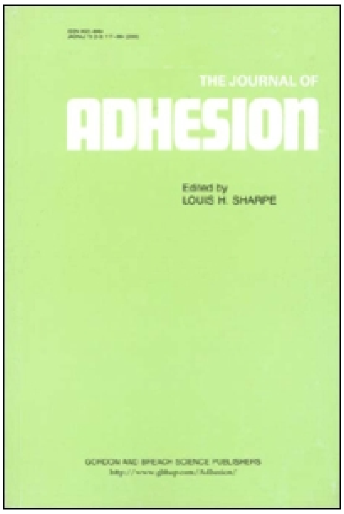

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Silyl Peroxide-Some Chemical and Physical Effects on Adhesion Promotion

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Silyl Peroxide-Some Chemical and Physical Effects on Adhesion Promotion †

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Silyl peroxides have previously been shown to promote the adhesion in a broad range of polymer/substrate and polymer/polymer systems. A correlation between the chemical composition of silyl peroxides and their ability to bond clearly exists. Their effectiveness is usually enhanced with increasing number of reactive sites. While many reactive functional groups are useful, the presence of at least one peroxy group appears to be a necessity. Silyl peroxides are heat-activated. Strength of joints made of silyl peroxides are shown to depend on the extent of their dissociation which can be accelerated or retarded with known radical accelerators or retarders, respectively. Adhesion is believed to result from a sequence of silyl peroxide initiated, free radical reactions taking place during the curing step. This hypothesis is consistent with the kinetic behavior of the silyl peroxides. Internal reflection infrared study reveals that the areas immediately surrounding the interface are diffused layers of siloxanes and the substrate molecules. The possibility of chemical linking of the silyl peroxide fragments to the polymeric phase(s) is suggested. Silyl peroxide promoted joints exhibit good hydrolytic and thermal stabilities. However, the measured adhesive strength is also affected by the morphology of the polymer employed in the system. Results of a quenching study are presented.

INTRODUCTION

Silyl peroxides have previously been shown to promote the adhesion in a broad range of polymer/substrate and polymer/polymer systems[1,2]. They differ from the more conventional silanes in two basic respects; (1) adhesion promotion is effected by heat while other silanes must be hydrolyzed;

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(2) a free radical mechanism is believed to be responsible in contrast to traditional silanes which couple via an ionic mechanism.

As adhesion promoters, silyl peroxides are self sufficient. They react with either thermoplastics or thermosetting resins without an external free radical source such as a peroxide. They can be applied either as primers, or used as integral blends. Adhesion promotion is effected by heating under contact pressures.

Some chemical and physical effects on adhesion promotion with the silyl peroxides are described in this paper. On the basis of our experimental findings, a mechanistic account for the silyl peroxide promoted adhesion is presented.

REACTIVITY vs. CHEMICAL CONSTITUTION

The simple silyl peroxides can be represented by the following formula: $R_{4-n}Si(OOR')_n$ where n is an integer from 1 to 4, R and R′ are organic residues. The behavior of a silyl peroxide as well as its ability to promote adhesion are affected not only by the number of peroxy group (or groups) present in each molecule but also the reactivity of its organic moieties[1,2].

For a given series of silyl peroxides where R and R′ are methyl and tertiary butyl respectively, the bonding efficiency of a silyl peroxide increases with an increasing number of peroxy radicals. This is illustrated by the peel strength data of several aluminum-polyethylene-aluminum (Al-PE-Al) composites containing these silyl peroxides (Table I). Each composite was made of two outer layers of 25 mil aluminum Q-panels and a 20-mil PE (Union Carbide DFDA-4141 NT) interlayer containing 2% by weight of a given silyl peroxide. Bonding was carried out at 210°C under a pressure of 75 psi for 5 min.

Some differences in bonding efficiencies of silyl peroxides containing the same number of, but different, substituent groups of peroxy radicals were also observed. The presence of a reactive substituent (or substituents), such

TABLE I

Effect of increase in peroxy radicals.

