

## **An investigation of the effects of a silicalite type zeolite on PDMS-composites**

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The aim of this paper was to investigate the effect of a silicalite type zeolite on PDMS-zeolite composites. The obtained results show that the introduction of a silicalite type zeolite into polysiloxane matrices results in a change of the equilibrium degree of swelling of the composites in toluene, their hardness and their thermal stability. With increasing amount of zeolite, the time required to achieve the equilibrium degree of swelling (DSe) is reduced, the DSe decreases and the hardness increases. Two ranges of the effect of the zeolite concentration on the composite characteristics were noted. At zeolite concentrations up to about 12 % there are significant changes of the DSe and the hardness with zeolite concentration, while these effects are considerably less pronounced at higher concentrations. The results obtained show that the silicalite type zeolite acts as a reinforcing filler. We believe that with increasing zeolite concentration in the composite the total number of established polymer-zeolite interactions increases, as does the spatial irregularity of the polymer network, but that the density of the interactions decreases. This could be the most probable explanation for the changes in the characteristics of the composite with changing zeolite concentration.

**Keywords:** PDMS-composite, silicalite type zeolite, degree of swelling, hardness, thermal stability.

### INTRODUCTION

Polysiloxanes are very suitable materials for combining with zeolites,<sup>1,2</sup> as, unlike with other organic polymers, no problem of zeolite dispersion appears.<sup>3</sup> Data on the preparation of various polysiloxane zeolite composites, which have prominent applications in the pervaporation of water/alcohol mixtures, are described in the works of Vankelcom,<sup>2</sup> Hennepe,<sup>4</sup> Adnadjević<sup>5</sup> and coworkers. The main reason for introducing zeolites or other types of fillers into polysiloxane matrices is to improve the mechanical properties, but it has also been established that the type of the zeolite used influences the pervaporation properties of the obtained membranes.<sup>2,5</sup> Depending on the composite preparation procedure and the type of zeolite used, it seems that the possibility for the real cross-linking of the zeolites, as in the cases of zeolite types: Y, ZSM-5 and silicalite,<sup>4</sup> as well as NaA,<sup>6</sup> exists.

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This paper investigates the possibility of obtaining polydimethylsiloxane (PDMS)-zeolite composites in the form of materials, both as membranes and significantly thicker material, using PDMS matrices obtained by hydrosilylation reaction and a silicalite type zeolite. The effects of the concentration of the silicalite on the following characteristics of the PDMS-zeolite composites were investigated: swelling in toluene, hardness and thermal stability.

#### EXPERIMENTAL

*Materials:* A bicomponent room temperature vulcanization (RTV) system was used to obtain composites based on polysiloxane matrices: RTV-615A and RTV-615B, purchased from General Electric Corp., USA. Component A consisted of polydimethylsiloxanes end-capped with vinyl groups. Component B consisted of polysiloxanes containing a few silylhydro groups per molecule which acted as cross-linkers, and platinum as a catalyst for the hydrosilylation reaction.

A silicalite type zeolite, synthesized and analyzed at the Institute of General and Physical Chemistry in Belgrade, was used for obtaining the PDMS-zeolite composites.

The most important physico-chemical characteristics of the zeolite used are presented in Table I. The zeolite was dried by heating at 120 °C for two hours, at 240 °C for an additional two hours and finally for four hours at 400 °C. The dried zeolite was stored in a vacuum desiccator.

TABLE I Main physico-chemical characteristics of the employed silicalite type zeolite

|   | Silicalite |
|---|------------|
| Crystallinity degree/%                    | 100        |
| Mean crystal size/ $\mu\text{m}$          | 1.8        |
| Specific area/ $(\text{m}^2/\text{g})$    | 400        |
| Specific volume/ $(\text{cm}^3/\text{g})$ | 0.18       |
| Kinetic diameter/nm                       | 0.56       |

*Procedure for obtaining the polysiloxane-zeolite composites:* To obtain the polysiloxane-zeolite composite, a mixture of the polysiloxane precursors, RTV-615A and RTV-615B, in the ratio 10:1 by weight and various quantities of the zeolite (from 5 % up to the maximum possible quantity of 50 % by weight in the polysiloxane zeolite mixture) were used. The composites were prepared as follows: the desired quantity of zeolite was added to the determined quantity of polysiloxane RTV-615A. This mixture was first homogenized by carefully stirring using a metal spatula, and then in an ultrasonic bath. At higher zeolite concentrations (50 %), toluene was used as the solvent. After satisfactory homogeneity was reached, the required quantity of polysiloxane precursor RTV-615B was added and the obtained mixture homogenized once again, and then poured into adequate metal molds, kept under vacuum for two hours and then heated to 80 °C for four hours. After cooling to room temperature, the vulcanized samples were removed from the molds. The obtained composite samples are denoted as PDMS-nS where  $n$  represents the weight percent of zeolite contained in the composite.

