

Development of Organosilicone–Polyurethanes as Stone Preservation and Consolidation Materials

MOSHE PUTERMAN,^{1*} BERNHARD JANSEN,² and HERMANN KOBER,³

¹Institut für Bauforschung, RWTH, 52056 Aachen, Germany; ²Bayer AG, ZF-MFP, 51368 Leverkusen, Germany;

³Bayer AG, LS-A2, 51368 Leverkusen, Germany

SYNOPSIS

Two organosilicone-modified polyurethanes are investigated as potential materials for the conservation and consolidation of natural stones. The materials are low molecular weight oligomers at the application stage and react with the humidity of the air to give polymers, forming continuous microlayers. The two differ in the length of the organosilicone chain, resulting in pronounced differences in their physical state: one forms a brittle glassy material ($T_g \approx 70^\circ\text{C}$), and the other, a soft rubbery material ($T_g \approx -100^\circ\text{C}$). The rate of the polymerization of the prepolymers was investigated at different conditions, showing a strong dependence on the presence of a catalyst and air humidity. Both these favorable conditions exist probably in the natural stone pores, enhancing the formation of the protective hydrophobic internal microlayer. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

The deterioration and decay of natural stone buildings are of major concern in Germany as well as all around the world. Sand stones and, to a limited extent, also limestones, have been for centuries the main building materials for large construction. Many cathedrals, and other ancient buildings of great cultural and archeological importance, are sometimes badly affected by the deterioration process, and their future survival is endangered.

The reasons for the deterioration and degradation of the stones are mostly weathering effects and atmospheric influences. The main damaging element is, no doubt, water and, in particular, rainwater. Water, which penetrates the stone's internal pores by capillary forces, has both a physical and chemical damaging effect. The physical damage is caused by freezing of the absorbed water—a transition accompanied by a volume increase of about 10% and resulting in crack development and layer peeling. The

chemical effect is mainly that of stone dissolution: the carbon dioxide-saturated water dissolves slowly the calcium carbonate components of the stone. This chemical effect was badly accelerated in the last few decades as a result of the atmospheric polluting gases (e.g., SO_2), which strongly increase the acidity of the water and its ability to dissolve the calcium carbonate.¹ It is assumed that the water in the stone pores enhances also the biological degradation effects as it supports the growth of microorganisms within the pores.

The common solutions, so far, to deal with the problems were by treating the external stone surfaces with hydrophobic materials. These were impregnated into the stone, forming a hydrophobic surface layer which prevented, for some time, the penetration of the rainwater and, hence, its deteriorating effects. These materials are based mainly on organosilicones and, to a lesser extent, derivatives of stearic acid, e.g., aluminum stearate. Yet, these materials give the stones only a hydrophobic effect and that for a limited time. The hydrophobic effect, though reducing the water impregnation into the stone pores, does not have any effect on the consolidation of the internally damaged stone. The materials which are used as stone strengtheners, i.e.,

* To whom correspondence should be addressed at National Building Research Institute, Technion-Israel Institute of Technology, Haifa 32000, Israel.

silica esters, form in the stone pores a hard silica gel with the disadvantage of forming a higher modulus layer, as well as forming a secondary pore network due to adhesive or cohesive failures.

It was hence suggested²⁻⁴ to use, for both the protection and consolidation of the stones, materials that can form an internal polymeric microlayer on the stone pore surfaces, a concept referred to as the "internal supporting corset." The polymeric corset should prevent the water penetration (by a hydrophobic effect) and the damage caused by it while forming a consolidating protective layer on the pore surfaces.

The applied materials should therefore have the ability for

- Good penetration into the stone,
- Formation of the required polymeric microlayer, as well as to be
- Usable at the building site, and
- Compatible with ecological demands.

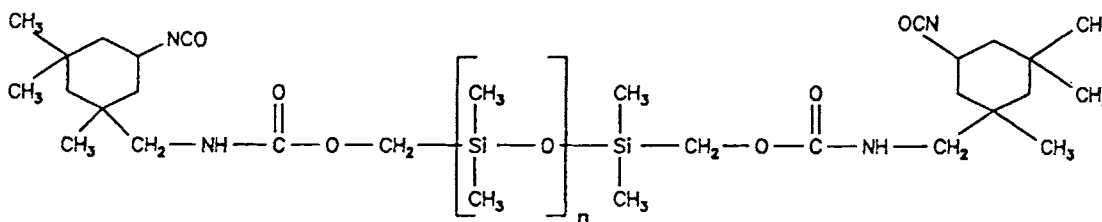
After the physical or chemical curing of the impregnated material, the formed microlayer should have the following properties:

- Water repellency and water resistivity (hydrophobic effect),
- Water impermeability,
- Resistivity against chemical and biological agents, and
- Rubber elasticity over a wide range of temperatures (-30° to 80°C), to prevent cracking as the temperature changes.

