



POLY(HEXAFLUOROISOPROPYLACRYLATE/DECYL)METHYLSILOXANE COPOLYMER: A NEW MATERIAL WITH THE LOW SURFACE ENERGY

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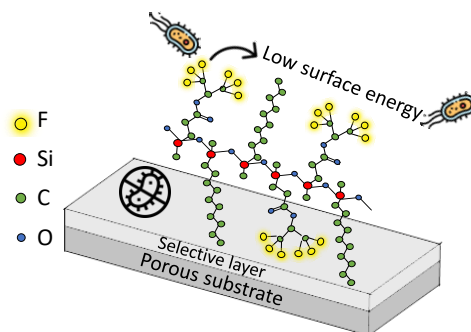
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Abstract

A copolymer of poly(hexafluoroisopropylacrylate)siloxane (F6) and polydecylmethylsiloxane (C10) was synthesized for the first time. The addition of 50 mol % of F6 groups into C10 led to a decrease in the surface energy from 25.5 to 16.5 mJ/m². Composite membranes M1 and M2 were made of C10 and F6–C10 copolymer. The gas transport properties of the membranes were studied before and after 2 months of exposure to pollutant solutions (ABE, lecithin, protein). Comparing the permeability of M1 and M2, it was found that M2 has higher resistance to fouling. Thus, a protein solution reduced the CO₂ permeability of M1 by 29% and that of M2 by 83%.

Key words: poly(hexafluoroisopropylacrylate)siloxane, polydecylmethylsiloxane, fouling, surface energy.



Introduction

One of the key challenges in the field of membrane materials and membrane development is the membrane fouling [1]. The development of new membrane materials with the low surface energy is crucial for improving the efficiency of separation processes, such as the extraction of bio-alcohols from fermentation mixtures. Among various types of polymers, fluoropolymers exhibit the lowest surface energy values [2]. Fluorinated polysiloxanes amount to a special type of polymers that combine the properties of amphiphobic fluoropolymers and alcohol-selective siloxanes. Due to their low surface energy and excellent performance characteristics, fluorine-containing polysiloxanes have great potential for use in the production of membranes for separating organic components from water, separating oils, and separating fermentation mixtures through pervaporation [3].

In this work, a copolymer of poly(hexafluoroisopropylacrylate)siloxane (F6) and polydecylmethylsiloxane (C10) was obtained for the first time.

Results and discussion

The hydrosilylation of polymethylhydrosiloxane (PMHS) by 1-decene and 1,1,1,1,3,3,3,3-hexafluoroisopropyl acrylate (F6-Acr) was assessed by analyzing the ¹H NMR spectra of the reaction mixtures of fluorinated polymethylsiloxanes (see Fig. S1 in the Electronic supplementary information (ESI)). The occurrence of the hydrosilylation reaction was confirmed, and it was demonstrated that the conversion degree over 90% was achieved for the copolymer.

The investigation of the wetting properties of the surfaces of

F6–C10 and C10 polymers showed that they exhibit water contact angles over 90°, indicating a hydrophobic character similar to that of polysiloxanes (112° for polydimethylsiloxane (PDMS) [4]). In particular, the contact angle of water on F6–C10 is 113°, and that for C10 is 101° (Table S1 in the ESI). Then we calculated the surface energies of these films. It was found that the incorporation of F6 groups into C10 results in a decrease in the surface energy from 25.5 to 16.5 mJ/m², which is comparable to the surface energy of Teflon being equal to 18–20 mJ/m². For comparison, the surface energy of PDMS is 19.4 mJ/m² [4].

The composite membranes based on F6–C10 and C10 (M1 and M2, respectively) were produced by contacting a porous substrate with a polymer solution by "kiss-coating" method. The permeability of individual gases (CO₂ and N₂) was studied for the resulting membranes before and after exposure to various pollutants.

