Silicone/Amine Resin Hybrid Materials as Abrasion Resistant Coatings

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Hydroxyl organofunctional silicone solutions were prepared by acid-catalyzed hydrolysis and condensation of tetraalkoxysilanes, alkoxysilane modified organic compounds, and hydroxyl functional trialkoxysilanes or epoxy functional silanes. These silicone solutions were mixed with methoxylated urea formaldehyde and methoxylated melamine formaldehyde to form silicone/amine resin hybrids and applied on bisphenol A polycarbonate substrates as coatings. After thermal curing at 100–125 °C for 2–3 h, several optically transparent hard coatings with excellent abrasion resistance were obtained.

Introduction

Sol–gel processing is a chemical technology based on hydrolysis and condensation of metal or semimetal alkoxides, chlorides, or nitrates, and it has been used to prepare powders, fibers, films, or porous solids of special glasses or ceramics.[1] One of the most attractive features of this technology is its low processing temperature, which allows organic compounds to be incorporated into inorganic structures without decomposition. For this reason, this technology has played an indispensable role in preparing novel inorganic–organic hybrid materials.[2,3]

Silicone hardcoatings are formulated as water–alcohol born systems by sol–gel reactions of organoalkoxysilanes.[4–7] If metal alkoxides and/or alkoxysilane modified polymer or organic compounds are incorporated, the resulting materials are often referred to as inorganic–organic hybrids.[8–13] Silicone or inorganic–organic hybrid coating compositions may be applied by traditional coating processes such as dip coating, spin coating, flow coating, etc. After vulcanizing at 80–150 °C, coatings with abrasion resistance significantly higher than organic polymers and many metals or alloys can

be obtained. Therefore, these coatings can be used to control the wear of optical plastics such as bisphenol A polycarbonate (Bis-A PC) and poly(methyl methacrylate), which are often used to replace inorganic glass windows or to make optical devices such as lenses.

Silicone hardcoatings and many other inorganic–organic hybrid coatings are mainly hardened by thermally induced SiOH–SiOH and SiOH–SiOR condensations, which generate highly cross-linked siloxane networks and water/alcohol byproducts. In inorganic–organic hybrids containing metal or semimetal salts (nitrates, alkoxides, etc.), reactions such as MOH–MOH and SiOH–MOH condensations (M represents the metal or semimetal atom) also occur. Other mechanisms may also exist if the system contains an organofunctional silane and/or other reactive organic compounds. With 3-methacryloxypropyltrimethoxysilane (MPTMS), free radical polymerization of the methacryloxy groups can be introduced by adding a free radical initiator.[9] With 3-glycidoxypropyltrimethoxysilane (GPTMS), another frequently used organofunctional silane, the epoxy groups can either undergo ring-opening polymerization[10] or react with a polyamine or polycarboxylic acid.[11] The sol–gel condensations, in conjunction with these organic reactions, often lead to materials with novel hybrid network structures. Silicone and other inorganic–organic hybrid systems are often generated by hydrolyzing alkoxysilanes and other related compounds in water-rich alcoholic solutions so that the alkoxysilane groups can be sufficiently hydrolyzed. To form a homogeneous hybrid network, the organic components incorporated should be soluble in the water–alcohol solution and an appropriate organofunctional alkoxysilane is a necessity to bridge the siloxane network and the organic species.

Amine resins such as urea formaldehyde (UF) and melamine formaldehyde (MF) resins are among the earliest and cheapest synthetic plastics and have been widely used as adhesives, laminating resins, molding compounds, coatings, and texture finishes.[14–17] These resins can self-condense and react with vehicle resins (the primary film formers) of celluloses, alkyds, acrylics,

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(1) Mackenzie, J. D. In *Ultrastructure Processing of Ceramics, Glass, and Composites*; Hench, L. L., Ulrich, D. R., Eds.; John Wiley & Sons: New York, 1984; pp 15–26.

(2) Schmidt, H.; Seiferling, B.; Philipp, G.; Deichmann, K. In *Ultrastructure Processing of Advanced Ceramics*; Mackenzie, J. D., Ulrich, D. R., Eds.; John Wiley & Sons: New York, 1988; pp 651–660.

(3) Wen, J.; Wilkes, G. L. *Chem. Mater.* **1996**, *8*, 1667–1681.

