



EFFECT OF THE TYPE OF A CROSS-LINKING AGENT ON THE SWELLING DEGREE OF POLYDECYLMETHYLSILOXANE

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Abstract

In this work, the effect of the type of a cross-linking agent for polydecylmethylsiloxane (C10) on its sorption and swelling in organic solvents was studied for the first time using toluene, octane, isooctane, and butyl acetate. Hydrocarbon (1,7-octadiene (OD), 1,9-decadiene (DD), 1,11-dodecadiene (DdD)), vinyl-terminated PDMS ($M_n = 500$ g/mol (Sil500), $M_n = 25000$ g/mol) and combined cross-links were used for membrane obtaining. It was shown that cross-linking with hydrocarbons leads to the least swelling in the solvents explored, while cross-linking with vinyl-terminated PDMS results in the greatest swelling. Apparently, the flexible siloxane cross-linking imparts greater mobility to C10, which leads to high absolute sorption values. At the same time, the rigid hydrocarbon cross-linking allows the formation of a structure specific to the comb-shaped polymer, which significantly contributes to its properties.

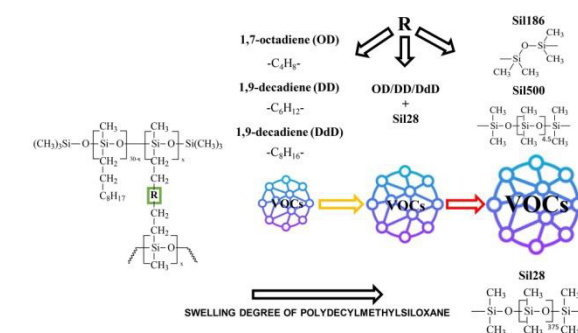
Key words: polydecylmethylsiloxane, membrane, cross-linking, swelling, hydrocarbon separation.

Introduction

Emissions of volatile organic compounds (VOCs) have a negative impact on the environment [1] and represent a direct loss for the manufacturing sector [2]. Utilization or recovery of these compounds is an important environmental task both in Russia and throughout the world. The membrane separation of vapor-gas mixtures is a competitive modern technology that allows for not only reducing the emission of VOCs into the environment, but also returning them to the production cycle. The choice of a membrane material is an important problem since it determines the separation properties of the entire membrane module.

Silicone rubbers are used as membrane materials, in particular, for the production of industrial membranes which are currently utilized for separating VOC vapor-gas mixtures. It was previously shown that the introduction of a decyl side group into the polysiloxane chain can significantly increase the selectivity of VOC separation from gas mixtures compared to classical polydimethylsiloxane (PDMS) [3]. However, this class of materials is characterized by a significant change in transport and separation properties on passing from individual gases to gas mixtures containing VOCs [4]. One of the approaches to reduce these changes is the chemical cross-linking [5]. Cross-linking of polysiloxanes gives them chemical resistance and mechanical strength.

In this communication, the effect of the type of a cross-linking agent for polydecylmethylsiloxane (C10) on its sorption and swelling in organic solvents was studied for the first time



using toluene, octane, isooctane, and butyl acetate. Hydrocarbon (1,7-octadiene (OD), 1,9-decadiene (DD), 1,11-dodecadiene (DdD)), vinyl-terminated PDMS ($M_n = 500$ g/mol (Sil500), $M_n = 25000$ g/mol), and combined cross-links were used for the production of membranes.

Results and discussion

The sorption and swelling degree of the resulting membrane materials were studied by measuring changes in the geometric dimensions and mass of the films after long-term exposure to organic solvents (Fig. 1). A clear dependence of the swelling degree on the nature and length of the cross-linking agent was observed: cross-linking with short and rigid hydrocarbons (the Kuhn segment for polyethylene (20.8) and PDMS (14)) led to the least swelling degree in the studied solvents, while cross-linking with flexible and long siloxanes resulted in the greatest swelling degree. Increasing the length of the hydrocarbon cross-link increased the sorption and swelling of C10 in toluene and reduced swelling in butyl acetate. For octane and isooctane, an increase in sorption and swelling was observed for C10-DD sample, which may be due to a more ordered arrangement of the side groups in the polymer [6]. C10 cross-linked with vinyl-terminated PDMS was characterized by a decrease in sorption and swelling in all solvents as the length of the cross-linking agent decreased. In the case of the combined (containing both a vinyl-terminated PDMS (Sil25) and a hydrocarbon cross-linking agent (OD, DD, DdD)) cross-links, a decrease in sorption and swelling in toluene was observed with increasing length of the

