TOWARD A BETTER UNDERSTANDING OF B72 ACRYLIC RESIN/METHYLTRIMETHOXYSILANE STONE CONSOLIDANTS

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ABSTRACT

B72 acrylic resin/methyltrimethoxysilane (MTMOS) mixtures are frequently employed as consolidants for deteriorated limestones, sandstones and marbles. The addition of B72 to MTMOS imparts adhesive properties to the consolidant but it is not known to what degree the B72 affects the reactions which MTMOS must undergo to form a solid polymer network. This paper examines the following chemical, physical, and mechanical properties in order to better understand B72/MTMOS systems: 1. viscosity 2. vapor pressure 3. reaction mechanism and kinetics 4. chemical nature of polymer solids 5. rupture moduli of polymer solids and 6. rupture moduli of stone/consolidant composites.

INTRODUCTION

Advancing the front of stone consolidation has proved difficult in recent years. Since the development of WACKER OH and H [1] and the Lewin method [2] in the 1960s, BRETHANE, [3] the "Bologna Cocktail," [4] and acrylic resins dissolved in methyltrimethoxysilane (or just neat MTMOS) [5] in the 1970s, there has been no evolution in stone consolidation. This fact was lamented in the closing remarks by V. Furlan at the Fifth International "Stone Conference" in 1985. [6] What was not pointed out at that time was how little is known about the chemical, physical, and mechanical properties of many of the above-mentioned consolidation systems. This paper purports to elucidate some of these properties for B72/MTMOS mixtures as they pertain to the usage of these mixtures as stone consolidants.

BACKGROUND

Acrylic resins hold important positions in the conservation repertoire as adhesives and consolidants for many materials. However, subsequent to the work of Larson acrylic resin/MTMOS mixtures attained near regal status for the consolidation of limestones and marbles in museums. [7] One reason Larson employed these resins was to impart adhesive properties to the consolidated stone. His experience indicated that it was difficult to cohere pieces of stone previously treated with MTMOS and that the addition of 1-10% w/v of the acrylic resin overcame the problem. Other workers found that alkoxysilanes in general could not consolidate stones with large grains - on the order of 3 mm or greater. [8] These kinds of stones can also be more successfully consolidated by adding B72 to MTMOS, again, presumably, relying on the adhesive properties of B72. It is not known to what degree B72 affects the physical properties of MTMOS such as viscosity and vapor pressure, the kinetics and mechanisms of the complex set of reactions which produce the solid network of MTMOS-derived polymers, or the mechanical properties of this solid network. Each is important to the successful consolidation of stone:

1. viscosity - controls depth of penetration; inadequate penetration usually considered to be less than 1 cm - can result if the viscosity of a consolidation system is "too high." Although what "too high" is will vary depending on the porosity and pore size distribution of a given stone, 4.0 centistokes at 20°C may be taken as a practical upper limit for viscosity.

2. vapor pressure - controls the amount of consolidant which remains in the stone. Higher vapor pressures cause more consolidant to evaporate before it can react to become a solid. In addition, vapor pressure can control depth of penetration. In solute/solvent systems such as B72/MTMOS a high vapor pressure solvent can cause the solute to be drawn to the surface of the stone. This can lead to surface sheen, darkening of the stone, and a thin consolidated layer - all of which are undesirable.

3. reaction kinetics and mechanisms (mechanical properties) - these chemical features can control depth of penetration, evaporation rate, the mechanical properties of the solid polymers as well as the resulting polymer/stone composite.

The problem of evaporative loss with MTMOS can be severe. Bradley reported [9] that the mass of solid material retained in limestone can be as low as 1% of the original mass of liquid absorbed during application. It has been suggested that by adding B72 to MTMOS evaporative loss may be reduced through solute/solvent interactions. The effect of the stone substrate on evaporation is also unknown; sandstone (i.e. quartz and feldspars) may reduce evaporative loss by surface reactions while the lack of these effects in limestone may increase evaporative loss.

The hydrolysis and condensation reactions of alkoxysilanes such as MTMOS are sensitive to Lewis and Bronsted acids and bases. To the extent that B72 or a stone substrate such as limestone or sandstone may function as such an acid or base, they may alter the kinetics and mechanisms of the MTMOS reactions and, hence, evaporative loss.

Finally, the mechanical properties of MTMOS-derived gels and B72/MTMOS-derived gels are not known. The B72/MTMOS gels may have enhanced mechanical properties as do many composite materials. These composites often employ MTMOS as a "coupling agent." In addition, the mechanical properties may be further enhanced or compromised by different stone substrates.

EXPERIMENTAL

Materials

B72 is the acrylic resin employed in all mixtures; it is a 50/50 co-polymer of methylmethacrylate and ethylacrylate produced by Rohm and Haas. The MTMOS (Dow Chemical Z6070 or Petrarch M9100) is double distilled directly before use. Wallace (Nova Scotia) sandstone and Salem (Indiana) limestone are employed in all experiments requiring stone samples. The sandstone contains silica-cemented clasts of quartz and feldspar and the limestone contains calcite-cemented calcitic oolites. The mineralogies of these stones were confirmed by x-ray diffractometry and petrographic thinsections. The porosities as determined by ASTM C97-83 are 9.42% for the sandstone and 9.45% for the limestone. For mechanical testing a bisphenol A epoxy resin (Epoxy Technologies EPO-TEK 301 - a two part system employing 2,4,4-trimethylhexamethylenediamine as the hardener) is used to consolidate limestone and sandstone samples for the purpose of comparison.

