

Synthesis and Application of a Novel Organosilane Modifier for Surface Paintability of Organosiloxane Sealants

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Abstract: A novel organosilane, *N-n*-butyl- γ -aminopropylmethylmethoxydimethylsilane was synthesized through aminization reaction and the chemical structure of resulting products was characterized by ^1H NMR, ^{13}C NMR, FT-IR and elemental analysis. The results of test on probation for this organosilane proved that it was effective to modify surface-paintability of organosiloxane sealants.

Keywords: Aminoalkylsilane, aminization, organosiloxane sealants, surface paintability.

Owing to having excellent weather ability, resistance to heat, maintaining their flexibility at low temperatures, ease of application, and rapid cure in place, organosiloxane materials have been widely used as sealants and caulking materials¹⁻². However, the application of these materials can seldom avoid decorative and protective coatings such as paints, lacquers and varnishes. Unfortunately, due to the low surface energy of polydiorganosiloxane, which has been usually used as the most basic and important composition of the silicone elastomer, the disadvantage of possessing unpaintable surface results in a considerable limitation for their application. In general, the improvement of the paintability for polydiorganosiloxane surfaces can be achieved by introducing isocyanate terminated polyurethane prepolymer into the polydiorganosiloxane. Nevertheless, there exist some difficulty arising from the poor the compatibility between these two materials³. Even though there have been a lot of methods for enhancing compatibility between components in polymer blends or composites, to our knowledge, few research reports concerning the organosilane modifier for surface paintability of organosiloxane sealants have been published until now. In this article, we attempt to synthesize a novel aminoalkylsilane, *N-n*-butyl- γ -aminopropylmethylmethoxydimethylsilane in order to improve the compatibility through coupling the polyurethane prepolymer and polydiorganosiloxane by the amino and alkyloxy radicals, and preliminarily evaluate the effect of surface paintability of organosiloxane sealant through modification by using the modifier synthesized.

The aminization reaction (**Scheme 1**) was carried out in bulk at 110 °C under dry nitrogen atmosphere. The desired amount of predistilled γ -chloropropylmethyl dimethoxydimethylsilane, along with a calculated amount of *n*-butyl amine (molar ratio: 2.5:1), was

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charged to a four-neck flask equipped with a mechanical stirrer, a nitrogen inlet, a reflux condenser and a thermometer. The reaction lasted approximately for 10 h, and precipitation appeared as it proceeded. Then the mixture produced was filtrated, and the liquid obtained was further distilled. The aminosilane compound was collected at 154 °C under a vacuum of 70 mmHg.

Test pieces were made in a mold with certain dimensions, and then exposed to a condition of 50% R.H. and 25°C for a period of time before coating with either an acrylic latex paint or an alkyl paint (oil based). The adhesion of the paint to the surface of the cured sealants was determined by the tape test method⁴. The amount of paint adhered was determined through observing the remaining sections of the cross-hatched area and the following rating system was used to compare the paint adhesion⁵: rating 0 meaning no paint adhesion; 1, less than 20% paint adhesion; 2, 20-40% paint adhesion; 3, 40-70% paint adhesion; 4, 70-95% paint adhesion; and 5, 95-100% paint adhesion.

The compounds of organosiloxane sealants were prepared through a high-vacuum-mixer following the formulations as given in **Table 1**.

NMR analysis was conducted on a Bruck Advance DMX500 spectrometer. The solvent was CDCl₃ and D₂O was used for the solvent and the deuterium exchange of the secondary amino proton respectively. FT-IR spectrum was obtained through Bruck Vector 22 spectrometer in NaCl tablet, and elemental analysis was performed through Eager 200 elemental analyzer.

The FT-IR spectrum of N-*n*-butyl- γ -aminopropylmethylmethoxydimethylsiloxane exhibited the presence of the characteristic absorption peaks of NH (3312 v/cm⁻¹, 729 ω /cm⁻¹), Si-O-CH₃ (1190 δ /cm⁻¹), Si-CH₃ (767 v/cm⁻¹) and Si-O (1087 v/cm⁻¹) revealed that the aminization reaction well took place.