(4) Clark, H. A. U.S. Patent 3,986,997, 1976.

(5) Clark, H. A. U.S. Patent 4,027,073, 1977.

(6) Ubersax, R. W. U.S. Patent 4,177,315, 1979.

(7) Frye, R. B. U.S. Patent 4,277,287, 1981.

(8) Wang, B.; Wilkes, G. L. U.S. Patent 5,316,855, 1994.

(9) Kasemann, R.; Schmidt H. *New J. Chem.* **1994**, *18*, 1117–1123.

(10) Kasemann, R.; Schmidt, H.; Arpac, E.; Gerhard, V.; Geiter, E.; Wagner, G. U.S. Patent 6,008,285, 1999.

(11) Havey, J. L.; Ho, T. H.; Guest, A. M.; Terry, K. W.; Sollberger, M. S. U.S. Patent 6,001,163, 1999.

(12) Wilkes, G. L.; Wen, J.; Jordens, K. U.S. Patent 6,072,018, 2000.

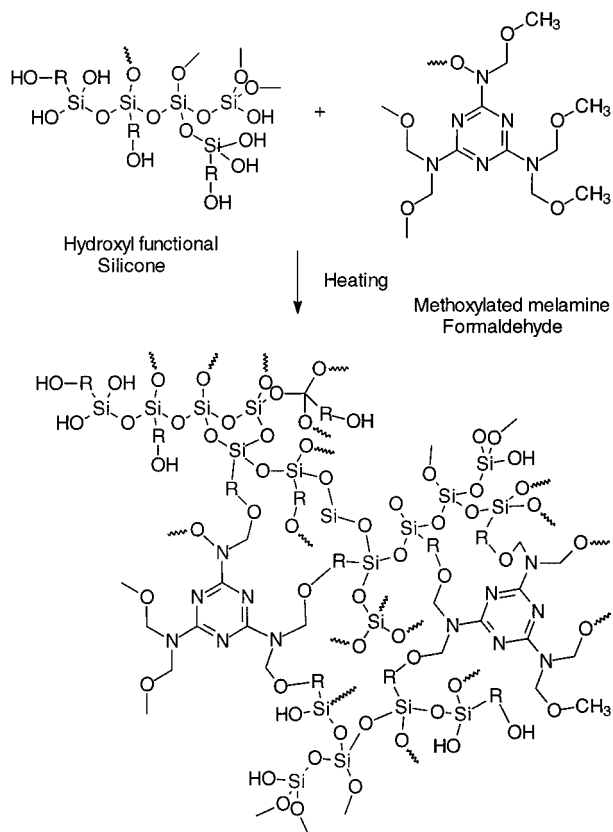(13) Li, C.; Jordens, K.; Wilkes, G. L. *Wear*, **2000**, *242* (1–2), 152–139.

Figure 1. Preparation of silicone/melamine formaldehyde hybrid materials.

Figure 2. Formation of hydroxyl functional alkoxysilanes.

Figure 3. Structure of tris(3-trimethoxysilylpropyl) isocyanurate.

polyesters, or epoxy, which contain hydroxyl, amido, ureido, or carboxyl groups. Nowadays, amine resins are often provided in alkoxylated low molecular weight forms or monomeric forms to increase the compatibility with organic polymers, to lower the viscosity, to hinder self-condensation, and to minimize the free formaldehyde concentration. Methoxysilylated UF and methoxysilylated MF resins are soluble in water and alcohol and widely used to formulate high solid concentration, water-born thermoset coatings or "baked enamels" for appliances and automobiles. Considering their high reactivity and compatibility with water and alcohol, we believe that amine resins can be incorporated into hydroxyl, urea, amido, or carboxyl functional silicone resins to form thermally curable hybrid coatings that can offer high optical transparency as well as better abrasion resistance than existing organic coatings (Figure 1).

Organofunctional silicones can be prepared by hydrolysis and condensation of alkoxysilane such as tetraethoxysilane with a related organofunctional alkoxysilane. However, hydroxyl functional alkoxysilanes such as 3-hydroxypropyltriethoxysilane are not commercially available because these silanes undergo intermolecular transesterification and polymerize. Stable

hydroxyl functional alkoxysilane can only exist in alcoholic solutions. These silanes can be obtained by hydrolyzing epoxyfunctional trialkoxysilanes such as GPTMS and 2-(3,4-epoxycyclohexyl)ethyltrimethoxysilane (ECHETMS) (Figure 2 A,B). Alternatively, they can also be prepared by reactions of 3-isocyanatopropyltriethoxysilane (ICPTES) with polyols or amino alcohols. Figure 2C shows the preparation of N,N'-bis(2-hydroxyethyl)ureidopropyltriethoxysilane (BHEUPTES). The objectives of this paper are to prepare hybrid coatings of hydroxyl functional silicones with UF or MF resins and to evaluate their abrasion resistance.