$(Me)_{4-n}Si(00\ t\text{-Butyl})_n$	Decomposition Temperature °C.	Peel strength ASTM D1876 lbs./in.
n = 1	114 (boiling)	2
2	185	6.5
3	150	31
4	135	36

TABLE II

Effect of substituent groups.

$RSi(OO\ t\text{-}Butyl)_3$	Decomposition temperature °C.	Peel strength* lbs./in.
R = H	120	18
Methyl	150	31
Vinyl	154	68 (CF)
Allyl	174	76 (CF)

* CF = Cohesive Failure

as an olefinic group, enhances the efficiency of a silyl peroxide (Table II). Silyl peroxides containing tertiary alkyl peroxy functionality usually exhibit better performance and stability than those containing aralkyl or aryl peroxy radicals (Table III).

TABLE III

Effect of nature of peroxy radical.

$CH_2{=}CH{-}Si(OOR)_3$	Decomposition temperature °C.	Peel strength lbs./in.
R = t-butyl	154	68 (CF)
cumyl	140	31
p-menthyl	140	10

KINETIC BEHAVIOR

Thermal decomposition of silyl peroxides has been shown to proceed primarily via a free radical mechanism[3]. The initial process involves a homolytic cleavage at the O—O bond to produce the corresponding siloxy and alkoxy (or aralkoxy) radicals. The generation of siloxy radicals, which are reactive toward either organic or inorganic substrate, is suspected to be responsible for the ability of the silyl peroxides to promote adhesion.

Silyl peroxides containing multiple peroxy radicals decompose in a more complex manner than the mono-peroxy silyl peroxides. Decomposition of vinyltris(*t*-butylperoxy) silane in cumene is essentially first order with respect to the silyl peroxide. However, its rate of decomposition is markedly dependent on the initial peroxide concentration indicating the occurrence of induced decomposition. In cumene-acrylonitrile solution where the induced decomposition is suppressed, its decomposition can be adequately described by the following Arrhenius equation: $t_{\frac{1}{2}} = 2.775 \times 10^{-10}\, e^{11{,}136/T}$ where $t_{\frac{1}{2}}$ is the half life in minutes at the temperature T in degree Kelvin. The extent of decomposition of vinyltris(*t*-butyl peroxy)silane during bonding applications can be roughly estimated using this equation.

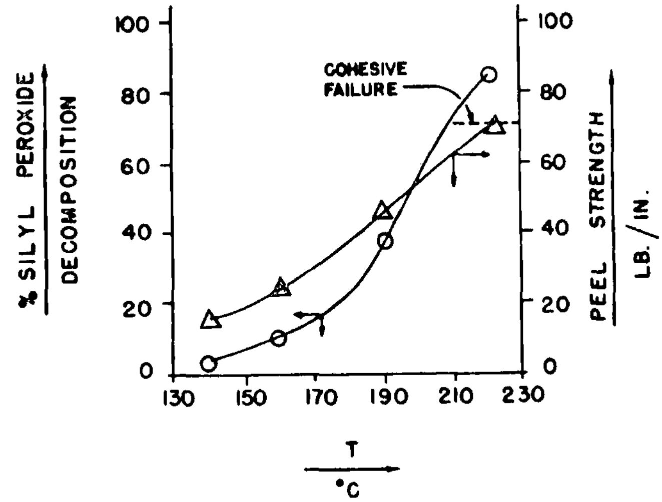


FIGURE 1 Effect of Vinyltris(*t*-butyl peroxy)silane decomposition upon the adhesive strength of an aluminum-polyethylene-aluminum composite.