This article presents the chemical and physical properties of an organosilicone–diisocyanate developed by Bayer AG, Germany, as a potential stone protection material, with the aim to suit the above-mentioned requirements.

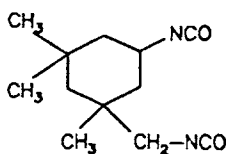
THE CHEMISTRY OF THE ORGANOSILICONE–POLYURETHANE MATERIALS

The basic organosilicone–diisocyanate developed is an oligomeric prepolymer material of the following chemical structure (I):

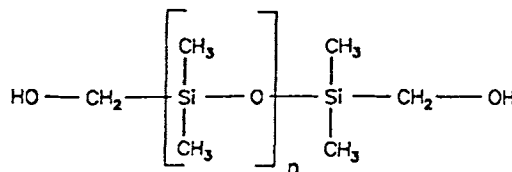


Structure I

This prepolymer is made from isophorondiisocyanate (II) and α,ω -alkyldihydroxy polysiloxane (III):



Structure II

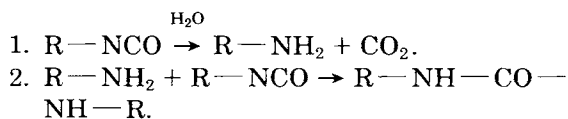


Structure III

Two products have been investigated: The first, referred to as material 1, has a short organosilicone chain with $n = 5,6$ and a theoretical molecular weight of about 1000; the other (material 2) has a longer chain with $n = 12,9$ and a theoretical molecular weight of about 1500. The values of n are not round numbers, as the basic products are not

pure substances, but mixtures of molecules of different chain length. Yet, it can be assumed that material 2 has a polysiloxane chain twice as long as that of material 1.^{5,6}

By reacting with the humidity of the air, the prepolymers condense in a two-step reaction to form long-chain macromolecules, as described hereby:



Obviously, this polymerization reaction proceeds not just with the air humidity, but with water molecules absorbed on a mineral surface as well.

After polymerizing, the shorter-chain originated material (1) forms a glassy brittle film, whereas the longer-chain originated material (2) forms a soft rubbery film. Figure 1 shows the thermal transitions of the two materials as recorded by a differential scanning calorimeter (DSC 30, Mettler, Switzerland). Material 1 has a transition at about +70°C, whereas material 2, at about -100°C. The brittle material shows also a relaxation peak close to the T_g (in the first thermal run). Such a relaxation does not exist in the softer material, as it is already well annealed at the ambient room temperature due to its very low glass transition. Relating to the mechanical requirements mentioned above, it is obvious that the softer material is more suitable as an "internal corset," yet other parameters have to be con-

sidered, too, in order to make the material suitable for technical application.

THE RATE OF POLYMERIZATION

To ensure a sufficient depth of impregnation and the proper functioning of the material according to the "supporting corset" concept, it is desirable that the viscosity of the material does not increase due to polymerization prior to its optimal capillary uptake under the specific impregnation conditions. Yet, the polymerization process should not be too slow either; otherwise, the short molecules can be washed away by penetrating rainwater. It was, hence, important to investigate the rate of polymerization under various conditions. The conditions chosen were

- Standard laboratory conditions: 23°C/50% RH,
- High humidity conditions: 23°C/95% RH,
- With a dibutyltin-dilaurate catalyst at 23°C/50% RH.

