Investigation of the Effects of NaA-Type Zeolite on PDMS Composites

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ABSTRACT: The aim of this article was to investigate the effect of a NaA-type zeolite on a polydimethylsiloxane (PDMS)–zeolite composite. The obtained results show that the introduction of a NaA-type zeolite into polysiloxane matrices results in a change of the equilibrium degree of swelling (DSe) of composites in toluene, their hardness, and their thermal stability. With increase in the zeolite, the time required to achieve the DSe is reduced, DSe decreases, and hardness increases. A double effect of the zeolite concentration on the change of the composite characteristics was noted. At zeolite concentrations of up to 20%, there is a drastic change of the DSe and hardness with zeolite concentration, while this effect is considerably less pronounced at higher concentrations. The results obtained show that a NaA-type zeolite plays the role of a reinforcing filler. A new mechanism of bonding the zeolite into the composite was suggested. According to this model, there is a possibility that bonds are established between the polymer and the zeolite via interaction of the π-bond of terminal vinyl groups of PDMS with the Na cation of the zeolite. With increase in the zeolite concentration in the composite, the total number of established polymer–zeolite bonds increases, but the density of the interaction decreases. This explains the change in the characteristics of the composite with the change of zeolite concentration. © 2000 John Wiley & Sons, Inc. J Appl Polym Sci 77: 1171–1176, 2000

Key words: PDMS composite; Na-type zeolite; degree of swelling; hardness; thermal stability

INTRODUCTION

Polysiloxanes are very suitable materials for combinations with zeolites,[1,2] unlike other organic polymers where the problem of zeolite dispersion appears.[3] Data exist on obtaining various polysiloxane zeolite composites which have prominent applications in the pervaporation of water/alcohol mixtures.[2,4,5] Vankelecom et al.[2] mentioned the possibility of chemical crosslinking of zeolites in cases of polydimethylsiloxane (PDMS)–zeolite membranes containing zeolites of the following types: Y, ZSM-5, and silicalite, according to procedures for membrane preparation.[4]

This study investigated the possibility to obtain polysiloxane–zeolite composites in the form of materials, both as membranes and significantly thicker, using polysiloxane matrices obtained by a hydrosylilation reaction and a NaA-type zeolite. The effect of the concentration of a NaA-type zeolite on the following characteristics of a PDMS–zeolite composite was investigated: swelling in toluene, hardness, and thermal stability.

Crystallinity degree (%)	100
Mean crystal size (μm)	4
Specific area (m^2/g)	780
Specific volume (cm^3/g)	0.3
Kinetic diameter (nm)	0.4

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 PDMSs end-capped with vinyl groups. Component B consisted of polysiloxanes, which contained a few silylhydro groups per molecule so that it acted as a crosslinker, and platinum, which acted as a catalyst for the hydrosilylation reaction.

Zeolite-type NaA was synthesized at the Institute of General and Physical Chemistry in Belgrade and used for obtaining the PDMS–zeolite composite. The most important physicochemical characteristics of the zeolites used are presented in Table I. The zeolites were dried by heating at 120°C for 2 h, at 240°C for an additional 2 h, and at 400°C for 4 h and were kept in a vacuum exicator.

Procedure for Obtaining Polysiloxane–Zeolite Composite

To obtain the polysiloxane–zeolite composite, a mixture of polysiloxane precursors, RTV-A and RTV-B, in a ratio of 10 : 1 by weight and various quantities of zeolite (from 1% to the maximum possible quantity of 50% by weight in the polysiloxane zeolite mixture) was used. Composites were prepared as follows: The desired quantity of the zeolite was added to the determined quantity of polysiloxane RTV-A. This mixture was first homogenized by careful stirring using a metal spatula and then in an ultrasonic bath. At higher zeolite concentrations (50%), toluene was used as the solvent. After reaching satisfactory homogeneity, the required quantity of the polysiloxane precursor RTV-615B was added and the obtained mixture homogenized once again and then poured into adequate metal molds, kept under a vacuum for 2 h, and then heated to 80°C for 4 h. After this time, vulcanized samples were, after cooling at room temperature, removed from the molds. The obtained composites are hereinafter denoted as PDMS-nA, where "n" represents the percent of zeolite contained in the composite.

Determination of Degree of Swelling (DS)

The DS of the composite was determined based on the change in weight of the sample submerged in toluene until swelling equilibrium was reached (denoted DSe), so that

$$\text{DS } (\%) = (G_t - G_0)100/G_0$$

where G_t is the weight of the swelled sample in time, and G_0, the initial sample weight.