hydrocarbon cross-link. It is worth noting that in terms of the absolute sorption and swelling values, C10 with combined cross-linking took an intermediate value between C10 with hydrocarbon and siloxane cross-links. For other solvents, a local minimum was observed for C10-Sil25-DD sample. Apparently, the flexible siloxane cross-linking imparts greater mobility to C10, which leads to large absolute values of sorption. At the same time, the rigid hydrocarbon cross-linking allows the formation of a structure specific to the comb-shaped polymer, which significantly contributes to its properties.

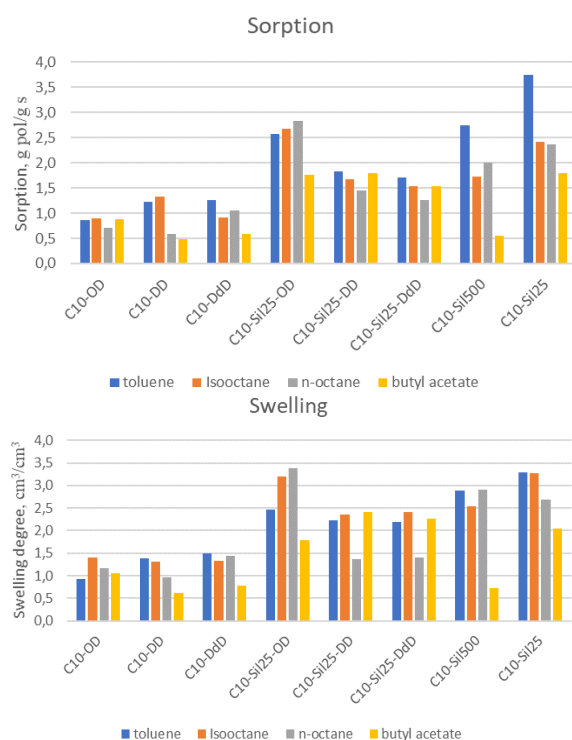


Figure 1. Dependence of the sorption and swelling on the type of a cross-linking agent.

Experimental section

Synthesis

The synthesis of cross-linked C10 was carried out according to the method previously developed at TIPS RAS and described in detail in Ref. [6], which is based on the hydrosilylation reaction [7]. The cross-linking agents represented the diene hydrocarbons 1,7-octadiene (C10-OD), 1,9-decadiene (C10-DD), 1,11-dodecadiene (C10-DdD) and vinyl-terminated PDMS with different molecular weights: 500 g/mol (C10-Sil500) and 25000 g/mol (C10-Sil25, C10-Sil25-OD, C10-Sil25-DD, C10-Sil25-DdD). The 1-decene/cross-linking agent ratio for C10-OD, C10-DD, and C10-DdD was 20 mol/mol, and that for C10-Sil500, C10-Sil25, C10-Sil25-OD, C10-Sil25-DD, and C10-Sil25-DdD was 15 mol/mol.

Methods

The sorption and swelling degrees of the membrane material were determined in toluene, isooctane, *n*-octane, and butyl

acetate. For this purpose, flat membrane films were obtained, the thickness of which was at least 150 μm, and their mass and geometric dimensions were measured before and after exposure in an organic medium until constant mass for 48 h. Before the measurements, excess organic matter was carefully removed from the surface using a filter paper. Sorption (S) and swelling degrees (Q) were calculated using equations (1) and (2):

$$S = \frac{m_s - m_i}{m_i} \quad (1)$$

$$Q = \frac{V_s - V_i}{V_i}, \quad (2)$$

where m is the mass of the polymer sample, V is the volume of the polymer sample, indices i and s refer to the initial sample and the sample after 48 h of exposure in an organic medium.

Conclusions

The sorption parameters and swelling degree of various membrane materials differing in the chemical cross-linking were studied in toluene, isooctane, *n*-octane, and butyl acetate. The dependence of the sorption properties and swelling degree of the membrane materials on the length and type of a cross-linking agent was outlined.

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