Experimental Section

Materials. TEOS (98%), GPTMS (98%), ICPTES (95%), diethanolamine (99%), and *p*-toluenesulfonic acid monohydrate (p-TSA, 98.5%) were purchased from Aldrich Chemical and used as received. ECHETMS and tris(3-trimethoxysilylpropyl) isocyanurate (TTMSPIC) were purchased from Gelest Inc. and used as received. TTMSPIC was used to form tertiary silicone resins with TMOS (or TEOS) and BHEUPTES (or GPTMS), and its structure is shown in Figure 3.

BHEUPTES was prepared by adding ICPTES to a diethanolamine solution in ethanol. A 500 mL Erlenmeyer flask was charged with 21.0 g of diethanolamine and 76.5 g of ethanol. When this mixture was quickly stirred, 55.5 g of 3-ICPTES were added dropwise through a dropping funnel in about 30 min. The mixture was further stirred for another 12 h at room temperature, and the transparent solution was a 50 wt % solution of BHEUPTES in ethanol.

RESIMENE 730 is a high solids methoxylated melamine formaldehyde (88–92% solids in 2-propanol). RESIMENE U-975 is a high solids methoxylated urea formaldehyde (>96% solids). Both RESIMENE 730 and RESIMENE U-975 were kindly provided by Solutia Inc. as free samples.

Bis-A PC sheets (Lexan, 24" x 12" x ¹/₁₆') for Taber abrasion tests were purchased from McMaster Carr Co. They were cut into a square shape (4" x 4" x ¹/₁₆") and used as coating substrates to evaluate the abrasion resistance of the coating.

Coating Compositions. *TEOS/GPTMS/Amine Resins.* A 250-mL Erlenmeyer flask was charged with 30.0 g of TEOS, 10.0 g of GPTMS, 20.0 g of water, 20.0 g of ethanol, and 5.0 g

(14) Updegraff, I. H.; Moore, S. T.; Herbes, W. F.; Roth, P. B. In *Kirk-Othmer Encyclopedia of Chemical Technology*; Grayson, M., Eckroth, D., Mark, H., Othmer, D. F., Overberger, C. G., Seaborg, G. T., Eds.; John Wiley & Sons: New York, 1978; Vol. 2, pp 440–469.

(15) Paul, S. *Surface Coatings, Science and Technology*; John Wiley & Sons: New York, 1985; pp 167–199.

(16) Hill, W. L.; Lee, S.-B. *J. Coatings Technol.* **1999**, *71* (879), 127–134.

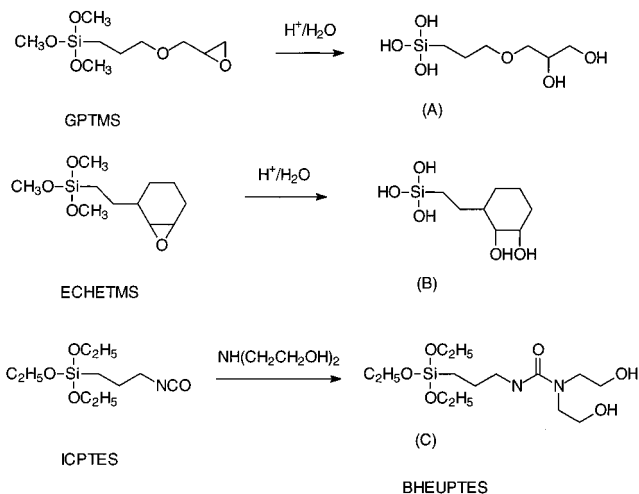(17) Diaz, I.; Jacquin, *J. Modern Paint and Coatings*, **1988**, *88* (7), 32–45.

of 0.5 M aqueous p-TSA solution. This mixture was hydrolyzed for 12 h at room temperature and the resulting transparent liquid was a TEOS/GPTMS silicone solution (GP). This silicone solution remained stable after aging at room temperature for two weeks, although it did show a slight increase in viscosity.