Experiments and Analyses

Manometry

Solutions of 0, 5, 10, and 30% B72/MTMOS w/v are freshly prepared for vapor pressure measurements. The samples are placed in a closed Erlenmeyer flask which is in turn placed in a thermostatted bath at 25.0°C ± 0.1°C. The temperature is controlled by a Fisher Model 70 circulator/heater and a water cooled copper coil. A Nalgene tube connects the Erlenmeyer flask to the manometer which is connected to a vacuum pump. The pump is turned on for one minute to remove the air and water vapor from the flask, tubing and manometer. The stopcock to the vacuum pump is then closed, the pump is turned off, the system is allowed ten minutes to reach equilibrium, and the measurement is taken. At least nine measurements are made for each solution. Measurements are also taken for the MTMOS dimer.

Viscometry

Viscosity measurements are conducted in Cannon-Fenske tube viscometers which are placed in the same thermostatted bath used for manometry. All measurements are conducted at 25.0°C ± 0.1°C. Each viscometer is calibrated with a liquid of known viscosity in the appropriate range of the viscometer. At least twelve readings are made for each liquid; the highest and lowest values are discarded and the average is reported. Viscosities are determined for 0, 5, 10, and 30% B72/MTMOS w/v mixtures and for the MTMOS dimer.

Gravimetry

Gravimetric analysis is conducted on five samples each of neat MTMOS, 0, 5, 10, and 30% B72/MTMOS w/v. In each case the original solution contains 100 ml of MTMOS. The procedure consists in noting the masses of the empty containers, weighing the containers with the solutions each day for one month, and then every few days for a total of four months.

In addition, cylinders of both limestone and sandstone measuring approximately 5.8 mm in diameter and 60 mm in length are produced with a diamond core drills. These cylinders are dried in a convection oven at 60°C for 48 hours. For each of the following solutions a minimum of five limestone and five sandstone cylinders are immersed for one hour to half the diameter of the cylinders in petri dishes containing the consolidants: 0, 1, and 10% B72/MTMOS w/v, 10% B72/toluene w/v, and epoxy resin. The solutions completed permeated the stone samples. The surfaces of the samples are dabbed with KIMWIPES and weighed at approximately thirty minute intervals up to four hours and then intermittently until constant weight is reached (the epoxy samples were not weighed).

Silicon Nuclear Magnetic Resonance (NMR)

Samples of neat MTMOS and 10% B72/MTMOS w/v are allowed to cure at approximately 40% RH and 20°C for three months in which time they became polymeric solids. Each was broken into small pieces suitable for silicon NMR analysis with magic angle spinning. The NMR experiments are performed with a Bruker CXP300 spectrometer operating at 59.6 MHz. Also, neat MTMOS and a 10% B72/MTMOS solution are reacted at approximately 50% RH and 20°C and spectra are collected at 160 and 236 hours. These NMR experiments are performed with a Bruker AM500 spectrometer operating at 99.328 MHz. Through these techniques the distribution of silicon linkages and therefore the reaction kinetics, mechanisms, and nature of the solids which are formed can be revealed.

Head Space Analysis - Gas Chromatography (HSA-GC)

The Hewlett-Packard 19395A head space analyzer coupled to a Hewlett-Packard 5890 gas chromatograph and 3396A Integrator are used for all analyses. Samples of 0, 5, 10, and 30% B72/MTMOS w/v are allowed to react in open HSA vials so that the mixtures could remain undisturbed during the reaction period. The temperature of the HSA bath is set at 40°C and the equilibration time - the time the sample is in the bath before injection into the GC - is 42 minutes. The transfer line from the HSA to the GC is set at 45°C to avoid cold trapping the sample during transfer. The GC injection temperature is 250°C and the temperature program is as follows: 40°C for five minutes, 10°C/minute ramp to 200°C and a 15°C/minute ramp to 300°C. The oven for the GC is then held at 300°C for five minutes for a total run time of 32.67 minutes. The column is a 25 m, 0.25 mm inner diameter and 0.32 μm film thickness Hewlett-Packard Ultra 2 which is slightly polar (5% phenylsilicone/95% dimethylsilicone). The carrier gas is chromatographic grade helium and the gas mix for the flame ionization detector is 2:1 hydrogen to oxygen. The split ratio is approximately 100:1.

During the equilibration time volatile material collects in the head space - the space in the closed vial above the solid or liquid sample. At the end of this time a probe enters the vial and transfers the head space vapor to the injection port and onto the GC column where it is separated into its components and quantified by the integrator.

Scanning Electron Microscopy (SEM)

Samples of neat MTMOS and 10% B72/MTMOS w/v are allowed to cure for two months and then prepared for SEM. The samples are coated with approximately 10 nm of spectroscopically pure carbon in an Edwards E306 vacuum evaporator and are viewed in an AMRAY 1100T SEM with a KEVEX Model 7000 X-ray spectrometer. Operating conditions are specified on the photomicrographs or, for energy dispersive x-ray spectroscopy (EDS) used to collect the dot map, the conditions are 20 or 30 kV, 200 s collection time and 1 to 100 μm² excitation areas.

Mechanical Testing

Samples of 0, 1, 4, 5, and 10% B72/MTMOS w/v are allowed to cure for two months. The specimens are prepared for testing by cutting small "planks" measuring approximately 53 mm x 3.0 mm x 2.0 mm from the larger pieces of cured gels. Cutting is carried out on a Buehler ISOMET saw with diamond wafering blades and a petroleum based lubricating fluid (Buehler ISOCUT Fluid).

The apparatus for determining mechanical properties (in this case the modulus of rupture - MOR) consists of a balance for determining applied load to 0.0001 g, a stepper motor for controlled application of the load at strain rates from 0.0004 to 0.4 mm/sec and a laser interferometer with 100 Å resolution for measurement of displacement or strain.