*Determination of the degree of swelling (DS):* The degree of swelling of the composite was based on the change in the weight of the sample submerged in toluene until swelling equilibrium was reached (denoted as  $DS_e$ ), so that:

$$DS(\%) = \frac{G_t - G_0}{G_0} \cdot 100$$

where:  $G_t$  is the mass of the swollen sample at time  $t$  and  $G_0$  the initial sample mass.

*Hardness determination:* The hardness of the composites were measured using the Shorr A method on a "Zwick" type 7206 apparatus.

*The thermogravimetric analysis (TG):* The thermal characteristics of the composites were determined using a "Stanton Redcroft" type 1000 apparatus, at a constant heating rate of 10 °C/min. The analyses were performed under a dynamic nitrogen atmosphere at a flow rate of 60 mL/min using 10 mg samples.

## RESULTS AND DISCUSSION

*Swelling behaviour:* The kinetic curves of the swelling of PDMS-silicalite composites in toluene at ambient temperature, expressed as the degree of swelling *DS* vs. time are presented in Fig. 1. As can be seen the kinetic curves all have the same shape, independent on the content of zeolite.

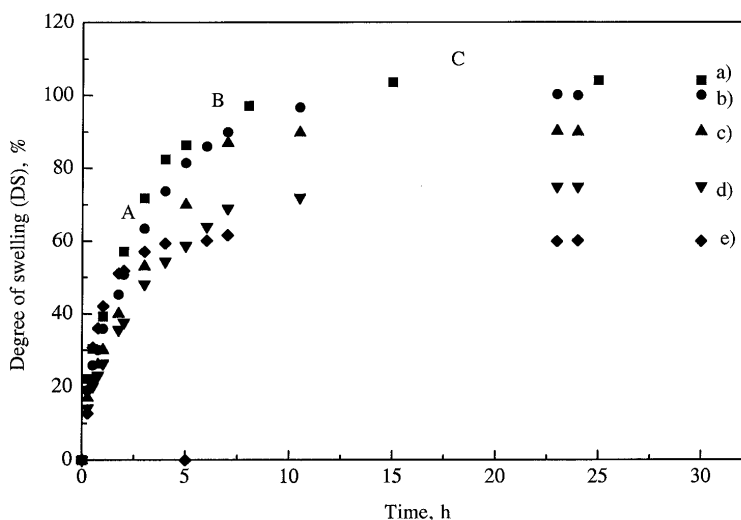


Fig. 1. Degree of swelling vs. time of swelling in toluene at ambient temperature: a) PDMS-5S, b) PDMS-10S, c) PDMS-20S, d) PDMS-35S, e) PDMS-50S.

Three characteristic stages can be distinguished in the kinetic curves of composite swelling. During the first stage, denoted as A in Fig. 1, the *DS* increases rapidly and linearly with swelling time. In the second stage, denoted as B in Fig 1, the *DS* increases non-linearly and not as rapidly with swelling time. In the so-called equilibrium phase of swelling, denoted as C in Fig. 1, there is no real change in the *DS* with swelling time.

The durations of the first and second characteristic phases of the investigated composites are presented in Table II. The concentration of zeolite affects the duration of the characteristic phases of the *DS* changes.

Compared with unfilled PDMS elastomer, the duration of the first characteristic phase is unchanged for 5 % zeolite concentration, although the duration of the second phase is considerably prolonged. As the zeolite concentration in the PDMS-nS composite increases above 5 %, the first characteristic phase of the *DS*

change with time becomes shorter and the duration of the second characteristic phase also becomes shorter, compared to its duration for the 5 % silicalite composite.

TABLE II Results of monitoring the swelling of the PDMS-nS composite in toluene at ambient temperature

| Sample   | Time A <sup>a</sup> /h | Time B <sup>b</sup> /h | DSe <sup>c</sup> /% | $\Delta DS^d$ /% | $\Delta DS/c^e$ |
|----------|------------------------|------------------------|---------------------|------------------|-----------------|
| PDMS-0   | 3.0                    | 4.5                    | 108                 | —                | —               |
| PDMS-5S  | 3.0                    | 13.0                   | 104                 | 3.7              | 0.74            |
| PDMS-10S | 2.8                    | 8.0                    | 100                 | 7.4              | 0.74            |
| PDMS-20S | 2.5                    | 8.0                    | 90                  | 16.7             | 0.83            |
| PDMS-35S | 2.0                    | 7.0                    | 75                  | 30.5             | 0.87            |
| PDMS-50S | 1.5                    | 2.5                    | 60                  | 44.4             | 0.88            |

<sup>a</sup>Time A (initial period): Period of rapid linear change of the degree of swelling. <sup>b</sup>Time B (transition period): Period of slower increase of the degree of swelling until the equilibrium degree of swelling (*DSe*) is reached. <sup>c</sup>*DSe*: Equilibrium degree of swelling. <sup>d</sup> $\Delta DS$  /% =  $\frac{DS_{PDMS-0} - DS_{PDMS-nS}}{DS_{PDMS-0}} \cdot 100$ . <sup>e</sup>*c*(weight %) zeolite concentration

Table II (column four) also shows the changes in the equilibrium degree of swelling (*DSe*) of the PDMS-zeolite composite with various zeolite concentrations. Based on the presented results, it can easily be concluded that increasing concentration results in a reduction of the *DSe* of the composites compared to unfilled elastomer.