Hardness Determination

The hardness of the composites obtained was measured using the Shorr A method on a "Zwick"-type 7206 apparatus.

Thermogravimetric (TG) Analysis

Thermal characteristics of composites were determined using "Stanton Redcroft"-type 1000 apparatus under a constant heating speed of 10°C/min. Analyses were done under a nitrogen atmosphere with a flow velocity of 60 mL/min and using 10-mg samples.

RESULTS AND DISCUSSION

Figure 1 presents the kinetics curves of the PDMS-nA composite swelling in toluene at ambient temperature (about 25 ± 1°C). Table II contains the times for the initial period of swelling (Time A) and times for period until equilibrium state is reached (Time B), the experimentally determined values for the degree of swelling (DSe, exp., %), calculated values for degree of swelling (DSe, calcd., %) based on the zeolite content in the composite as the inert filler, and the difference between experimental and calculated values for the degree of swelling (ΔDSe (exp. − calcd.), %).

Based on the demonstrated kinetic curves for the swelling of the PDMS-nA composites, it can easily be concluded that they have an equal shape regardless of the zeolite quantity in the PDMS-composite. Three characteristic phases were evident on these curves pertaining to DS change with swelling time. In the first phase (so-called
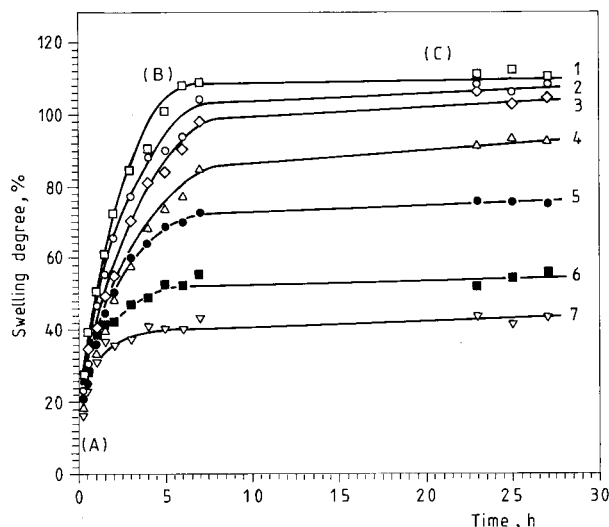
Figure 1 Monitoring of swelling behavior of PDMS-nA composites in toluene at 25°C: (1) PDMS-0; (2) PDMS-1A; (3) PDMS-5A; (4) PDMS-10A; (5) PDMS-20A; (6) PDMS-35A; (7) PDMS-50A.

Figure 2 Influence of zeolite concentration on the hardness of PDMS-nA composites.

initial period, denoted Time A in Table I), which lasts 1–3 h, DS grows abruptly and virtually linearly with the swelling time. Increase of the swelling time after completion of the initial period (so-called transitory period, denoted Time B), in the interval from 7 to 25 h, depending on the composite, leads to a slowing of DS growth. After this period, an equilibrium swelling state is reached and the DS does not change any more with time.
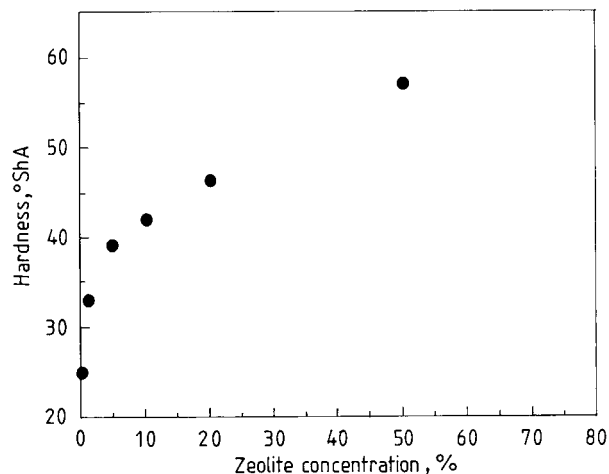
The increase of zeolite concentration in the composite decreases the duration of the initial and the transitory period, while the difference between the calculated and the experimentally determined DSe increases.

