Adhesion Between Addition-Curable Silicone Elastomer and Nylon Using Diallylbisphenol A as Adhesion Promoter

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ABSTRACT: It was found that the incorporation of a small amount of 2,2'-diallylbisphenol A in a two-component room-temperature vulcanizing (RTV) silicone produced excellent adhesion on nylon substrates, whereas no adhesion was observed when this additive was excluded from the formulation. The effect of the chemical structure and the functionalities of this adhesion promoter were investigated by evaluation of several other molecules bearing both allylic and phenolic groups. No adhesion improvement was observed when 2-allyl 4-cumylphenol or 2-allylphenol was used as the adhesion promoter, whereas with 2-allylbisphenol A there was good adhesion between the two surfaces. Although it is quite clear that allyl groups react with the adhesive through the hydrosilylation reaction during the cure process of the RTV material, the interaction of the phenolic group with polymer surfaces seems to be largely dependent on the steric effect, that is, the ability of the OH group to be close enough to the plastic surface to develop a strong hydrogen bond. The minimum temperature required for adhesion to occur between nylon and RTV was determined to be in the range of 50°C–60°C. This temperature corresponds to the glass-transition temperature of the amorphous part of the nylon. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3496–3499, 2003

Key words: silicone elastomer; addition reaction; adhesion promoter; nylon

INTRODUCTION

Addition-curable silicone coatings are formed by the reaction of multifunctional silicone hydride polymers with multifunctional silicone vinyl polymers in the presence of a hydrosilylation catalyst such as Karstedt's catalyst, $Pt_2(M^{vi}M^{vi})_3$, where $M^{vi}M^{vi}$ = 1,3-divinyl-1,1,3,3-tetramethyldisiloxane. Coatings prepared in this manner typically do not adhere to surfaces for a variety of reasons, including the low surface free energy of the coatings,[1] their low polarity, and the high flexibility of the polymer backbone and their incompatibility with organic polymers.[2] Surface treatments or priming of the adherent surface enhances the adhesive nature of these materials,[3] but sometimes those techniques cannot be used for various reasons such as the cost and the negative impact on the environment from using primers (high levels of volatile organic compounds). An alternative method for obtaining the adhesion of addition-curable silicone to substrates is by incorporation of adhesion promoters into the precured silicone. A coupling agent, a product added to the coating formulation or used in surface treatment, which improves adhesion by creating stronger interfacial interaction between the coating and the substrate, is usually considered as an adhesion promoter. The adhesive bond strength of a coating to the substrate can be increased by mechanical alteration of the substrate, polar interactions with the bonding agent, or chemical bonding, facilitated by an adhesion promoter. It is usually suggested that adhesion promoters need to have functionalities reactive with both substrates and polymer networks in order to achieve good adhesion.[4] Many kinds of adhesion promoters have been proposed in order to improve the adhesion between addition-cured silicone elastomers and plastic or metal substrates. Generally, it has been claimed that these adhesion promoters should contain at least one functionality selected from a group consisting of alkoxy, alkenoxy, epoxy, acryl, alkenyl, and SiH residues. Those functionalities react with both the silicone and the substrate surface.[5–8] In this article we describe a new self-priming addition-curable silicone. In this case, the adhesion promoter did chemically bond to the silicone network and physically interact with the plastic surface.
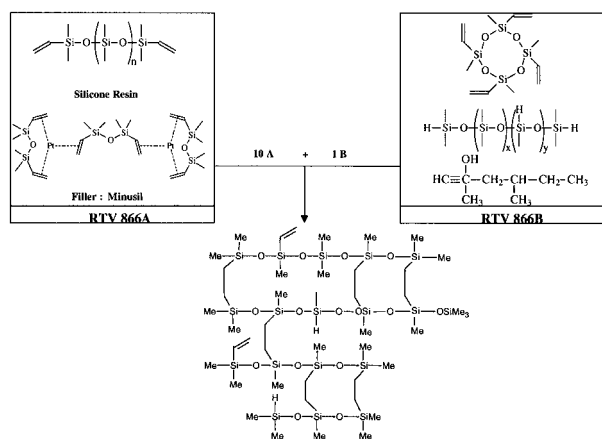
EXPERIMENTAL

Materials

Nylon

Quarter-inch thick nylon sheets (nylon 6,6) cut into 1-by 4-inch coupons were provided by McMaster-Carr

Scheme 1 Addition-cured network formation.