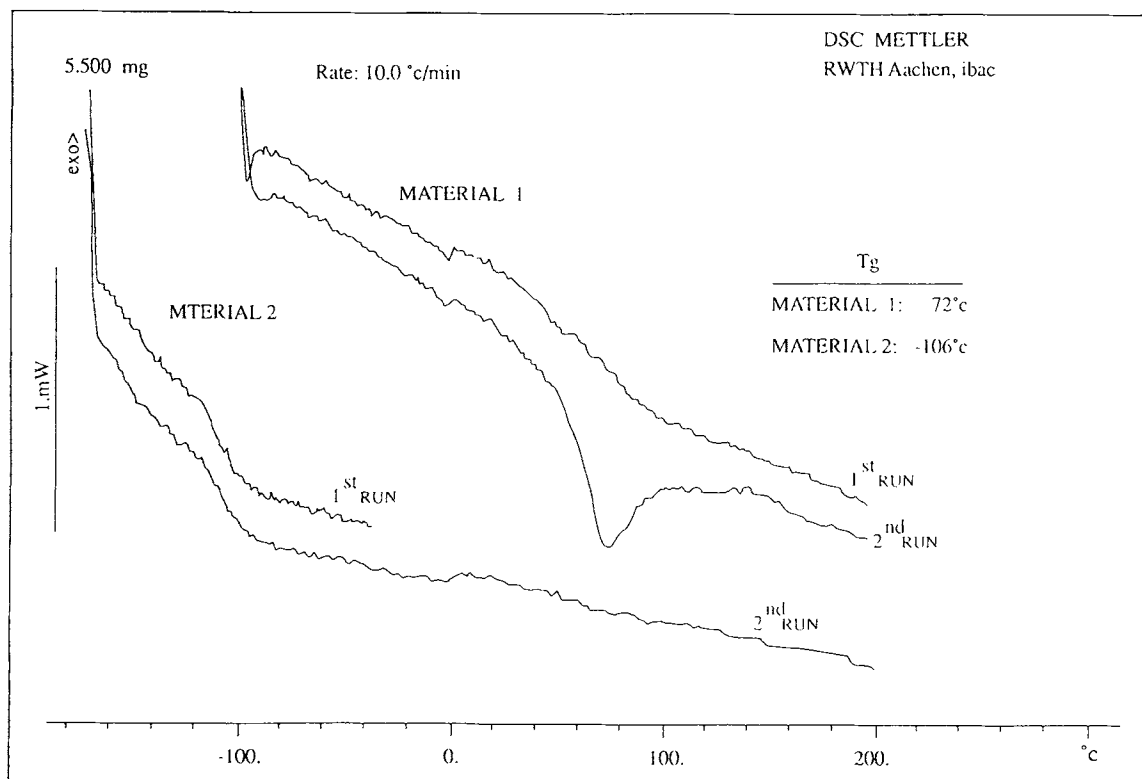


Figure 1 Thermal transitions of the polymerized organosilicone-polyurethanes. First and second runs are shown for each material.

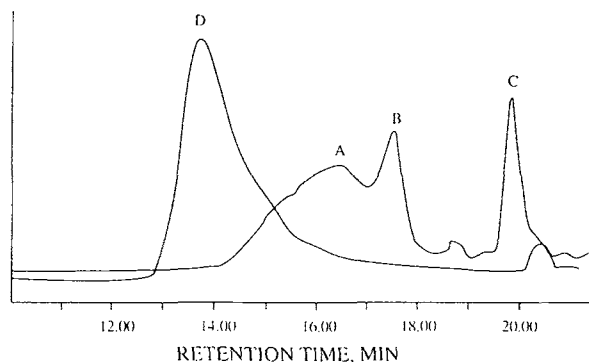


Figure 2 GPC curves of material 1 before (peaks A, B, and C) and after (peak D) polymerization.

The starting materials were, in all cases, 30% solutions of the basic oligomers in methoxypropylacetate. A gel permeation chromatography (GPC) method, utilizing polystyrene gel columns (Merk-Hitachi, Germany) was used to measure the apparent molecular weights. These were determined by comparing the measured retention times with those of polystyrene standards of narrowly distributed molecular weights. (The molecular weight of the tested materials is therefore referred to as PSU = polystyrene units).

An example of a GPC curve of a freshly prepared material 1, before and after polymerization, is shown in Figure 2. The original oligomeric material has a relatively wide molecular size distribution with the main peak (A) at about 1000 PSU and a shoulder toward the 2000 PSU. The sharper peak to the right (B) with a molecular weight of a few hundred PSU is probably unreacted starting material in the form of cyclic four-member Si—O rings. The IPDI, having a molecular weight of 222, is also detected as a sharp single peak (C) at their right. After polymerization, the peak shifts to a much shorter retention time, corresponding to a molecular weight of 8000 PSU, with a relatively narrow distribution (D). A similar situation exists with material 2; nevertheless, the molecular weight of the oligomer is somewhat higher, in the order of 2000 PSU.