Composite Hardness

Figure 2 shows the effect of the concentration of the zeolite-type NaA employed on the hardness of the investigated composites. The results obtained show that an increase of zeolite concentration resulted in an increase in the composite hardness,

Table II   Results of Monitoring Composite PDMS-nA Swelling in Toluene at 25°C

Sample	Initial Period[a] Time A (h)	Transition Period[b] Time B (h)	DSe, exp[c] (%)	DSe, calcd[d] (%)	ΔDSe[e] (%)
PDMS-0	3	7.5	108	—	—
PDMS-1A	3	25	106	106.92	0.87
PDMS-5A	3	18	101	102.6	1.58
PDMS-10A	2	13	93	97.2	4.52
PDMS-20A	1.5	10	75	86.4	15.2
PDMS-35A	1.2	8.5	52	70.2	18.2
PDMS-50A	1	7	44	54	22.73

[a] Initial period (Time A): Period of abrupt linear change of degree of swelling.
[b] Transition period (Time B): Period of slower increase of degree of swelling until DSe is reached.
[c] DSe, exp: Equilibrium degree of swelling determined experimentally.
[d] DSe, calcd: Equilibrium degree of swelling, semitheoretical, calculated based on content of zeolite in composite and known DSe of unfilled PDMS elastomer as

$$\text{DSe, calcd} = \text{DSe, } o \, Xi \tag{1}$$

where DSe, o = 108 (for PDMS-0) and Xi is the mass proportion of polymer in the composite:
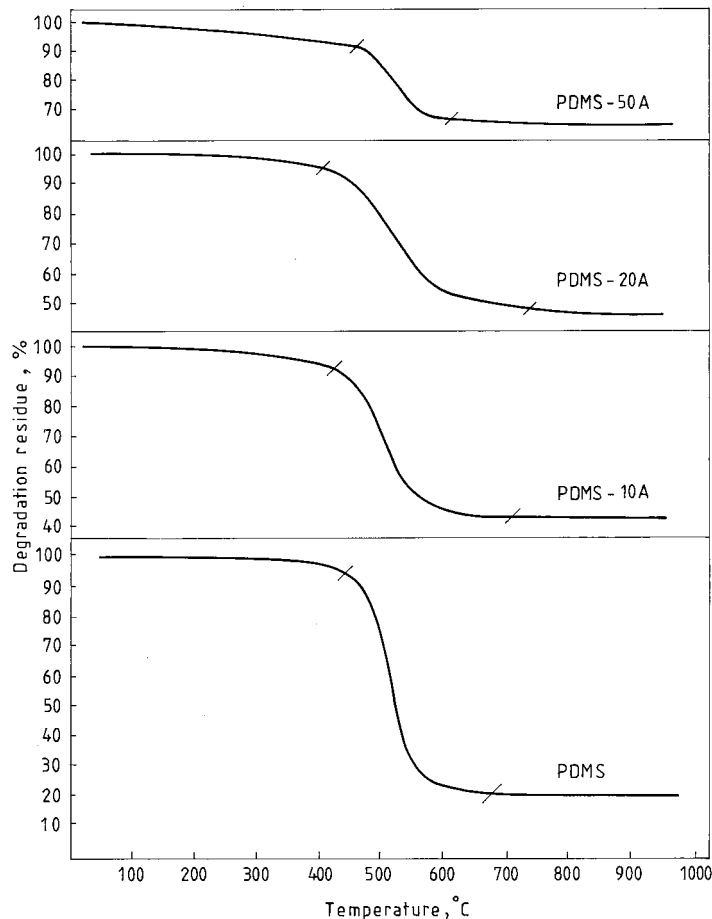[e] ΔDSe, % = (DSe, exp − DSe, calcd)/DSe, exp. $\tag{2}$

Figure 3   TG curves of PDMS-nA composites.

in such a manner that in ranges of lower zeolite concentrations there is a significant increase in the composite hardness. At higher concentrations, this increase becomes less pronounced.

For composites in which the zeolite content does not exceed 5%, there is a very abrupt increase in hardness (as compared to unfilled elastomer), when the composite becomes over 50% harder. In zeolite concentration ranges from 5 to 50%, there is still a very pronounced effect on the increase of the hardness. The addition of 50% zeolite results in an increase of the composite hardness of about 130% as compared to the unfilled elastomer.

Thermal Analysis

Figure 3 shows TG curves for the PDMS-nA composite with various contents of the NaA zeolite. The starting and end temperatures of the degradation and mass residue of degradation of the composite are presented in Table III.

Based on the obtained results, it can be concluded that the temperatures at which degradation begins (loss of 5% of initial mass) of the composite containing up to 20% zeolite are constant (420°C). For composites containing over 20% zeolite, temperatures at which degradation begins are significantly lower (340°C) (see Table III).

