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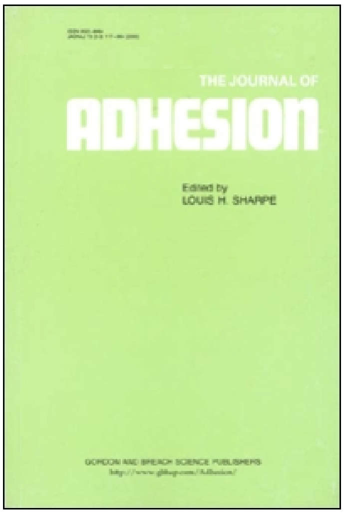

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Vapor Deposited Silanes and other Coupling Agents

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INTRODUCTION

Coupling agents are primarily used to: (a) promote adhesion between the adherends and adherates‡[1] or reinforcing media in the case of composites; (b) maintain improved adhesion as a function of aging; and (c) protect against the deleterious effects of water and corrosive environments. Silanes are the most commonly used coupling agents, and the adhesion of polymers to glass and metals can be significantly improved by applying certain trialkoxysilanes to the adherend surface.[2, 3]

Most of the work involving coupling agents has been done by depositing silanes from a solution onto glass surfaces and the mechanisms by which these coupling agents function are summarized by Cassidy and Yager.[4] Less information is available on the use of coupling agents on metal surfaces. If the silanes are deposited from the solution phase, the following difficulties are encountered: (1) corrosion of the metal surface; (2) non-uniformity of the deposited silane film thickness; (3) poor control of the rate of deposition, and in some cases, the rate of deposition is very slow. Eakins[5] accomplished the vapor phase application of alkylalkoxy silanes by mixing the silanes with moist air for hydrolysis and applying them to nascent glass surfaces while the temperature is held near the decomposition point of the silanes.

In the present paper, we describe a technique for the vapor phase deposition of the coupling agents and the subsequent deposition of polymeric adherates.

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‡ A general term for any material which adheres to an adherend.

EXPERIMENTAL

The tested coupling agents are summarized in Table I. The adherends were thin films (30 nm) of an iron-cobalt alloy deposited on metallic substrates. A plasma surface treatment described earlier[6] was used to remove traces of contaminants before the deposition of the coupling agents. Figure 1 describes the system used to apply the thin layer of coupling agents prior to the deposition of a polymer overcoat. Each of the coupling agents shown in Table I was vaporized under vacuum, usually by heating, and deposited on the metal surface which was at room temperature. The chamber pressure was usually less than 0.1 Torr (13.3 Pa) during the coupling agent deposition. The film thickness of the coupling agent was measured with a quartz crystal thickness sensor. The rate of deposition depends upon the temperature of the silane reservoir and is generally in the range of 0.5 to 1.0 nm/min. Usually 20 minutes were allowed for the thickness of silanes reported.

FIGURE 1

Subsequently, poly-chloro-p-xylylene (Parylene C) was deposited by chemical vapor deposition. The thickness of Parylene C varied from <25 nm to 175 nm, as measured by the Gould microtopographer on coated samples. The water vapor required to react with the silanes can be obtained by vapor diffusion through the polymer overcoat after the deposition process is complete. The contact angle of deionized water (θ_{H_2O}) on the coupling agent coated surface was measured with a contact angle goniometer (Model A–100, Rame–Hart, Inc.). A 12 μl water drop was placed on the surface at 25°C

TABLE I

Coupling agents tested

Trade name	Chemical name	Source	Boiling point at 760 Torr	Density (g/cc)	Film thickness (nm)	Deposition pressure (Torr)*
Z–6076	γ-Chloropropyltrimethoxysilane	Dow Corning	196°C	1.077	0.6	0.03
A–187	γ-Glycidoxypropyltrimethoxysilane	Union Carbide	290°C	1.064	11.5	0.02
A–151	Vinyltriethoxysilane	Union Carbide	160°C	0.965	2.6	0.01
A–174	γ-Methacryloxypropyltrimethoxysilane	Union Carbide	255°C	1.041	4.8	0.02
A–1100	γ-Aminopropyltriethoxysilane	Union Carbide	217°C	0.945	7.8	0.01
—	4-Methylpiperidine	Reilley	—	—	1.1	0.6
—	4-Aminomethylpiperidine	Reilley	—	—	1.2	0.02

* 1 Torr = 133.3 Pa

and the contact angle measured within 1 minute. The adhesion of polychloro-p-xylylene on metal surfaces coated with coupling agents was measured, using a scratch test procedure. The details of this test are described in recent articles by Mittal.[7, 8] In this test, essentially, a smoothly rounded point or stylus is drawn across the coated sample, and a vertical load applied to the point is gradually increased until the film is completely removed and the corresponding load is taken as a measure of adhesion.