Supply Company Inc. (New Brunswick, NJ). They were used without any drying or surface treatment except a simple cleaning with isopropanol.

Room-temperature vulcanizing silicon

The addition-curable silicone compositions (RTV866-A and B) were generously supplied by GE Silicones (Waterford, NY). RTV866 has two components, as depicted in Scheme 1. The silicone networks were prepared by reaction of silicone hydride polymers with silicone vinyl polymers in the presence of a hydrosilylation catalyst. A cure inhibitor was also incorporated into the formulation to avoid the mixture to cure too quickly after the mixing of the two components.

Adhesion promoter

The different compounds evaluated as adhesion promoters in this study are shown in Figure 1; 2,2′-diallylbisphenol A and 2-allylphenol (compounds 1 and 2) were commercially available and were obtained from Aldrich (St. Louis, MO). 2-Allyl 4-cumylphenol (compound 3), 2-allylbisphenol A (compound 4), and 2,2-bis-(3-allyl-4-hydroxyphenyl) hexafluoropropane (compound 5) were synthesized according the procedure depicted in Table I.

Characterization

Lap shear sample preparation and adhesion measurement

Lap shear specimens were prepared and tested according to ASTM Standard D 1002. Samples of 1 inch × 1 inch were cured at 100°C for 1 h and tested using an Instron 4202 with a crosshead speed of 5 inches/min.

Note: To obtain reproducible results, control of the bond line was needed, which was achieved by intro-

ducing a small amount (0.05% by weight of the total formulation) of calibrated glass beads into the formulation (maximum diameter of 0.0234 inches; obtained from Potters Industries, Inc., Canby, OR).

RESULTS

Optimization of the formulation

The diallylbisphenol A was expected to react with the RTV during the hydrosilylation reaction, and the ratio of allylic bond to hydride in the RTV formulation was optimized to provide the silicone network with optimal properties to. The level of adhesion promoter has to be low enough to avoid unbalance between the two reactive species, which might compromise the cure and the final properties of the silicone, but high enough to ensure good adhesion with the nylon surface. Based on these considerations, the optimal formulation was determined by varying the percentage of diallylbisphenol A from 0.25% to 2.5% (by weight) of the total formulation. Six lap-shear samples were prepared from each formulation, cured 1 h at 100°C, and evaluated 24 h after their preparation. The results are depicted graphically in Figure 2.
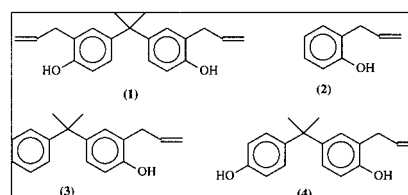
All formulations with diallyl-BPA in the range of .5–2.5 wt % of the total formulation gave cohesive failure in the tests. The best formulation was found to be the one with 1.25% of additive.

Shelf-life stability of the formulation

A premixed formulation consisting of RTV B amended with 1.25% of diallyl-BPA was prepared. Every month an evaluation of the adhesion between the nylon and RTV866 prepared from this premixed component was conducted. No decrease in the strength of the adhesion was observed during the 6 months of this shelf-life study.

Effect of cure temperature

Based on the hydrosilylation reaction, the RTV cure required 1 week at room temperature after mixing the two parts or less time when cured at a higher temperature (1 h at 100°C). The effect of the cure conditions on adhesion was investigated by varying time and

Figure 1 Structure of the compounds evaluated as adhesion promoter.