End temperatures of the thermal degradation decrease with increase in the zeolite content in the composite, and the mass residue of degradation increases with increase in the zeolite content in the composite. Such results can be explained by the assumption that there are additional, specific interactions between the polymer and zeolite. The obtained results clearly indicate that this zeolite behaves as an active filler in the investigated composites, that is, that it establishes specific interactions with the polymer.

The dimensions of the entrance pores of the NaA-type zeolite are 0.4 nm, and it has no surface OH groups.[6] Therefore, the only possible type of

Table III   Results of TG Analysis of PDMS-nA Composites

Sample	Beginning of Degradation[a] (°C)	End of Degradation (°C)	Mass Residue of Degradation (%)
PDMS-0	420	750	19.7
PDMS-5	420	720	29.7
PDMS-10	420	700	40.7
PDMS-20	420	695	45.8
PDMS-35	380	650	50.2
PDMS-50	340	600	60

[a] For mass loss of 5%.

polymer–zeolite interaction is bonding of the end vinyl groups of α,ω-divinyl telechelic PDMS (RTV-A) to Na cations in the structure of the NaA-type zeolite. This "bond" is achieved by interaction of the π-bond of the vinyl group with the Na cation of the zeolite.[7]

For all the investigated characteristics of the PDMS-nA composites in this article, that is, the DSe, hardness, and thermal stability, two characteristic phases of influence of a change in the zeolite concentration on the degree of a change of the composite characteristics can be noted. In the first characteristic phase of influence of the zeolite concentration in the zeolite on its characteristics (zeolite concentration ≤20%), an increase of concentration results in a drastic change of the investigated characteristics, especially of the DSe and hardness.

At zeolite concentrations in the composite of >20%, the effect of the change of concentration on the investigated characteristics is much less pronounced. The noted effect of zeolite concentration on the characteristics of the PDMS-nA composite can be explained by a specific interaction of the zeolite–polymer, in keeping with the postulated assumption of the possibility to establish bonds between the polymer and zeolite via the interaction of the π-bond of end vinyl groups of PDMS with Na cation of the zeolite. At low zeolite concentrations, the number of such bonds established per unit zeolite mass (density of interaction) is high.

An increase of zeolite concentration in the composite results in an increase in the total number of established polymer–zeolite bonds, but the density of the interaction decreases. Therefore, with increase of the zeolite concentration in the composite, the portion of the zeolite which is not incorporated into the polymer matrix in the fashion described (crosslink within the crosslink of the

polymer matrix), but which is only "trapped" in the polymer matrix, grows.

Therefore, a change of zeolite concentration also results in an alteration of the composite characteristics. A polymer "bonded" to zeolite, of which there is more at lower zeolite concentrations, causes pronounced changes in the composite characteristics, thus causing a pronounced increase of hardness and reduction of the degree of swelling. A polymer unbonded to zeolite has no significant influence on the composite characteristics (does not increase crosslink density); therefore, an increase of its concentration does not result in significant changes of the composite.

As a consequence, it is not the increase of zeolite concentration but the proportion of the polymer "bonded" to the zeolite which is decisive for the application of its characteristics. The results of thermal analysis of the investigated composites confirm the postulated hypothesis of the establishment of polymer–zeolite interaction and the change of the proportion of "bonded" and "unbonded" polymer with change in the zeolite concentration.

CONCLUSIONS

- Introduction of NaA-type zeolite into polysiloxane matrices causes changes in the equilibrium degree of swelling, hardness, and thermal stability.
- Increase of the zeolite concentration shortens the time required to achieve the DSe (both in the initial and the transitory periods), increases reduction of the DSe, and increases the composite hardness.
- A double effect of zeolite concentration on the alteration of the investigated characteristics was established. At low zeolite concentrations (≤20%), the hardness and the DSe of

the composite change significantly, while at concentrations >20%, these changes are much less pronounced.

- A model of bonding of the zeolite into the polysiloxane matrix, via specific interactions of the π-bond of PDMS end vinyl groups with the Na cation of the zeolite, was suggested. Increase of the zeolite concentration results in increase in the total number of polymer–zeolite bonds, but the density of interaction decreases. For this reason, a change of the zeolite concentration results in a change of the composite characteristics.

- The bonding of a polymer to a zeolite, the proportion of which is higher when zeolite concentrations are low, causes changes of the composite's characteristics.

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