Loading is accomplished by the stepper motor attached to a silica impinging rod. This rod is positioned so that as it moves down it hits the center of a sample resting on a holder in a three-point bend configuration. The motor is interfaced to a computer.

In addition, mechanical testing is conducted on the stone cylinders used for the gravimetry experiments. These samples are also allowed to cure for two months. Both treated and untreated stone samples are tested.

RESULTS AND DISCUSSION

Manometry

The results of the vapor pressure measurements are found in Table I.

Table I. Vapor Pressures in mm Mercury

Methyltrimethoxysilane	31
1,2 Dimethyltetramethoxydisiloxane	7
5% B72/Methyltrimethoxysilane	31
10% B72/Methyltrimethoxysilane	31
30% B72/Methyltrimethoxysilane	29

As can be seen from the data only a 2 mm lowering is found for a 30% solution whereas the 5 and 10% solutions show no measureable reduction in vapor pressure of MTMOS. Therefore, from the point of view of controlling evaporative loss, no advantage is gained by adding B72 to MTMOS. The data indicate, however, that the MTMOS dimer - 1,2 dimethyltetramethoxysilane - has less than one-fourth the vapor pressure of the monomer. Therefore, evaporative loss is reduced at the dimer stage of the reaction.

Viscometry

The results of the viscosity measurements are found in Table II.

Table II. Viscosity in Centistokes at 25.0°C

Methyltrimethoxysilane	0.3750
1,2 Dimethyltetramethoxydisiloxane	0.9554
5% B72/Methyltrimethoxysilane	1.851
10% B72/Methyltrimethoxysilane	4.625
30% B72/Methyltrimethoxysilane	74.82

One of the reasons for the interest in alkoxysilanes for stone consolidants can easily been seen by examining Table II: the viscosity of MTMOS is 0.3750 cSt and the viscosity of the dimer is only slightly greater than water at 25°C. These low values mean that flow through small capillaries is not restricted by the viscosity of the liquid. Even the 5% solution is still low in viscosity while the 10% B72/MTMOS solution is noticeably viscous; the 30% solution would be impractical as a stone consolidant.

Gravimetry

The results of the gravimetry experiments employing neat MTMOS and B72/MTMOS *without* stone samples are shown graphically in Figure 1. The graph plots the mass of retained material *minus the mass of acrylic resin present in the original solution* versus time. It is assumed that no acrylic resin evaporates. Through this graph one can readily see the effect of the acrylic resin on the mass of the reacting MTMOS system.

As might have been guessed from the vapor pressure data for the B72/MTMOS solutions, the presence of B72 makes little difference in the weight loss profile in the early stages of reaction; the graphs for neat MTMOS and the 5 and 10% solutions are virtually identical for the first ten days. At longer times that the B72 appears to have a greater attraction for the MTMOS-derived oligomers that are formed. Ultimately, a 2% difference in mass retention is noted for the 5% solution and a 4% difference for the 10%

solution. The 30% solution exhibits a 12% increase in mass retention. The effect is approximately linear - for every 5% of B72 a 2% increase in mass retention is achieved.
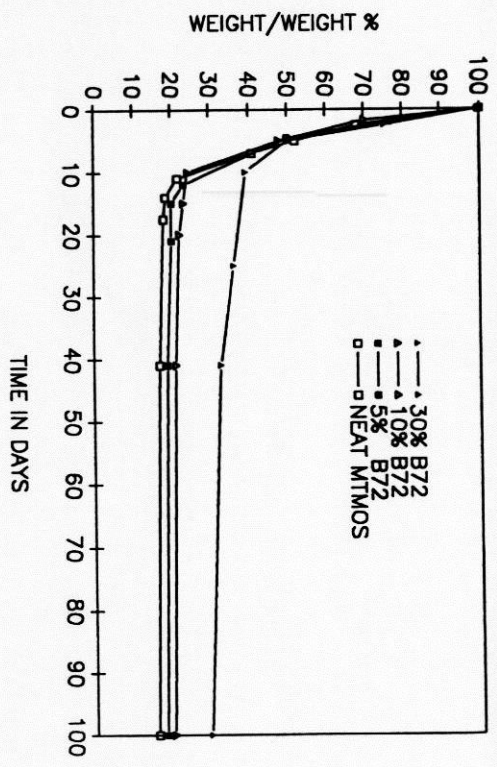

Figure 1
Gravimetry for B72/MTMOS Mixtures

(Legend: 30% B72, 10% B72, 5% B72, NEAT MTMOS; axes: WEIGHT/WEIGHT %, TIME IN DAYS)

The results of the gravimetry experiments employing consolidants with stone samples are presented in Figures 2-6 and Table III. Figure 2 for neat MTMOS demonstrates that the rate of loss of MTMOS in limestone far exceeds that in sandstone. Also, Table III demonstrates that the residue both in actual mass and percent is greater in sandstone (0.02 g/25% of the original mass of liquid imbibed by the stone) than in limestone (0.005 g/3.3%).