Five samples, 15 g each, were taken from a GP solution that was aged at room temperature for about 24 h. To the five samples were added 0.5, 1.0, and 2.0 g of RESIMENE 730 and 0.5 and 1.0 g of RESIMENE U-975, respectively. The five mixtures were labeled as GP/MF-A, GP/MF-B, GP/MF-C, GP/UF-A, and GP/UF-B, respectively, and stirred at room temperature for 3 h so that clear coating compositions were obtained. After aging at room temperature for ca. 24 h, the five compositions, along with the remaining GP solution (as a control), were used to prepare coatings on Bis-A PC substrates.

The GP/MF solutions were less stable than the GP solution, they often gelled in 5−7 days at room temperature. However, for the GP/UF solutions under the same condition, no gelation was observed in 2 weeks.

TEOS/ECHETMS/Amine Resins. Using ETHETMS instead of GPTMS in the above procedures, a TEOS/ECHETMS silicone solution was prepared. The stability of this silicone solution was similar to that of the TEOS/GPTMS silicone solution.

Five 15-g samples were taken from an EC solution that was aged at room temperature for about 24 h and mixed with the same amounts of RESIMENE 730 and RESIMENE U-975 as stated above, respectively. The five compositions were labeled as EC/MF-A, EC/MF-B, EC/MF-C, EC/UF-A, and EC/UF-B, respectively. After aging at room temperature for ca. 24 h, the five coating compositions, along with the remaining EC solution, were used for coating preparations.

The EC/amine resin solutions were more stable than their GP/amine counterparts. No gelation was observed when the EC/amine resin solutions were aged at room temperature for 2 weeks.

TMOS/TTMSPIC/BHEUPTMS/MF Resins. A 250-mL Erlenmeyer flask was charged with 5.0 g of TMOS, 5.0 g of TTMSPIC, 20.0 g of 50 wt % BHEUPTES, 10.0 g of ethanol, and 10.0 g of water. The mixture was hydrolyzed for 24 h using 2.0 g of 0.5 M aqueous p-TSA solution as a catalyst and a TMOS/TTMSPIC/BHEUPTMS tertiary silicone resin solution (T-BH) was obtained. The T-BH solution gelled at room temperature in about 2 weeks.

Three 15-g samples were taken from a T-BH solution that was aged at room temperature for 24 h and mixed with 0.5, 1.0, and 1.5 g RESIMENE 730, respectively. These mixtures were labeled as T-BH/MF-A, T-BH/MF-B, and T-BH/MF-C and stirred at room temperature until homogeneous solutions were obtained. After 24 h of aging at room temperature, the three silicone/MF resin compositions, along with the remaining T-BH solution, were used to prepare coatings for abrasion resistance evaluation. The T-BH/MF resin solutions gelled at room temperature in 3−5 days.

A slightly different silicone resin solution (T-BH′) was prepared by using 5.0 g of TMOS, 5.0 g of TTMSPIC, and 10.0 g of 50 wt % BHEUPTES. This silicone solution was prepared by the same procedure as stated above except that only 10.0 g of 50 wt % BHEUPTES was used here. By doing this, the ratio of TMOS:TTMSPIC:BHEUPTES was changed to 5:5:5 from 5:5:10 for the previous silicone solution. With a low concentration of BHEUPTES, the gelling time of the T-BH′ solution at room temperature was 3−4 days.

Two samples, 14.0 g each, were taken from a T-BH′ solution that was aged for 24 h and mixed with 0.5 and 1.0 g of RESIMENE 730 and the mixtures were labeled as T-BH′/MF-A and T-BH′/MF-B. Similarly, these two samples, along with the remaining T-BH′ solution, were used to prepare coatings for abrasion resistance evaluation. The gelling time of the T-BH′/MF resin solutions at room temperature was 2−3 days.

TEOS/TTMSPIC/GPTMS/MF Resins. A 500-mL Erlenmeyer flask was charged with 20.0 g of GPTMS, 30.0 g of water, and 10.0 g of 0.5 M p-TSA. The mixture was stirred at room temperature for about 18 h to hydrolyze the alkoxysilane and

epoxy groups. TTMPIC, 10.0 g, and TEOS, 28.0 g, were added into the hydrolyzed GPTMS. The combined mixture was stirred at room temperature to hydrolyze for another 24 h and a TEOS/TTMSPC/GPTMS tertiary silicone solution (T-GP) was obtained. No gelation was observed when the T-GP solution was aged at room temperature for about 2 weeks.

