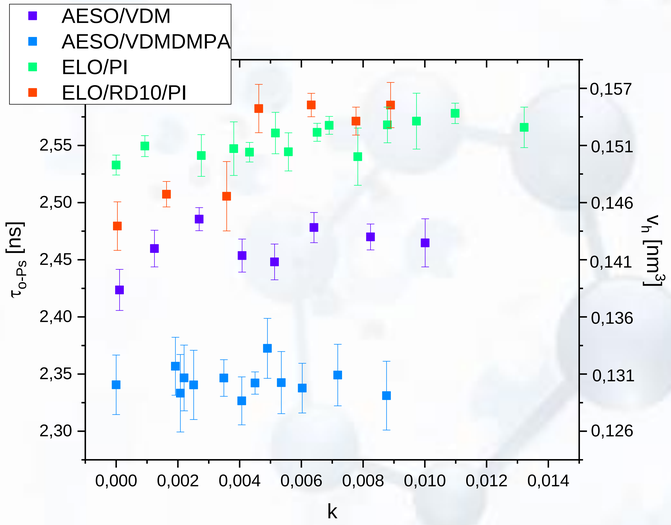

Fig. 2 o-Ps lifetime as a function of water content expressed by k for the investigated samples.

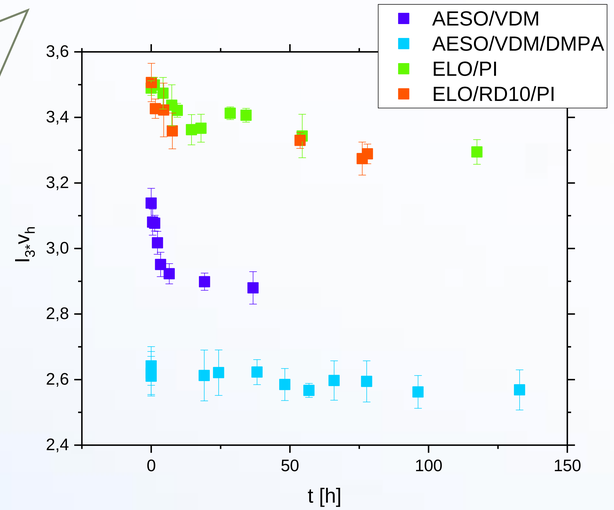

Fig. 3 Reduced free volume fraction f_v/C (I_3*v_h) for four investigated samples*h*

INTRODUCTION

Laccase-based biosensors are third-generation biosensors containing a retention polymer matrix and a laccase enzyme. This enzyme is bound by covalent bonds, adsorption or crosslinking to the retention matrix so as to allow maximum activity of the enzyme with sufficient stability and reusability. They are copper-containing oxidases that are able to catalyze the oxidation of several phenolic compounds and aromatic amines. Laccases are very promising natural compounds in the manufacture of biosensors for monitoring large amounts of phenol-containing compounds, including some xenoestrogens. In recent years, photopolymers have become increasingly important, due to their considerable practical and economic advantages. It has been shown that free volumes and pores of polymer matrices with immobilized enzyme have the impact on the increased sensitivity and selectivity of the biosensors.

The aim of our work is to determine the size and changes of free volumes depending on the amount of absorbed water in samples of crosslinked photopolymers based on epoxidized linseed oil (ELO) or acrylated epoxidized soybean (AESO) oil using positron annihilation spectroscopy. These samples are thoroughly investigated due to their potential use as retention matrices in biosensor systems.

EXPERIMENTAL

The analyzed samples were marked as AESO/VDM, AESO/VDM/DMPA, ELO/PI and ELO/RD10/PI [1]. The weight of each sample was recorded to the nearest 0.01 mg. Then the sample was placed in a Petri dish with deionized water and sealed. After approximately six hours, the samples were removed from the water, shortly dried from surface water, and then weighed again. This procedure was repeated several times until the samples were completely saturated with water. Subsequently, lifetime spectra were measured for different amounts of absorbed water in all samples.The samples were hermetically sealed during the measurements. The water content was expressed by coefficient $k = m_w/(m_w+m_M)$, where m_w is a mass of water and m_M is a mass of dry polymer.

RESULTS AND DISCUSSION

Fig. 1 shows the swelling process of all samples in time where m(t) is the weight of the sample at time t (swollen sample) and m_0 is the weight of the original sample (i.e. the sample before swelling). The lifetime spectra were analyzed using the program LT Polymers ™. Ortho-positronium lifetimes were measured at known coefficients k and subsequently the free-volumes v_h of the cavities were determined (**Fig. 2)** using the semiempirical quantum-mechanical model of Tao and Eldrup [2,3]. The time dependences of o-Ps intensity I_3 and v_h were reconstructed from known k and the time dependence of swelling curves. **Fig. 3** shows the estimated reduced free volume fractions (***f_v/C, C*** is a material constant) during a swelling process in investigated polymers. It reflects the fact that the smallest changes in free volume (smallest sorption capacity) are in the sample AESO/VDM/DMPA, on the contrary the larger changes of ***f_v/C*** are in other samples.

CONCLUSION

Changes in the free volume of the cavities as well as changes in the free volume fraction during swelling of the samples in water were determined. The presence of other additives in AESO based polymers greatly affects the sorption properties of water in the matrix. AESO/VDM/DMPA sorbs water very poorly. For ELO based polymers, these properties do not change significantly. Furthermore, it has been shown that with the amount of water in the sample, local free volumes clog at the same time and the polymer chains expand in their vicinity.

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