The rates of loss for the 1% B72/MTMOS solution Figure 3 are similar to the neat MTMOS samples although the mass return was 0.04 g/36.6% for sandstone while for limestone the mass return is 0.002 g/2.0%. This indicates that the B72 discourages the loss of MTMOS in sandstone while in limestone little difference is noted. For the 10% B72/MTMOS solution in limestone the mass return is 0.123 g/60% - again the B72 causes entrapment of MTMOS and then apparently allows for in situ reaction in sandstone; the limestone retains 0.026 g/14.5%. For the 10% B72/toluene solution in Figure 5 and Table III the mass return drops to its lowest values for sandstone - 0.0178 g/17.7% - while the values are similar to the 10% B72/MTMOS case - 0.021 g/13.7% - for limestone. Table III also demonstrates that in all but the 10% B72/MTMOS example the limestone imbibes more liquid than the sandstone and ultimately gives up more of that

Figure 2
Gravimetry for Neat MTMOS-Treated Limestone and Sandstone

(Legend: SANDSTONE, LIMESTONE; axes: WEIGHT/WEIGHT %, TIME IN min)

liquid to evaporation. Finally, it has been postulated that in limestone an initial treatment with MTMOS may have a priming effect which would encourage added deposition of MTMOS-derived solids in a second treatment. Figure 6 indicates that no such priming occurs for limestone and that a second treatment on sandstone produces a similar mass return to the first treatment (22.4% vs. 25%).

Table III. Mass Return for Consolidated Stone Samples

Consolidant		Retained Grams/Percent After 4 Days
MTMOS	Sandstone	0.02/25
	Limestone	0.005/3.3
1% B72/MTMOS	Sandstone	0.04/36
	Limestone	0.0028/2.0
10% B72/MTMOS	Sandstone	0.123/60
	Limestone	0.026/14.5
10% B72/Toluene	Sandstone	0.0178/18.5
	Limestone	0.021/13.7

Figure 3
Gravimetry for 1% B72/MTMOS-Treated Limestone and Sandstone

WEIGHT/WEIGHT %
TIME IN min
□ SANDSTONE
■ LIMESTONE
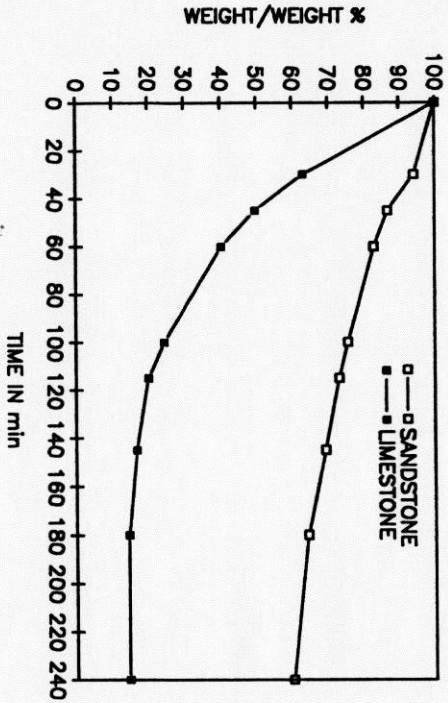
Figure 4
Gravimetry for 10% B72/MTMOS-Treated Limestone and Sandstone

WEIGHT/WEIGHT %
TIME IN min
□ SANDSTONE
■ LIMESTONE
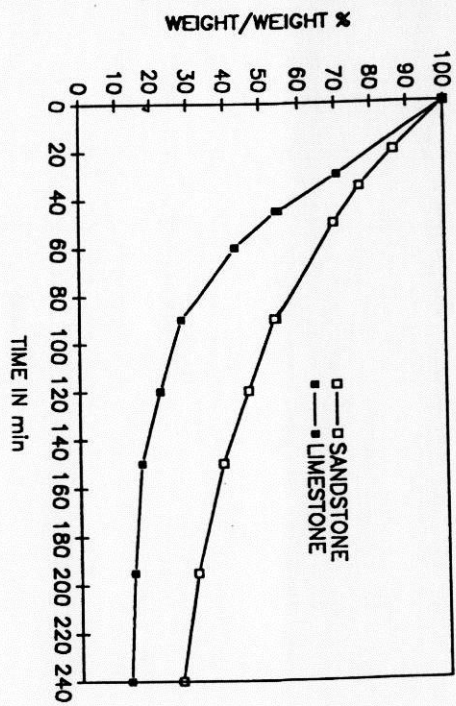
Figure 5
Gravimetry for 10% B72/Toluene-Treated Limestone and Sandstone

WEIGHT/WEIGHT %
TIME IN min
□ SANDSTONE
■ LIMESTONE
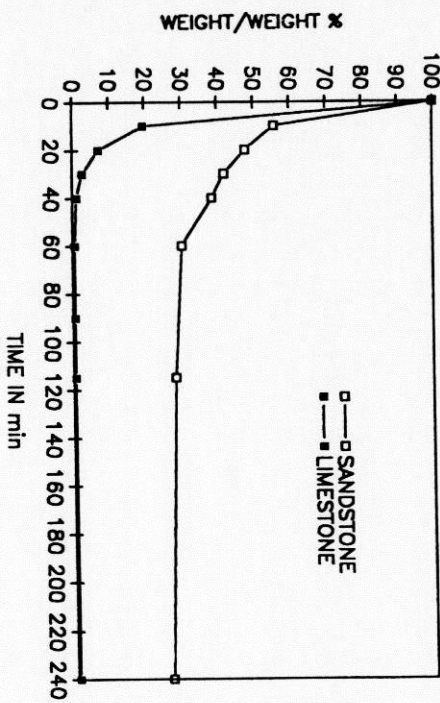
Figure 6
Gravimetry for Second Application of Neat MTMOS to Limestone and Sandstone

WEIGHT/WEIGHT %
TIME IN min
□ SANDSTONE
■ LIMESTONE

Silicon NMR Spectroscopy

Silicon NMR employs a "Q" identification terminology: Q_0 represents silicon atoms attached to no other silicon atoms through oxygen; Q_1 represents silicon atoms attached to one silicon atom through oxygen - i.e. an end group Si-O-Si; Q_2 are two silicon linkages - i.e. linear or monocyclic polymer groups; Q_3 are three linkages; and Q_4 are four linkages. For MTMOS the possibilities range from Q_0 to Q_3; no Q_4 can be present because the methyl group directly attached to silicon does not react.