Three samples, 15.0 g each, were taken from a GP solution that was aged at room temperature for 24 h, diluted with 3.0 g of ethanol, and then mixed with 0.23, 0.446, and 1.00 g of RESIMENE 730, respectively. The three mixtures were labeled as T-GP/MF-A, T-GP/MF-B, and T-GP/MF-C. After 24 h of stirring at room temperature, the three mixtures, along with the remaining T-GP solution (as a control), were used to prepare coatings for abrasion resistance evaluation. The gelling time of the T-BH′/MF resin solutions at room temperature was 3−5 days.

Surface Treatment and Coating Preparation. To improve the adhesion of the silicone/amine resin hybrid coating to the Bis-A PC substrates, a 5 wt % 3-aminopropylmethyldiethoxysilane solution in ethanol was first applied on the substrates (4" x 4" x $^1/_{16}$") by spin coating using a spin-off rate of 600−800 rpm. Then the treated substrates were immediately placed in a forced convection air oven and dried at 100 °C for 20 min.

The silicone/amine resin hybrid solutions or silicone solutions alone (as controls) were spin coated on the pretreated Bis-A PC substrates using a spin-on rate of 500 rpm and a spin-off rate of 800 rpm. After drying at room temperature for about 30 min, the coated substrates were placed in a forced convection air oven and cured at 100 °C for 3 h or 125 °C for 2 h. After curing, 3−5-μm-thick coatings with good adhesion to the substrate were obtained. These coatings were normally crack-free and highly transparent. However, if the amine resin concentration was more than 25 wt % by the estimated total resin solids (TRS), coatings were often slightly hazy (∼2% haze).

Test Methods. A Taber Abrasion Tester from the Tabor Industries, Inc., was used to estimate the abrasion resistance of the silicone/amine formaldehyde hybrid coatings according to ASTM D 4060. A pair of CS10 wheels, with a 500-g load per wheel, was used in the Taber abrasion test. The abrasion resistance of the coating was graded using the difference of haze between the wear track and unabraded regions after 500 cycles of abrasion. The haze measurement was conducted according to ASTM D 1044 and ASTM D 1003. An aperture ($^5/_{16}$" in diameter) was used to select circular regions for the haze measurement. The haze value of the wear track and unabraded region was given as the average for five randomly selected locations and the difference between these two average values was used as an index of abrasion resistance of the coating.

Results and Discussions

The structures of silicones resins prepared by sol−gel reactions depends on the concentration and relative reactivity of all alkoxysilane species, the pH, the nature of the solvent, etc. Silicone solutions formed in acidic media are generally lightly cross-linked cluster sols, while those formed in basic media are generally heavily cross-linked particulate sols.[18a] Unless stabilized sterically or electrostatically, silicone sols undergo gradual SiOH−SiOH or SiOH−SiOR condensations and eventually become gels. Gels obtained from less cross-linked silicones sols often have lower porosity than those obtained from heavily cross-linked particulate sols,[18b] so acid-catalyzed silicone sols should be more suitable for coating applications. The presence of bulky organo-

(18) Brinker, C. J.; Scherer, G. W. *Sol−Gel Science: The Physics and Chemistry of Sol−Gel Processing*; Academy Press: Boston, MA, 1990, (a) pp 213-215, (b) pp 802−819.
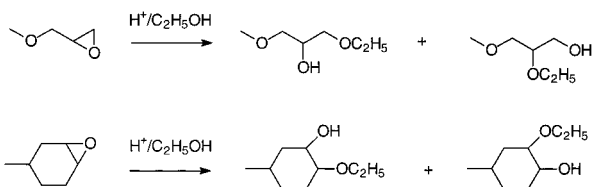
Figure 4. Alcoholysis of epoxy groups in GPTMS and ECHETMS.

functional groups usually lowers the cross-link density of the silicone clusters and hence helps reduce porosity.