*Hardness*: The changes in the hardness of the investigated PDMS-nS composites with changing zeolite concentration in the composite are presented in Table III, from which it can be concluded that the introduction of this type zeolite into the PDMS matrix leads to an increase of the composite hardness.

TABLE III Results of the effect of silicalite concentration of the hardness of the PDMS-nS composites

| Sample   | Hardness/ <sup>o</sup> ShA | $\Delta H^a$ /% | $\Delta H/c^b$ |
|----------|----------------------------|-----------------|----------------|
| PDMS-0   | 25                         | —               | —              |
| PDMS-5S  | 31.5                       | 26              | 5.2            |
| PDMS-10S | 34                         | 36              | 3.6            |
| PDMS-20S | 39                         | 56              | 1.8            |
| PDMS-35S | 40                         | 60              | 1.42           |
| PDMS-50S | 41                         | 64              | 1.28           |

<sup>a</sup> $\Delta H = \frac{H_{PDMS-0} - H_{PDMS-nS}}{H_{PDMS-0}} \cdot 100$ ; <sup>b</sup>*c* zeolite concentration/weight %

*Thermal analysis*: Figure 2 presents two typical TG curves of the investigated PDMS-zeolite composites. Table IV shows the temperatures of the beginning and end of degradation, as well as the residues at 800 °C of the investigated composites.

With increasing zeolite concentration the end temperature decreases. The degradation residue of the composites increases with increasing zeolite content in

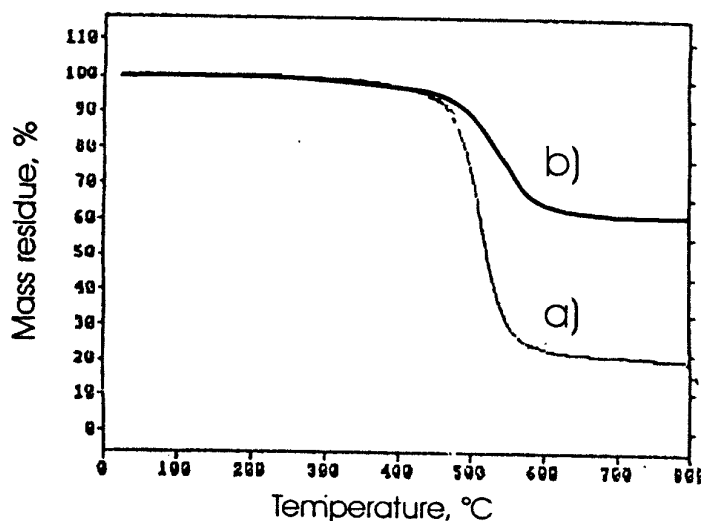


Fig. 2. TG curves of a) PDMS-0 and b) the PDMS-50S composites.

the composite as expected. The difference in the change of the residue with zeolite concentration ( $\Delta R/c$ ) decreases with zeolite concentration.

There is no change in the temperature of the beginning of degradation of the composites up to about 35 % of silicalite. Further increase of the zeolite concentration leads to a lowering of this temperature.

The established changes in the  $DS$ , hardness and mass residue of thermal degradation with zeolite concentration, clearly indicate that some interaction between the polysiloxane and the zeolites exists.

As there are no free OH groups on the outer surface of the silicalite and the dimensions of the entrance pores ( $d = 0.56 \text{ nm}$ )<sup>8</sup> are much smaller than the polysiloxane radius of gyration,<sup>9</sup> the main question is what type of interaction is possible between PDMS and the silicalite type zeolite.

We believe that in the case of silicalite there is some unspecific interaction of the outer surface of the zeolite with polydimethylsiloxane.

The observed differences in the  $DS$ , hardness and thermal stability of the composites, which are caused by different zeolite concentrations, could be explained in terms of changes in the number of established polymer-zeolite interactions, the density of the polymer-zeolite interactions (the number of polymer-zeolite interactions per mass unit of zeolite) and spatial irregularity in the polymer network.