It is worth noting that the greatest decrease in the CO₂ permeability, more than 2 times, for both membranes was observed after a contact with a lecithin solution. At the same time, M2 membrane showed a larger decrease of the CO₂ permeability from 0.28 to 0.03 m³/(m²·h·bar) than its counterpart M1, for which a decrease from 0.28 to 0.16 m³/(m²·h·bar) was observed. The effect of a protein contaminant was similar to lecithin but slightly less pronounced, with the lowest decrease in the permeability observed for M1 membrane (from 0.25 to 0.18 m³/(m²·h·bar)) and the greatest decrease for M2 membrane (from 0.29 to 0.05 m³/(m²·h·bar)). The selectivity of CO₂/N₂ separation for sample M1 remained unchanged after a contact with the protein and lecithin and was 9, while for sample M2 it decreased by 2.5 times (from 9.5 to 3.8). When considering the effect of the prolonged contact between the surface of the selective layer and the deactivated

ABE fermentation mixture, it was found that membrane M1 was more resistant to fouling. A decrease in the CO₂ permeability after a contact with this contaminant composed 32% (from 0.28 to 0.19 m³/(m² h bar)). On the other hand, its counterpart M2 showed the greatest decrease in the gas transmission properties upon investigation of the effect of the prolonged contact with various pollutants. The permeability of CO₂ decreased by 40.91% (from 0.22 to 0.13 m³/(m² h bar)).

Experimental section

Syntheses

The synthesis of F6–C10 copolymer (Fig. 1) was accomplished by the hydrosilylation according to the one-step *in situ* methodology previously suggested for polyalkylmethylsiloxanes [4]. PMHS was mixed with a 15 wt % solution of F6-Acr and 1-decene in toluene in 1:1 ratio and Karstedt's catalyst. The catalyst was added at the PMHS/catalyst molar ratio of 4. The resulting mixture was stirred at 60 °C for 2 h. In order to cross-link the polymer, a 10 wt % solution of PDMS in toluene was added to the reaction mixture. The stirring was continued at 60 °C for 1 h. At the final step, a 3 wt % PMHS solution was added until the PMHS:PDMS molar ratio of 0.16 was reached. The full synthetic scheme is presented in Fig. S2 in the ESI.

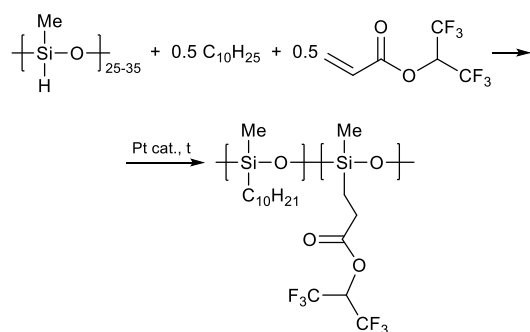


Figure 1. Synthesis of the copolymer.

Methods

NMR spectroscopy was used to study the composition of the reaction mixture after the interaction of PMHS and side substituents. The high-resolution ¹H NMR spectra were recorded on a Bruker AVANCE III HD 400 NMR spectrometer for CDCl₃ solutions using the standard procedures.

The advancing contact angles (θ) of water and diiodomethane were measured by sessile drop method (Contact Angle System OCA apparatus, DataPhysics, Germany) at 20 °C. The specific free surface energy $\gamma_{sv} = \gamma_{sv}^d + \gamma_{sv}^p$ of the polymer surfaces and its dispersive γ_{sv}^d and polar γ_{sv}^p components were calculated according to the molecular theory of wetting in the Owens–Wendt–Kaelble approximation [5].

The selective layer of siloxane was deposited from the polymer solutions onto an MFFK-1 microfiltration support by the "kiss-coating" method similar to the described process [6].

To study the effect of the long-term contact with various

pollutants on the transport properties of the composite membranes, they were treated with 1 g/L pollutant (protein, lecithin) solutions and real deactivated ABE fermentation mixture for 2 months at room temperature. To prevent the pollutant solution from getting into the support pores, only the selective layer of the membranes was in contact with it.

The fouling was observed by comparing the CO₂ permeability of the composite membrane before and after its exposure to a pollutant solution. The gas permeability of the composite membranes for individual gases (N₂, CO₂) was determined by the variable volume method [6].

Conclusions

Thus, copolymer F6–C10 was synthesized for the first time. It was shown that the resulting copolymer features a low surface energy and high resistance to the prolonged exposure to pollutants.

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Electronic supplementary information

Electronic supplementary information (ESI) available online: the ¹H NMR spectra, synthetic scheme, and water contact angles. For ESI, see DOI: 10.32931/io2522a.

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