When hydrolyzing in aqueous solution, a glycidoxy group yields a primary hydroxyl group and a secondary hydroxyl group. For the cyclic epoxy group in ECHET-MS, however, two secondary hydroxyl groups are generated. In water–alcohol media, the epoxy groups also undergo alcoholysis (Figure 4), so the yield of the hydroxyl groups should be slightly reduced.

In water–alcohol media in which transesterification is limited, the presence of bulky hydroxyl functional organic groups significantly increases the stability of the silicone resin solutions by steric stabilization. Hydroxyl functional silicone solutions prepared by cohydrolyzing GPTMS (or ECHETMS) with TEOS or TMOS using an acid catalyst such as p-TSA were stable for 2 weeks or longer. Silicones derived from BHEUPTES, however, were only stable for 3 days to 2 weeks, depending on the compositions. The relatively poor stability of the latter silicone solutions can be ascribed to the hydrolysis of the urea group in BHEUPTES. The amine groups formed by hydrolysis could neutralize the acid catalyst and increase the pH. The sol–gel condensation rates are usually much higher in the pH range 6–8 if no stabilizers are present.[18b]

Without amine resins, the hydroxyl functional silicone solutions are thermally cured by sol–gel condensations as well as reesterification and transesterification (Figure 5).

Amine resins contain $-NH-$, $-NCH_2OH$, $-NCH_2OR$ (R = a methyl, isobutyl, or butyl group), or other reactive groups that allow them to self-condense or react with hydroxyl, ureido, or carboxyl groups of the vehicle resins.[19] The $-NCH_2OH$ or $-NCH_2OR$ groups can react with hydroxyl functional silicones to form $-NCH_2OR'$ bonds (R′ represents a residual group from the functional silicone) and hence bridge the silicone and the amine resin. The major reactive groups in highly methoxylated amine resins are $-NCH_2OCH_3$ groups. These systems do not appreciably self-condense but react with hydroxyl functional vehicle resin in the presence of a strong acid catalyst (free or blocked form). The reaction of a GP hydroxyl functional silicone with a methoxysilyated MF resin can be represented by Figure 6.

As expected, the hydroxyl functional silicone solutions had rather good miscibility with methoxylated UF and methoxylated MF. In the presence of p-TSA and water, methoxylated MF can be hydrolyzed into $-NCH_2OH$ groups, which can self-condense or react with the silicone. Therefore, after mixing the amine resins, the

silicone/MF hybrid solution often gelled within 3–7 days. However, a longer gelling time may be obtained if a blocked acid catalyst is used.

Estimating the TRS of the silicone and amine resin solutions is difficult because the degrees of condensation for both species are uncertain (never 100%). This is especially true for the silicone resin, which loses large amounts of water and alcohol during hydrolysis and condensation. The weight ratio of the silicone to amine resin provided for comparison was estimated based on the weight of completely condensed silicone (no free silanol and alkoxysilane groups) and the net weight of the amine resin (no condensation loss).

Crack-free coatings were generally obtained by following the aforementioned procedures. However, for the silicone/amine resin hybrid coating, drying of the coated substrates at room temperature for over 12 h sometimes led to coatings with a few 2–3-mm-wide cracks. This phenomenon was not observed for the silicone coating controls. Transparent coatings were obtained if the concentration of the amine resin was less than about 25 wt % by the estimated TRS. With a higher amine resin concentration, the coatings became less transparent (with ~2% haze) due to slight phase separation. We believe that the capillary forces that lead to shrinkage and densification of the sol–gel system also cause the separation of some unreacted MF resin from the silicone matrix. After phase separation, the unreacted MF resin in MF-rich domains can still self-condense or react with surrounding hydroxyl groups and become part of the continuous three-dimensional hybrid network.

Table 1 lists the Taber abrasion resistance values of the GP/MF and GP/UF hybrid coatings after curing at 100 °C for 3 h or 125 °C for 2 h. The coatings with the MF additive had rather good abrasion resistance, indicating the GP/MF resins had been reasonably cured. As the MF concentration was increased, the hybrid coating showed gradually decreasing abrasion resistance. Those cured at the higher temperature, 125 °C, typically showed much better results. However, the coatings with the UF additive showed unexpectedly poor results. Considering both MF and UF resins, if vulcanized alone, form very hard and brittle materials, these systems are speculated not to have cured sufficiently under the experimental conditions. As a cross-linker for high solids coatings, UF resins typically require a lower curing temperature than MF resins, but they also require a high acid catalyst concentration. After solvent evaporation, the percentage of p-TSA by TRS was about 0.5–1% in the GP/MF or GP/UF resins, which is about the normal catalyst level for MF resins but significantly lower than that of UF resins (6–10 wt %).[19,20]

The coatings based on the EC/MF resins were much less abrasion resistant than those based on similarly formulated GP/MF resin coatings (Table 2). Apparently, this is because the EC silicone only contained secondary hydroxyl groups, which are less reactive than the primary hydroxyl groups that exist in the GP silicone. Similar to the GP/UF systems, the EC/UF systems failed to cure into hard coatings.