In our opinion, an increase of the zeolite concentration in the composite results in an increase in the total number of established polymer-zeolite interactions, but the density of the interactions decreases. Therefore, with increasing zeolite concentration in the composite, the fraction of zeolite not incorporated into the polymer

matrice in the fashion described (by means of the previously mentioned polymer-zeolite interaction) but is only "trapped" in the polymer matrice increases. Hence, one can distinguish between so-called "bonded" and "unbonded" zeolite.

As can be seen from the obtained results, a change of the zeolite concentration alters the composite characteristics, but only at lower zeolite concentrations. It can be concluded that "bonded" zeolite, of which there is more at lower zeolite concentrations, causes pronounced changes in the composite characteristics, resulting in a pronounced increase of the hardness and a reduction of the degree of swelling. "Unbonded" zeolite does not significantly influence the composite characteristics (does not increase the cross-link density), therefore increasing its concentration does not result in significant changes of the composite properties.

Hence, it can be said that, most probably, it is not the increase in zeolite concentration, but the proportion of "bonded" zeolite which is decisive for the alteration of the composite characteristics.

TABLE IV Results of the thermal analysis of the PDMS-nS composites

| Sample   | $T_1^a/^{\circ}\text{C}$ | $T_2^b/^{\circ}\text{C}$ | Mass residue at 800 $^{\circ}\text{C}/\%$ | $\Delta R^d/\%$ | $\Delta R/c^e$ |
|----------|--------------------------|--------------------------|---|-----------------|----------------|
| PDMS-0   | 420                      | 750                      | 19.7                                      | —               | —              |
| PDMS-5S  | 420                      | 730                      | 26.0                                      | 6.3             | 1.26           |
| PDMS-10S | 420                      | 720                      | 32.0                                      | 10.3            | 1.00           |
| PDMS-20S | 420                      | 710                      | 40.0                                      | 20.3            | 1.00           |
| PDMS-35S | 420                      | 670                      | 48.0                                      | 28.3            | 0.81           |
| PDMS-50S | 405                      | 620                      | 60.0                                      | 40.3            | 0.80           |

<sup>a</sup> $T_1$ : Temperature of the beginning of degradation (for 5 % mass loss), <sup>b</sup> $T_2$ : Temperature of the end of degradation, <sup>c</sup> $\Delta R = R_{\text{PDMS-nS}} - R_{\text{PDMS-0}}$  where  $R$  is the mass residue after degradation, <sup>d</sup> $c$ : zeolite concentration

The most probably explanation for such a large influence of low zeolite concentrations (up to about 12 %) is that, due to the fact that small amounts of zeolite are able to disperse in the polymer well, the influence of spatial disorders in the network on the  $DS$ , hardness and thermal stability is small. So, in this concentration range, changes in the  $DS$ , hardness and thermal stability are a consequence of only two effects: the number of established polymer-zeolite interactions and the density of the polymer-zeolite interactions. In this concentration range, there is a real increase in the composite hardness which can be explained as being a direct consequence of the increased density of the polymer-zeolite interactions.

With increasing zeolite concentration in the range from about 12 % to about 35 %, there is a slower increase in the hardness as well as of  $\Delta DS/c$ , which can be explained in the following manner: although the number of established polymer-zeolite interactions increase, the density of the interactions is significantly decreased, so that the changes in  $\Delta DS$ , and hardness are not so expressed.

In the third range of concentration (more than about 35 %), we believe that the increase of spatial irregularity in the polymer network affects the previously

mentioned number of interactions and the density of interaction polymer-zeolite, so there are no real changes in  $\Delta DS$  and hardness, and the thermal stability of the composites is significantly lower.

#### ИЗВОД

#### ИСПИТИВАЊЕ УТИЦАЈА ЗЕОЛИТЕ ТИПА СИЛИКАЛИТА НА PDMS-КОМПОЗИТЕ

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Циљ овог рада је био испитивање утицаја зеолита типа силикалита на PDMS-зеолит композите. Добијени резултати су показали да увођење зеолита типа силикалита у полисилоксанске матрице има за последицу промене у равнотежном степену бубрења композита у толуену, њихове тврдоће и термичке стабилности. Са повећањем количине зеолита време потребно за постизање равнотежног степена бубрења ( $DSe$ ) смањује се,  $DSe$  опада, а тврдоћа расте. Запажен је двоструки ефекат концентрације зеолита на промене у карактеристикама композита. При концентрацијама зеолита до око 12 % постоје значајније промене у  $DSe$  и тврдоћи са концентрацијом зеолита, док је овај ефекат знатно мање изражен при вишим концентрацијама. Добијени резултати показују да зеолит силикалит делује као појачавајући пунилац. Сматрамо да повећањем концентрације зеолита у композиту укупан број успостављених интеракција полимер-зеолит расте, као и просторна нарушеност полимерне мреже, али густина интеракција опада. Ово би могло бити највероватније објашњење за промене у карактеристикама композита са променом концентрације зеолита.

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