The silicon NMR spectra for the liquid state experiments employing neat MTMOS and 10% B72/MTMOS solutions are shown in Figures 7 and 8. Figure 7 shows the solutions after 160 hours reaction time: the top spectrum is the B72/MTMOS mixture and the bottom spectrum is neat MTMOS. In the B72/MTMOS system only monomer (Q_0) is present which is represented by the large peak at -39.8 ppm. For neat MTMOS only 2% of the spectrum is represented by monomer while 56% is in the form of end groups (i.e. Q_1 from -46 to -49 ppm), 34% in linear groups (i.e. Q_2 from -56 to -59 ppm), and 8% in crosslinking groups (i.e. Q_3 at -67 ppm).

Q_0

10% B72/MTMOS
160 hours

Q_0

Q_1

Q_2

Q_3

neat MTMOS
160 hours

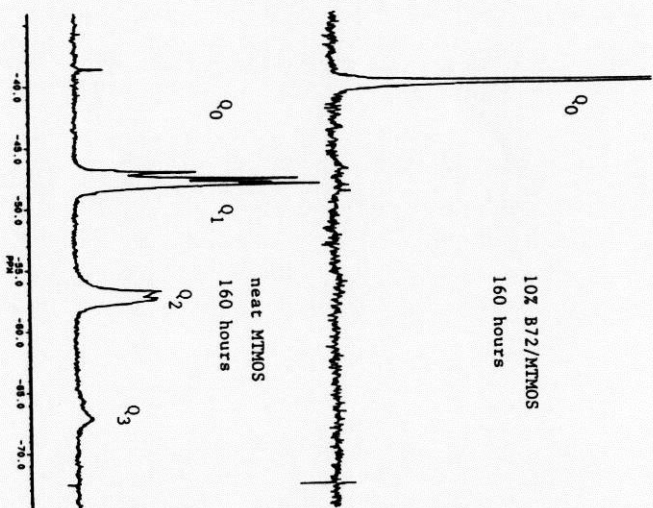-40.0   -45.0   -50.0   -55.0 PPM -60.0   -65.0   -70.0

Figure 7
Silicon NMR Spectra for 10% B72/MTMOS (top) and Neat MTMOS (bottom): 160 hours

After 236 hours (Figure 8) 76% of the B72/MTMOS mixture (top spectrum) is still in the form of monomer and 9% is end groups, 11% linear groups, and 4% crosslinking groups. With neat MTMOS (bottom spectrum) no monomer remains and 46% of the sample is end groups, 42% is linear groups, and 12% is crosslinking groups.

Q_0

10% B72/MTMOS
236 hours

Q_1

Q_2

Q_1

Q_2

Q_3

neat MTMOS
236 hours

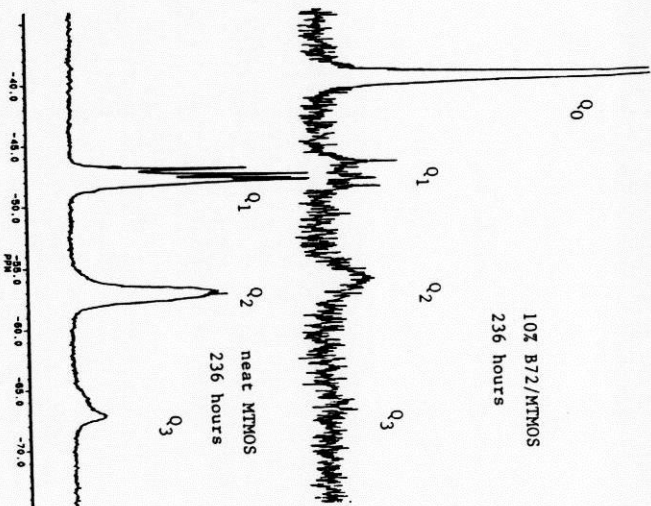-40.0   -45.0   -50.0   -55.0 PPM -60.0   -65.0   -70.0

Figure 8
Silicon NMR Spectra of 10% B72/MTMOS (top) and Neat MTMOS (bottom): 236 hours

It can be seen from these spectra that the hydrolysis and condensation of MTMOS have been dramatically slowed by the addition of B72. The slowing of the reaction is probably due to the fact that water cannot as easily hydrolyze the MTMOS and its oligomers due to the added hydrophobicity imparted to the solution by B72.

Figure 9 shows the results for two solids samples produced from neat MTMOS and from a 10% B72/MTMOS solution reacted at laboratory conditions (60% RH, 20°C) and examined by silicon NMR with magic angle spinning. No monomer is present in either sample; some Q_1 must be present but their number is too few to be detected. (No Q_1 implies no linear polymers or only cyclic or fully crosslinked polymers.)
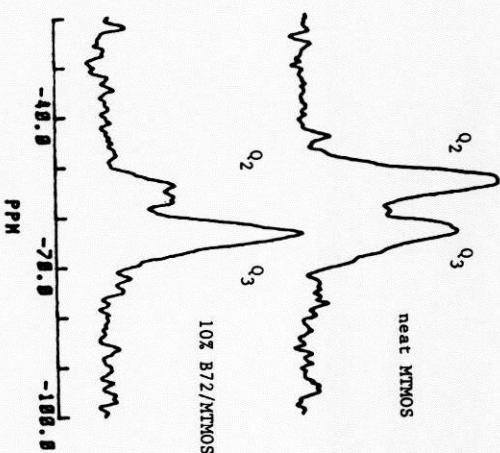
Figure 9