(19) *Resimene® High Solids Amino Resin Recommendation with Nacure & K–Cure Acid Catalysts*; Technical Bulletin, Pub No. 2029261A, Solutia Inc., St. Louis, MO, URL: http:\\www.coatings-solutia.com\index.html.

(20) *Maprenal® & Resimene®*; Technical Bulletin, Pub No. 2029665, Solutia Inc., St. Louis, MO, URL: http:\\www.coatings-solutia.com\index.html.
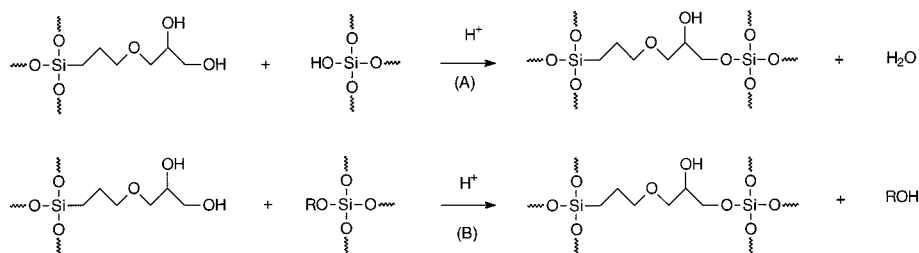
Figure 5. Reesterification (A) and transesterification (B) of a GP hydroxyl functional silicone resin.
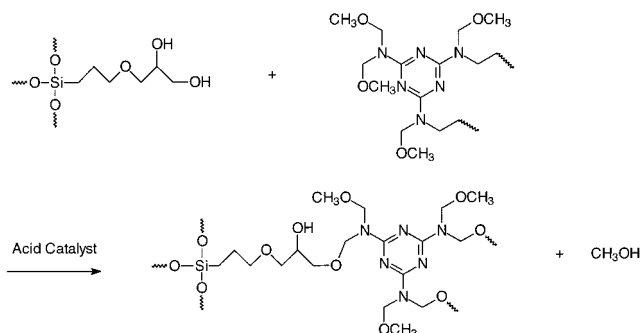

Figure 6. Condensation reaction between a methoxylated melamine formaldehyde resin and a GP silicone resin.

Table 1. Taber Abrasion Resistance Results of the GP/ Amine Resin Coatings

sample ID	estimated ratio of silicone to amine resin	curing condition	haze, %
GP	100:0	100 °C/3 h	9.4
		125 °C/2 h	3.4
GP/MF-A	86:14	100 °C/3 h	4.8
		125 °C/2 h	3.2
GP/MF-B	76:24	100 °C/3 h	7.2
		125 °C/2 h	5.3
GP/MF-C	67:33	100 °C/3 h	15.5
		125 °C/2 h	9.1
GP/UF-A	85:15	100 °C/3 h	~40
		125 °C/2 h	~40
GP/UF-B	74:26	100 °C/3 h	~40
		125 °C/2 h	~40

Table 2. Taber Abrasion Resistance Results of the EC/ Amine Resin Coatings

sample ID	estimated ratio of silicone to amine resin	curing condition	haze, %
EC	100:0	100 °C/3 h	8.6
		125 °C/2 h	7.9
EC/MF-A	86:14	100 °C/3 h	22.9
		125 °C/2 h	10.3
EC/MFB	76:24	100 °C/3 h	16.9
		125 °C/2 h	8.7
EC/MFC	67:33	100 °C/3 h	17.6
		125 °C/2 h	7.1
EC/UF-A	85:15	100 °C/3 h	~40
		125 °C/2 h	~40
EC/UFB	75:25	100 °C/3 h	~40
		125 °C/2 h	~40

According to the above results, coatings derived from the hydroxyl functional silicones alone often had similar or even better resistant resistance than some of silicone/ amine resins. However, these coatings may not be hydrolytically stable because the Si−OR′ bonds formed by reesterification or transesterification are susceptible to moisture. By adding MF resins, more hydrolytically stable −NCH$_2$−OR′ groups are formed instead of the Si− OR′ groups, so the resulting hybrid resins should improve the water resistance. UF resins have poor weatherability and are mainly used as primers, so they were not used as an additive in our latter experiments.