The change in the molecular size distribution, as a function of time for material 1 at high humidity conditions, is presented in Figure 3. The four curves show the originating material and those resulting after 3, 8, and 13 days of polymerization. The shift of the main peak from longer retention times, i.e., low MW molecules, to shorter retention times, i.e., higher MW molecules, can easily be detected, as well as the narrowing of the size distribution as the polymerization progresses to completion.

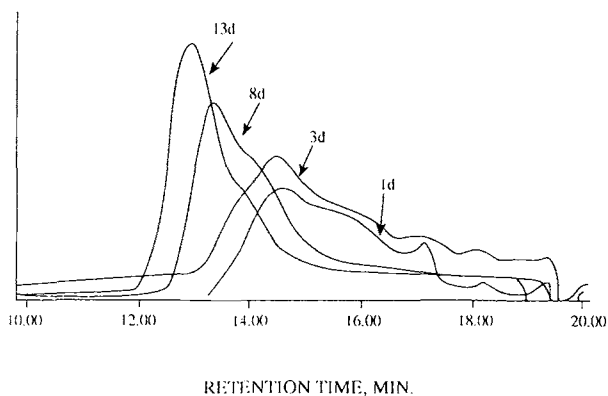


Figure 3 GPC curves of material 1 after 1, 3, 8, and 13 days of polymerization in high-humidity conditions (23°C/95% RH).

An interesting comparison is between the distribution curves of the materials after a similar polymerization period, but under the different conditions. Figure 4 shows the curve of material 1 after 9 days of polymerization at the standard conditions, the high humidity conditions, and with the organotin catalyst. (Due to experimental limitations, the curve of 23°C/95% RH presents the situation after 8 days.) The catalyzed reaction produces the highest molecular weight (ca. 16,000 PSU) with the narrower distribution. The high humidity enhances the reaction in comparison to the low-humidity condition, giving a main fraction of long molecules (ca. 12,000 PSU) with a “shoulder” of shorter molecules. The 50% RH, on the other hand, has mainly molecules of lower molecular weight (ca. 5000 PSU), with a “shoulder” of a fraction of higher MW molecules.

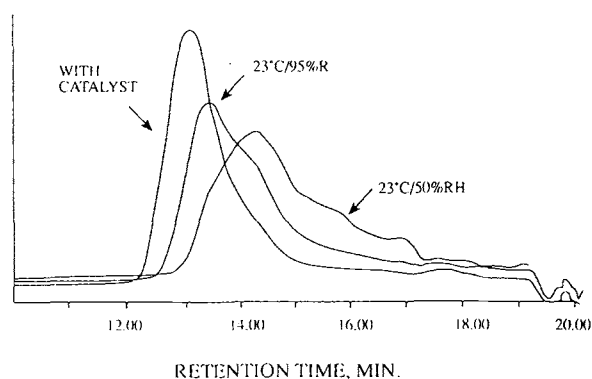


Figure 4 GPC curves of material 1 after 9 days of polymerization at (1) normal laboratory conditions (23°C/50% RH); (2) high humidity conditions (23°C/95% RH), and (3) with organotin catalyst at 23°C/50% RH.

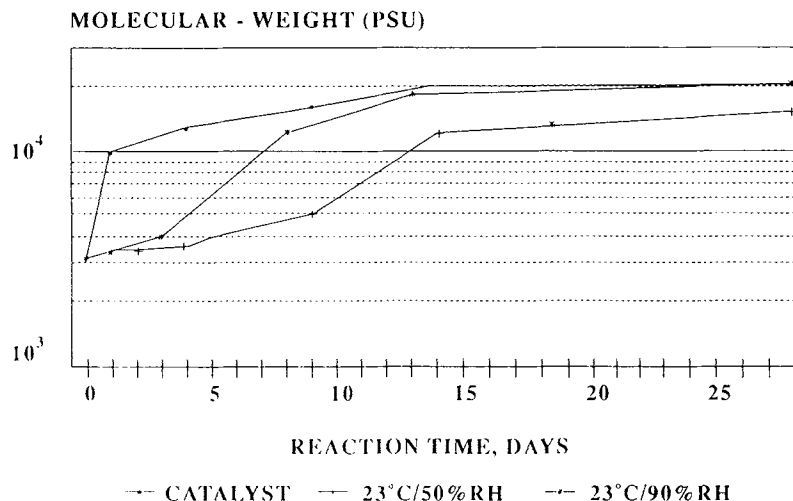


Figure 5 Polymerization rate of material 1 at the three different conditions.