RESULTS AND DISCUSSION

The deposited film thickness and the deposition pressure are listed in Table I for each of the coupling agents tested. The thickness of the coupling agents increased by about 3 nm when the film was returned from vacuum to atmospheric pressure. This is based upon the increase in thickness of the quartz crystal thickness sensor, and it takes about 1 minute for this increase. This may be attributable to water absorption. One hour after the coupling agent coated metal surfaces were removed from the deposition chamber, the water contact angle was measured on the surface. θ_{H_2O} values between 39° and 59° indicated the presence of coupling agents on the previously clean metal surfaces ($\theta_{H_2O} < 5$). The A–1100 had the lowest contact angle (39°) and the A–174 had the highest value (59°). The contact angle increased after storage of the silane coated surfaces in nitrogen. The increase in θ_{H_2O} on various silane coated samples is shown in Table II.

TABLE II

Water contact angles on silane coated surfaces as a function of aging

Silane	Time Zero	 24 hour	 48 hour	 72 hour
A-1100	39°	44°	44°	54°
A-151	57°	59°	68°	—
A-174	60°	61°	—	—

Ideally, one should measure γ_C, the critical surface tension of wetting, of these silane films, as the absolute values of θ_{H_2O} cannot be used to learn much about the surface configuration. The abnormality of water (used to measure contact angles) was found to be caused partially by the water sensitivity of some of these films.[9] Furthermore, θ_{H_2O} on these silane films depends upon the medium used for deposition and whether or not a catalyst is used. For example, θ_{H_2O} values on vinyltriethoxysilane deposited on steel plates are reported to be 86°, 34° and 43° for cyclohexane, methylethyl ketone, and propanol media respectively.[10] Also, Bascom[10] found an appreciable contact angle hysteresis, as the value for θ_{H_2O} (adv) and θ_{H_2O} (receding) varied considerably. No values could be found in the literature for γ_C's or θ_{H_2O} for silanes deposited from the vapor phase. It is likely that the surface configuration of silane films deposited from vapor and solution phases is different.

The adhesion of a 100 nm thick Parylene C film on the metallic surfaces was improved by the presence of A–1100, Z–6076, 4-methyl-piperidine, and 4-aminomethylpiperidine. In the absence of a coupling agent, Parylene C does not adhere to a smooth metal surface (CLA = 4.5 nm, RMS = 8.25 nm). This smoothness is equivalent to a smooth glass surface. The A–1100 coating improved the Parylene C adhesion if the polymer film was exposed to air for 16 hours before scratch testing. This probably permitted water vapor to diffuse through the polymer film and react with the silane at the metal surface. It is very important to point out that A–1100 did not improve adhesion if film adhesion was tested immediately after removal from polymer deposition chamber. This indicates the necessity of water diffusion through the film and the attendant hydrolysis of silane layers.

In the case of Fe/Co alloy surfaces, the vapor deposition of coupling agents offers the following advantages: (1) avoids the corrosion of the metal surface caused by aqueous solutions of coupling agents; (2) coupling agent film thickness is controlled, uniform, and generally less than 10 nm; (3) the rate of deposition is faster than that from the solution phase; (4) the technique is applicable to a variety of adherends; and (5) deposition can be carried out in a chamber at room temperature followed immediately by polymer deposition.

Obviously, more work is needed to understand the surface configuration and the nature of the bonding to the substrate of these silane films deposited from the vapor phase. Also, it will be interesting to compare these findings vis-à-vis behavior of silanes deposited from the solution phase.

References

1. K. L. Mittal, *J. Adhesion* **6,** 377 (1974).
2. S. Sterman and J. G. Marsden, *Ind. Eng. Chem.* **58** (3), 33 (1966).
3. E. P. Plueddemann, *J. Adhesion* **2,** 184 (1970).
4. P. E. Cassidy and B. J. Yager, *J. Macromol. Sci.-Rev. Polymer Technol.* **D1,** no. 1, 1 (1971).
5. W. J. Eakins, U.S. Pat. 3,276,853 (October 1966); *Chem. Abstracts* **65,** 18785d (1966).
6. D. F. O'Kane and K. L. Mittal, *J. Vac. Sci. Technol.* **11,** 567 (1974).
7. K. L. Mittal, "A critical appraisal of the methods for measuring adhesion of electrodeposited coatings, in *Properties of Electrodeposits: Their Measurements and Significance*, R. Sard, H. Leidheiser, Jr. and F. Ogburn, Eds. (The Electrochemical Society, Princeton, N.J., April 1975.) Chap. 17, pp. 273–306.
8. K. L. Mittal, Electrocomponen Sci. Technol. in press.
9. L. H. Lee, *J. Colloid Interface Sci.* **27,** 751 (1968).
10. W. Bascom, *Macromolecules* **5,** 792 (1972).