TABLE I
General Procedure for Allyl Phenol Preparation

Allylbromide K$_2$CO$_3$ / Acetone T = 60C → T = 200–210C

Compound	Starting material	Steps	Product
(3)	Paracumylphenol	1. Allyl bromide + base 2. Thermal rearrangement	Viscous liquid[9]
(4)	Bisphenol A	1. Monoprotection (THP)[10] 2,1-Allyl bromide + base 3. Thermal rearrangement 4. Deprotection (acidic treatment)	Viscous liquid
(5)	2,2-bis-(3-allyl-4-hydroxyphenyl) hexafluoropropane	1. Allyl bromide + base 2. Thermal rearrangement	Viscous liquid[9]

temperature from 1 week at room temperature to 15 min at 150°C. Six lap-shear samples for each condition were evaluated, and the results are given in terms of failure modes (cohesive or adhesive) in Table II.

The results suggest that the mechanism of adhesion required a minimum temperature of 50°C (at which temperature the cure process is longer). This temperature corresponds to the glass-transition temperature (T_g) of the amorphous part of the nylon (T_g = 50°C, and T_m = 285°C). This aspect will be discussed later.

Effect of chemical structure of adhesion promoter

The most probable mechanism for adhesion is that the RTV silicone can react with the allylic groups of the adhesion promoter by a hydrosilylation reaction. The link with the nylon surface was through strong physical bonds (i.e., hydrogen bond) between the phenolic groups of the adhesion promoter and the polar groups of the nylon. According to this mechanism, other structures bearing both allylic and phenolic groups should be efficient adhesion promoters for this system. Such compounds as depicted in Figure 1 were qualitatively evaluated, and the results are given in Table III.

proves adhesion by creating stronger interfacial interaction between the coating and the substrate, is usually considered an adhesion promoter. The adhesive bond strength of a coating to the substrate can be increased by (1) mechanical alteration of the substrate, (2) polar interactions with the bonding agent, or (3) chemical bonding, facilitated by an adhesion promoter. In the present case the most probable mechanism involved hydrosilylation of the allylic bond and polar interaction between the substrate (nylon) and the phenolic groups. (Note: it was previously shown that the *O*-silylation sometimes describes in the literature does not occur during the hydrosilylation of diallyl-BPA.) Quite unexpectedly, replacement of diallyl-BPA with a simpler molecule that contains both allylic and phenolic functions (2-allylphenol, compound 2) resulted in poor adhesion. One possible reasons was that 2-allylphenol was able to dissolve the nylon whereas diallyl-BPA did not. For compound 2 it is possible that the level of the adhesion promoter in the interface was very low because of diffusion into the substrate, leading to very weak adhesion. To avoid this problem, one solution is to prepare a molecule with a structure similar to 2,2'-diallylbisphenol A in

DISCUSSION

A coupling agent, a product added to the coating formulation or used in surface treatment that im-
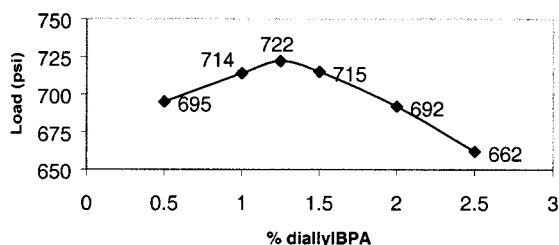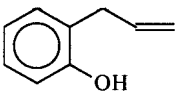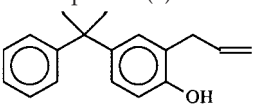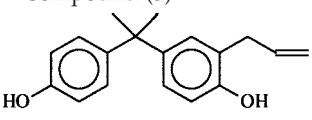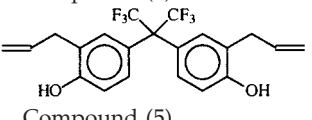

Figure 2 Effect of the levels of diallyl-BPA on adhesion.