Table 3. Taber Abrasion Resistance Results of the T-BH/ MF and T-BH′/MF Hybrid Coatings

sample ID	estimated ratio of silicone to amine resin	curing condition	haze, %
T-BH	100:0	125 °C/2 h	3.9
T-BH/MF-A	87:13	125 °C/2 h	4.4
T-BH/MF-B	77:23	125 °C/2 h	5.5
T-BH/MF-C	70:30	125 °C/2 h	6.8
T-BH	100:0	125 °C/2 h	2.3
T-BH/MF-A	87:13	125 °C/2 h	2.9
T-BH/MF-B	76:24	125 °C/2 h	4.0

Tertiary silicone systems were also formulated by using TMOS (or TEOS), TTMSPIC, and BHEUPTES (or GPTMS). Replacing portions of TMOS or TEOS by TTMSPIC should reduce the amount of volatile organic compound released during drying and curing and lower the shrinkage of the coating. Our experiments demonstrated that TMOS/TTMSPIC/methyltrimethoxysilane tertiary systems could form transparent coatings of excellent abrasion resistance (<1% in haze by the Taber test) when cured at 100 °C for 3 h, but these systems were rather brittle. As an extension, TTMSPIC modified silicones were used to form hybrid systems with MF resins.

Table 3 lists the abrasion resistance results for the T-BH/MF and T-BH′/MF hybrid coatings. With the same silicone resin, increasing the concentration of the MF resin caused a slight decrease in the abrasion resistance. The T-BH′/MF hybrid coatings, which contained a lower amount of BHEUPTES (with TMOS:TTMSPIC:BHE- UPTES = 5:5:5), showed obviously higher abrasion resistance than the T-BH/MF hybrid coatings. However, the T-BH solution (with TMOS:TTMSPIC:BHEUPTES = 5:5:10) had a significantly longer gelation time than the T-BH′ solution (~14 days vs 3−5 days).

BHEUPTES has twice the amount of primary hydroxyl groups as the same moles of the hydrolyzed GPTMS. In addition, it may condense with MF resin via the urea groups. However, the urea group in BHEUPTES may also undergo hydrolysis in the water− alcohol medium and the associated pH change often destabilized the silicone solution. Although TTMSPIC also contains urea groups, this cyclic compound is usually much less susceptible to hydrolysis.

As expected, the T-GP silicone was significantly more stable than the T-BH silicone. Table 4 lists the abrasion resistance of the T-GP/MF hybrid coatings. Apparently, the T-GP/MF hybrid coatings provided abrasion resistance comparable to other systems described in this paper.

Conclusions

Preliminary experiments indicated that the hydroxyl functional silicones aforementioned and the RESIMENE

Table 4. Taber Abrasion Resistance Results of the T-GP/MF Hybrid Coatings

sample ID	estimated ratio of silicone to amine resin	curing condition	haze, %
T-GP	100:0	100 °C/3 h	9.6
		125 °C/2 h	4.5
T-GP/MF-1	96:4	100 °C/3 h	11.2
		125 °C/2 h	5.1
T-GP/MF-2	91:9	100 °C/3 h	10.5
		125 °C/2 h	4.1
T-GP/MF-3	83:17	100 °C/3 h	16.1
		125 °C/2 h	4.8

730 resin were miscible and could be used to develop water–alcohol borne coatings. Some of the hydroxyl functional silicone solutions were found stable at room temperature for at least 2 weeks. Coating compositions derived from these silicone solutions and the MF resin had a gelling time of 3–7 days and they can be thermally cured at 100 °C or higher to form hard transparent abrasion resistant coatings. The hydroxyl functional silicones also formed transparent solutions with the RESIMENE U-975 resin; however, these silicone/UF hybrid systems failed to cure sufficiently under the experimental conditions and showed poor abrasion resistance.

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