Silicon NMR Spectra of Neat MTMOS (top) and 10% B72/MTMOS (bottom) Solid State with Magic Angle Spinning: 3 Months

neat MTMOS — Q_2, Q_3
10% B72/MTMOS — Q_2, Q_3

PPM: -40.0, -70.0, -100.0

The distribution between Q_2 and Q_3 for neat MTMOS is 57 to 43% - i.e. there are more linear and cyclic silicon atoms than tri-condensed silicon atoms. Surprisingly for the 10% B72/MTMOS sample there is a 3:1 ratio of Q_3 to Q_2 silicons indicating more condensation in the B72 sample than in the neat sample. Once in the solid state the B72 appears to promote condensation reactions.

Head Space Analyses - Gas Chromatography (HSA-GC)

As a basis for HSA-GC of neat MTMOS and B72/MTMOS mixtures a 1:1:1 molar mixture of water, MTMOS, and MeOH was run on the Hewlett-Packard 5890 GC and the peaks identified on a Hewlett-Packard 5970 B Mass Selective Detector. The results of this run demonstrated that a collection of species from monomer through cyclic hexamer are present in the mixture. To see which of these species might appear in head space analysis an identical mixture was run by HSA-GC at 40°C. This is approximately the lowest possible temperature of analysis for this instrument and is close enough to ambient to suggest which species in a mixture might be evaporating as it reacts in an open container. The mixture exhibited only methanol, monomer (with smaller amounts of the monomer silanol - $CH_3Si(OMe)_2OH$) and the dimer in the head space. Therefore, for the mass profiles in the gravimetry section evaporative loss can only be accounted for by monomer, monomer silanol, and dimer.

Table IV. contains the data for HSA-GC for each of the solutions: 0, 3, 5, 10, 30% B72/MTMOS. The table shows the area of the volatile components in the chromatogram and the percentage of these areas accounted for by methanol, monomer, and dimer. In the stages of the reaction of MTMOS before gelation the 3 and 5% solutions are not very different from

the neat MTMOS. After gelation more monomer appears to be present in the head space of the 3 and 5% solutions which signifies that the B72 is serving to slow the reaction. At the 10 and 30% levels it is quite clear that B72 slows hydrolysis by the small quantities of MeOH in the head space. The overall area of head space vapor in the 10 and 30% is three to ten times higher than the neat. Again, this indicates that the reaction is much slowed by the presence of B72.

Table IV. Head Space Analysis - Gas Chromatography

Days	Neat MTMOS %MeOH	Monomer	Dimer	Area*	3% B72/MTMOS %MeOH	Monomer	Dimer	Area
0	0.64	99.36	-	4.02	0.66	99.34	-	4.41
1	9.21	90.79	-	4.35	10.93	89.07	-	4.47
2	17.10	82.90	-	4.61	16.37	83.63	-	4.70
4	19.49	80.59	-	3.62	17.76	82.24	-	3.87
6	14.29	85.79	-	3.48	10.06	89.94	-	3.96
8	5.99	94.01	-	3.24	3.66	96.34	-	3.65
10	5.78	93.02	1.18	2.72	5.90	94.10	-	2.03
...gelation...								
14	37.09	46.88	16.03	0.33	37.62	57.18	5.20	0.27
26	48.94	51.06	-	0.05	84.31	11.70	3.99	0.03

Day	5% B72/MTMOS %MeOH	Monomer	Dimer	Area	10% B72/MTMOS %MeOH	Monomer	Dimer	Area
0	0.87	99.13	-	4.52	1.59	98.41	-	4.51
1	11.74	88.26	-	4.48	1.02	98.98	-	4.63
2	19.64	80.36	-	4.61	2.04	97.96	-	4.33
4	17.77	82.23	-	3.93	3.35	96.65	-	3.81
6	11.18	88.82	-	4.17	3.31	96.69	-	4.61
8	3.92	96.08	-	3.57	3.98	96.02	-	4.59
10	5.80	94.20	-	2.36	6.66	93.34	-	3.43
...gelation...								
14	25.47	71.17	2.81	0.40	23.26	76.64	-	0.85
26	79.20	19.06	1.74	0.05	82.79	17.21	-	0.16

Day	30% B72/MTMOS %MeOH	Monomer	Dimer	Area
0	2.35	97.65	-	5.32
1	2.20	97.80	-	4.30
2	3.05	96.95	-	4.30
4	4.48	95.02	-	3.68
6	4.63	94.61	-	4.24
8	5.39	92.52	-	3.75
10	13.48	86.52	-	2.13
...gelation...				
14	24.71	75.29	-	1.22
26	58.88	41.22	-	0.42

*each area should be multiplied by one million for actual count

Scanning Electron Microscopy

Figure 10 shows the SEM photomicrograph of the material derived from 1% B72/MTMOS. The sample has few structural features. The 10% B72/MTMOS in Figure 11 exhibits a very different texture; it shows 5-20 micron structures. These structures are MTMOS-derived polymers as confirmed by the silicon dot map in Figure 12 in which the distribution of

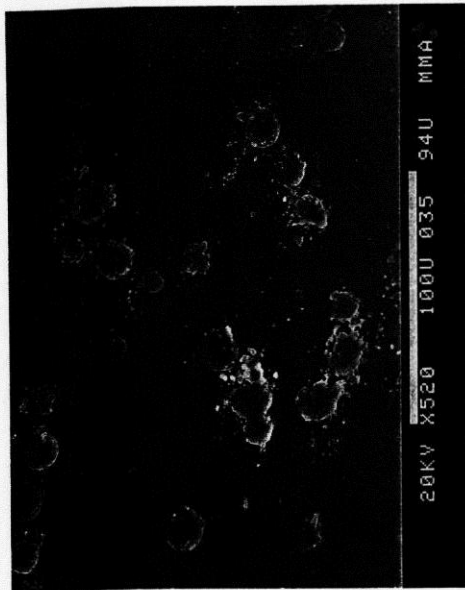silicon is clearly linked to the nearly spherical structures.