Figures 5 and 6 summarize graphically the changes in the molecular weight of materials 1 and 2, correspondingly, as a function of time and the conditions of polymerization. As can be seen, in both cases, the polymerization proceeds at the fastest rate in the catalyzed systems and at the slowest rate under the standard conditions. At these conditions (23°C/50% RH), the reaction has a relatively long induction time of 7–10 days, and even thereafter, the buildup of the molecular weight is slow. It reaches the size of 10,000 PSU only after 10–12 days. In the catalyzed system, the reaction is quick as from the start, without any induction time, and it reaches the 10,000 value after 1 day or so. The high-humidity reaction has an in between polymerization rate, with a short induction time of 3–4 days. It reaches the

10,000 PSU molecular size after 6–8 days. It is interesting to note that under the high-humidity conditions the molecular weight reaches, after 2–3 weeks, the same value as in the catalyzed reaction. The standard conditions polymerization, on the other hand, lags behind throughout the entire process and does not build these large molecules even after 4 weeks and more.

Although the basic behavior of the two materials is very similar, material 2 builds somewhat higher polymers, probably due to the fact that its starting oligomers are also longer. It should be noticed that the MW of the starting materials, 1 and 2, were about 3000 and 4000 PSU, correspondingly. The deviation from the lower theoretical values, or the values exhibited in Figure 2, can be a result of the par-

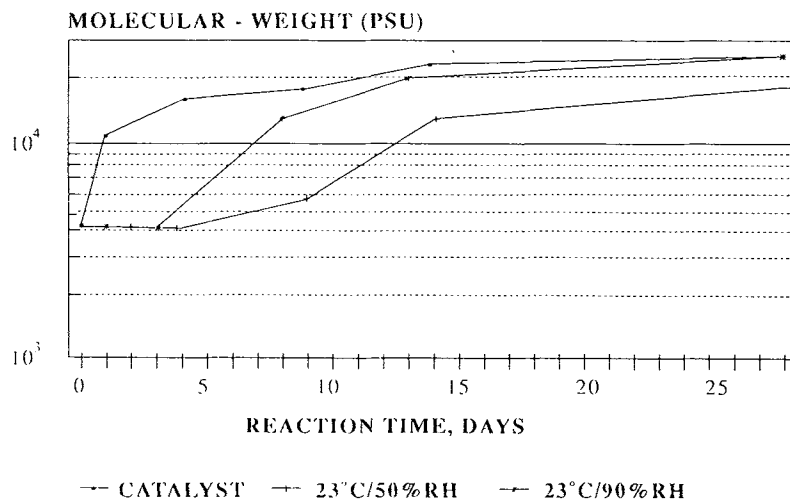


Figure 6 Polymerization rate of material 2 at the three different conditions.

ticular batch preparation or that of some "shelf" polymerization.

The conditions that most probably resemble the real conditions inside the stone are those of the high humidity, as it is assumed that water in liquid form exists in the capillary-size pores and channels. The polymerization behavior of the materials, under these conditions seems to be very favorable for the application and cure process. The induction time is long enough to enable good penetration of the oligomeric material prior to the polymerization of the molecules, yet short enough to form the polymeric film in due time. Also, the higher MW of the molecules, reached under these conditions in comparison to the lower humidity conditions, is a very favorable feature. It is, nonetheless, possible that the metal ions existing in the stone might act as catalysts to accelerate the polymerization reaction; yet, this question must still be verified.

REFERENCES

1. E. M. Winkler, *Stone: Properties, Durability in Man's Environment*, Springer, Wien, 1973.
2. H. R. Sasse, *Bautenschutz und Bausanierung*, Sonderausgabe: Bausubstanzerhaltung in der Denkmalpflege, 1st Statusseminar des BMFT, Mainz, 1986, pp. 65-68.
3. H. R. Sasse and D. Honsinger, in *Proceedings of the International Conference on Protection of Concrete*, Dundee, Scotland, UK, Sept. 1990, pp. 177-190.
4. H. R. Sasse, D. Honsinger, and M. Puterman, in *Proceedings of the 1st International Colloquium on Role of Chemistry in Archeology*, Hyderabad, India, Nov., 1991, pp. 87-94.
5. B. Jansen, H. P. Muller, R. Richter, D. Schapel, and R. Schmidt, EP-B-0259644 (to Bayer AG, Germany) 1988.
6. B. Jansen, M. Puterman, and H. Kober, *Bautenschutz und Bausanierung*, **16**, 1-4 (1993).

Received December 14, 1994

Accepted August 21, 1995