TABLE II
Effect of Cure Conditions on Failure Mode

Cure conditions	Failure mode
1 week RT	100% Adhesive
1 week 40°C	100% Adhesive
30 h at 50°C	100% Cohesive
1 h at 60°C	95% Cohesive
4 h at 60°C	100% Cohesive
1 h at 80°C	100% Cohesive
2 h at 80°C	100% Cohesive
15 h at 60°C	100% Cohesive
1 h at 100°C	100% Cohesive
0.25 h at 150°C	Cohesive
0.50 h at 150°C	Cohesive
0.75 h at 150°C	Cohesive

TABLE III
Effect of Chemical Structure of Adhesion Promoter on Failure Mode

Structures	Failure
Compound (2)	No adhesion
Compound (3)	No adhesion
Compound (4)	100% Cohesive
Compound (5)	100% Cohesive

order to decrease the solubility. Accordingly, compound 3 was prepared, and it was observed that this liquid did not dissolve the nylon. However, no improvement in the adhesion between the nylon and the silicone network was observed, suggesting an influence of the steric effect. After reaction and incorporation of the allylic bond into the silicon network, the OH in the ortho position was too hindered and not able to interact with the plastic surface. However, with 2,2'-diallyl-BPA the second OH group can be the link with the plastic because the allylic group has not reacted. To confirm this hypothesis, compound 4, with the same structure as compound 3 but with a sterically free OH, was prepared. It was observed that the efficiency of compound 4 was comparable to that of 2,2'-diallylBPA.

The explanation concerning the minimum temperature required to obtain good adhesion is probably related to the structure of the nylon. Many commercial polyamides are highly crystalline ($T_m = 285°C$), and repeating units within each crystalline region are generally inaccessible to water and other reagents. The maximum sensitivity of the amide is seen in the amorphous part ($T_g = 55°C$), where individual repeat units are accessible to the adhesion promoter. In this case it appears that the interaction and the association of the adhesion promoter with the nylon occurred mainly in the amorphous part of the nylon and was maximized when the temperature was greater than the glass-transition temperature of that part. This explains why there was no adhesion when the samples were cured at a temperature below 50°C.

CONCLUSIONS

The adhesion between nylon and RTV silicone can be dramatically improved by incorporation of as little as 1.25% by weight of diallylbisphenol A into the RTV prior to the cure. The premixing of this adhesion promoter with the vinyl polymer containing part of the RTV led to a stable mixture for at least 6 months without any decrease in adhesion performance. This adhesion promoter linked the two interfaces through chemical bonds with the silicon network (hydrosilylation reaction) and through strong hydrogen bonding with the nylon. The hydrosilylation reaction occurred at room temperature, but the association between the phenolic groups and the polar part of the nylon was activated by temperature, which needed to be greater than 50°C (T_g of nylon). The most probable mechanism for this is the increase of the mobility in the amorphous domains of the nylon and reassociation of the polar functional groups with the phenolic groups.

References

1. Noll, W. Chemistry and Technology of Silicones; Academic Press: New York, 1968.
2. Stein, J.; Grade, H.; Williams, E. A.; Codella, P. J.; Smith, J. F. J Appl Polym Sci 1993, 47, 2257.
3. Plueddmann, E. P. Silane Coupling Agents; Plenum Press: New York, 1982.
4. Suzuki, T.; Kasuya, A. J Adhes Sci Technol 1989, 3, 463.
5. General Electric. U.S. Pat. 4,311,739 (1982).
6. Dow Corning. U.S. Pat. 4,087,585 (1978).
7. Toray Silicone. U.S. Pat. 4,677,161 (1987).
8. Dow Corning. U.S. Pat. 4,737,562 (1988).
9. Abraham, M. H.; Hamerton, I.; Rosa, J. B.; Grate, J. W. J Chem Soc Perkin Trans 1991, 2, 1417.
10. General Electric. U.S. Pat. 4,273,717 (1981).