Figure 10
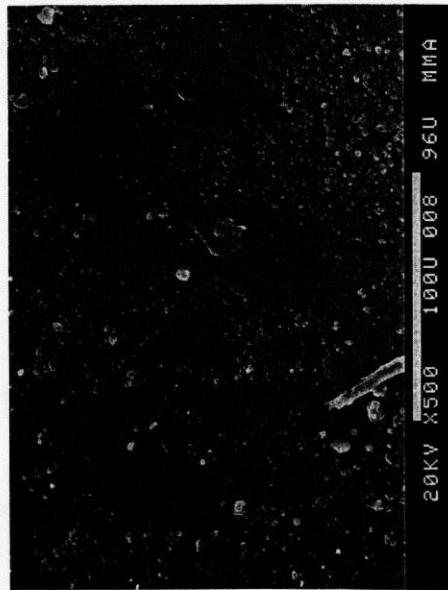SEM Photograph of 1% B72/MTMOS:
3 Months

Figure 11
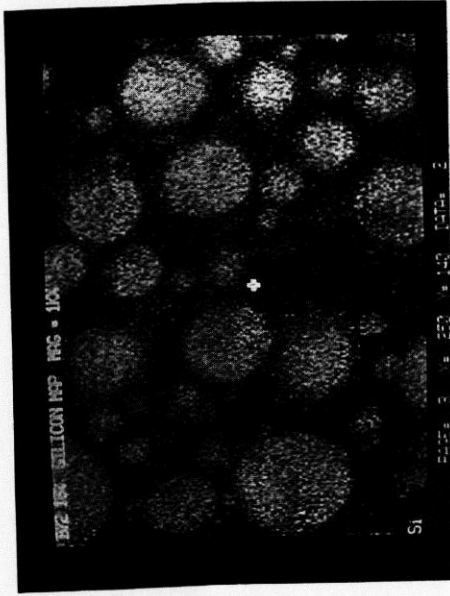SEM Photograph of 10% B72/MTMOS:
3 Months

Figure 12
SEM Dot Mapping for Silicon (Light Areas) in 10% B72/MTMOS:
3 Months

Mechanical Testing

The results of the mechanical testing of the MTMOS and B72/MTMOS-derived gels are found in Table V.

Table V. Modulus of Rupture (MOR) in MPa

Sample	MOR
Neat MTMOS	58
1% B72/MTMOS	20
4% B72/MTMOS	12
5% B72/MTMOS	10
10% B72/MTMOS	14

The samples derived from neat MTMOS are the strongest and the addition of B72 weakens the solid dramatically. A good composite material should show enhanced mechanical properties such as MOR and these kinds of composites have excellent bonding between filler and polymer. In our case the filler is MTMOS-derived polymer spheres and the polymer matrix is B72. No coupling exists and no improved mechanical properties result from the B72/MTMOS interaction.

The results of the mechanical testing of the consolidated stone samples are presented in Figure 13. The untreated sandstone has a larger modulus of rupture (MOR) than the untreated limestone. The effect of neat MTMOS on the sandstone is substantial - a 74% increase in MOR - while in limestone it is only 11.7%. The addition of the 1% B72 w/v provides a 124% increase in MOR for sandstone while in limestone the increase is virtually

CONCLUSIONS

The experiments reveal several interesting features for neat MTMOS and B72/MTMOS mixtures which are important to their use as stone consolidants:

1. Adding B72 to MTMOS does not lower the vapor pressure of MTMOS enough to reduce evaporative loss.

2. A 5% B72/MTMOS w/v mixture has a viscosity of 1.8 cSt. Therefore, mixtures of 5% or less can safely be used as consolidants for most stones.

3. B72/MTMOS-derived solids are NOT good composite materials. In fact, the rupture moduli of these gels are much lower than for neat MTMOS-derived gels.

4. Limestones promote a faster and more complete evaporation of MTMOS than sandstones. This difference is even greater when B72 is present.

5. Mixtures of B72 and toluene consolidate the limestone samples used in these experiments as well as or better than B72/MTMOS mixtures.

6. B72 slows the hydrolysis and condensation reactions of MTMOS in the liquid state. Once a gel is formed B72 appears to promote condensation.

7. MTMOS is a much better consolidant for sandstone than it is for limestone.

An important question arises from the data for the consolidation of limestone, "Why add MTMOS to B72 or alternatively why not use other solvents for B72?" B72 in toluene is clearly as good a consolidant for the Salem limestone as B72 in MTMOS. The importance of evaporation rate and solubility parameters of a solvent for resin containing systems is well known and MTMOS and its oligomers may offer a good transport system for B72 - i.e. the combination of viscosity and vapor pressure may be ideal. However, solvents such as toluene with a similar viscosity and vapor pressure are known. Furthermore, some clay-bearing limestones are not suitable to be consolidated with MTMOS due to adverse reactions between the clay component and the MTMOS. [10] These adverse reactions could be avoided by replacing MTMOS with another solvent.