Scheme 1

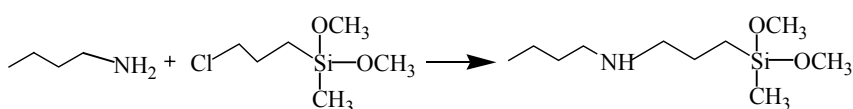
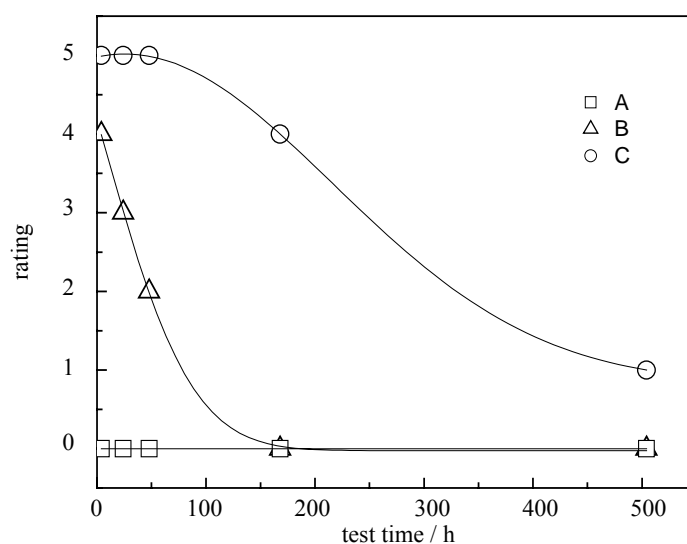


Table 1 Formulation for specific organosiloxane sealants

Components	Samples		
	A	B	C
PDMS	100	100	100
Filler (CaCO ₃)	100	100	100
Catalyst (dibutyltin dilaurate)	0.02	0.02	0.02
Crosslinker (methyltrimethoxysilane)	6	6	6
polyurethane prepolymer	0	10	10
N- <i>n</i> -butyl- γ -aminopropylmethylmethoxydimethylsiloxane	0	0	1

Figure 1 The relationship between time period (after test piece was made and before paint was applied to the surface of the test pieces) and paint adhesion rating



On the basis of the ^1H NMR spectrum, we can classify attribution of the spectrum as $\delta = 0.90\text{--}0.93$ (t, CH_3 , 3H), 1.55–1.56 (d, CH_2 , 2H), 1.45–1.46 (d, CH_2 , 2H), 2.59–2.60 (t, CH_2 , 2H), 3.42 (m, NH, 1H), 2.56–2.58 (t, CH_2 , 2H), 1.32–1.34 (d, CH_2 , 2H), 0.60–0.64 (t, CH_2 , 2H), 0.12–0.13 (d, Si– CH_3 , 3H), 3.51–3.52 (d, 2OCH_3 , 6H). Moreover, according to the ^{13}C NMR spectrum of the compound, it can be claimed as $\delta = 0.0006$ (Si– CH_3), 16.49 (OCH_3), 19.89 (CH_3), 26.40 (CH_2), 29.17 (CH_2), 38.27 (CH_2), 56.51 (Si– CH_2), 56.05 (NH– CH_2), 58.87 (NH– CH_2) for the different attribution of the carbon atoms in the compound. The results of elemental analysis indicated that C: 54.18%, N: 6.35%, H: 11.27% (calculated value: C: 54.37%, N: 6.38%, H: 11.50%).

In combination with above data, the structure and composition of *N-n*-butyl- γ -aminopropylmethyltrimethoxysilane could be well identified. We believed that the products synthesized were satisfactory even though a slight deviation from the theoretic calculation due to some experimental restrictions.

After the same paint drying time period (24 h), the paint adhesion rating was evaluated and the test results were shown in **Figure 1**.

It can be seen that the unmodified organosiloxane sealants (sample A) can hardly accept any paint during the whole test time. However, for sample B, which was incorporated with polyurethane prepolymer, the surface paintability was significantly improved within the initial 48 h despite a deteriorating tendency later. Moreover, in the case of sample C, the co-existence of the polyurethane prepolymer together with the modifier had further enhanced the surface paintability of the final product, indicating a paint adhesion rating up to 5 and this good surface adhesion will maintain this level throughout the test time period from 4 to 48 h. After 48 h, sample C began to exhibit a decreasing adhesion rating upon testing time, while sample B comparatively showed a

steeper varying trendy. This phenomenon had clarified the novel application of the modifier, N-*n*-butyl- γ -aminopropyl- methylmethoxysilane. We owed this observation to the respective reaction of the amino and alkyloxy radicals of the modifier with the isocyanate groups of the polyurethane prepolymer and hydroxyls of polydimethylsiloxane. Also, we believe this is resulted from enhancing the compatibility between polydimethylsiloxane and polyurethane prepolymer, and restricting the transference of polysiloxane segments to the surface of the sealants.

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