As can be inferred from the clay-MTMOS interaction cited above, a stone's mineralogy is important to its ability to be consolidated. The calcite which comprises the limestone used in our experiments is not well consolidated by MTMOS whereas the quartz and felspar-bearing sandstone is well consolidated by MTMOS. It has long been suggested that alkoxysilanes should be good consolidants for sandstones because of the chemical similarity between silicate minerals and silicate polymers. In addition, surface condensation reactions between silanols and hydroxylated silicate mineral surfaces have been proposed but not demonstrated. Given the greater mass return and the improved mechanical properties noted with sandstones it must be concluded that some type of surface effects - catalysis, co-condensation, or other - are operative. The exact nature and extent of these effects are however not known.

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identical to neat MTMOS (11.6%). The 10% B72/MTMOS solution and the epoxy treated sandstone were beyond the testing capability of the instrument; each provided greater than a 143% increase in MOR. For limestone the 10% B72/MTMOS solution brought about a 74% increase while the epoxy increased the MOR by 192%. The 10% B72/toluene gave a nearly 100% increase for sandstone and a 79% increase for limestone - the best for limestone except for the epoxy resin.
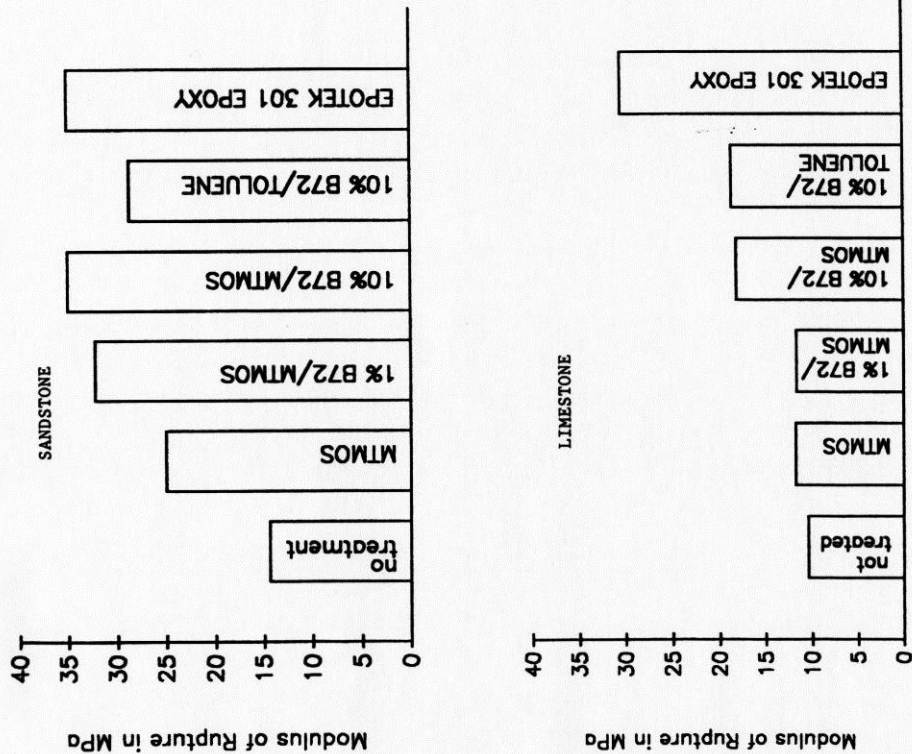

Figure 13

MORs for Sandstone (top) and Limestone (bottom)

PROTECTIVE COATINGS FOR MEDIEVAL STAINED GLASSES

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ABSTRACT

The corrosion protective effect of the surface modification of corrosion sensitive glass surfaces and of ORMOCER (= organically modified ceramic) coatings is investigated. The surface modification provides a modest protection, perhaps useful for additional protection in combination with external glazing. The advantage is the "invisability" of the modification due to the thickness of several molecular layers. An effective protection can be obtained by a diffusion barrier pigmented ORMOCER coatings. First outdoor results on medieval glasses are very hopeful, but long period experience is necessary for wider application.

INTRODUCTION

The corrosion of glass under the influence of H_2O is a well known phenomenon. An ion exchange process takes place between a proton and an alkali ion, as a rule, according to (1).

$$\equiv Si\text{-}O^- \ Na^+ + H^+ \rightarrow + NaOH \rightarrow \equiv Si\text{-}OH + Na^+ \qquad (1)$$

The sodium ion in an aqueous environment forms NaOH, which can lead to a network dissolution of the silica matrix (2).

$$\equiv Si\text{-}O\text{-}Si\equiv \ + NaOH \rightarrow \equiv Si\text{-}ONa + HO\text{-}Si\equiv \qquad (2)$$
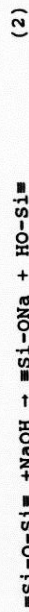
In presence of CO_2, sodium carbonate will be formed. Potassium containing glasses basically react in the same way. Whereas in hydrolytic stable glasses, e.g., modern calcium silicate glasses the ion exchange is mainly restricted to the alkaline ions [1, 2], in glasses with high potassium and high calcium contents calcium ions are exchanged, too, as shown in [3] by ESCA measurements. In these glasses with about 18 mole-% of K_2O as well as of CaO, in a corrosion experiment in humid air, K_2O as well as Ca is leached out. As shown in this investigation, too, the leaching out of Ca is enhanced in the presence of SO_2. This can be explained by the formation of syngenite, a potassium-calcium sulfate, which is almost unsoluble in water. This leads to a drastic decrease of the Ca^{2+} ion concentration in the diffusion path and to an increased driving force for the process in equation (3).

ACKNOWLEDGEMENTS

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