Because adhesion promotion with silyl peroxides is brought about with heat, their degree of dissociations affect directly the extent of adhesion developed. In Figure 1, the adhesive strength of an Al—PE—Al composite bonded with vinyl tris(*t*-butyl peroxy)silane, which was applied as an integral blend at a 2% by weight loading, and the extent of decomposition of this silyl peroxide calculated from the Arrhenius equation given above are plotted against the bonding temperature of the composite at a constant cycle of 5 min. The adhesive strength of the composite increases with increasing extent of thermal decomposition of the silyl peroxide until cohesive failure of PE takes place. A similar result was also obtained by varying the length of bonding cycles at a fixed temperature at 140°C as shown in Figure 2. However, at a similar level of silyl peroxide decomposition, different values in adhesive strength were obtained in the two instances showing that the resulting adhesion is influenced not only by the extent of silyl peroxide reacted but also the mode of reaction at different temperatures as well as the properties of the resulted PE interlayer.

For the purpose of comparison, performance of a vinyltriethoxysilane/dicumyl peroxide mixture[4] (1/1 mole ratio) for bonding the above composites was also determined. In Figure 3, the adhesive strength of the resulting composites and the extent of decomposition of dicumyl peroxide[5] are plotted against the bonding temperature of the composite at a constant cycle of 5 min. Although a very slight increase in adhesive strength was measured with

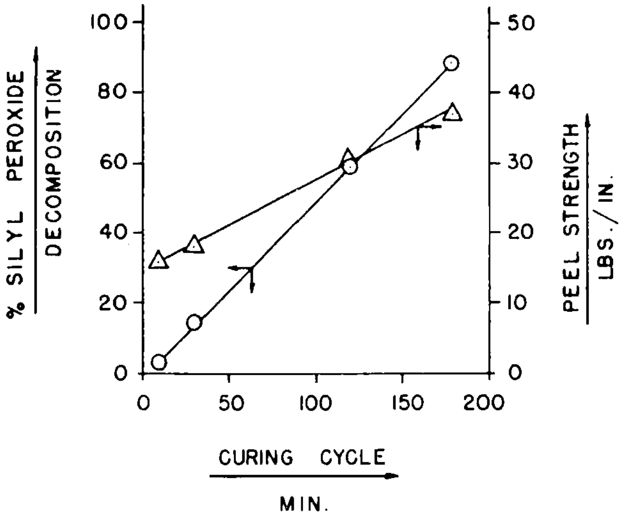


FIGURE 2 Effect of vinyltris(*t*-butylperoxy)silane decomposition on adhesive strength of an aluminum-polyethylene-aluminum composite.

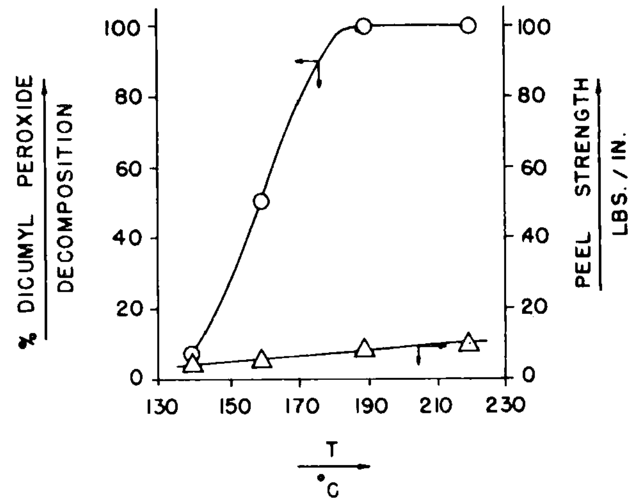


FIGURE 3 Effect of dicumyl peroxide* decomposition upon the adhesive strength of an aluminum-polyethylene-aluminum composite.

* $^1/_1$ Mole mixture of dicumyl peroxide/Vinyltriethoxysilane

increasing dicumyl peroxide decomposition, the resulting adhesive strength was nevertheless marginal throughout the temperature range studied.

ACCELERATORS AND INHIBITORS

The free radical mechanism of silyl peroxide promoted adhesion is consistent with their response to some known radical accelerators and inhibitors. Two types of accelerators have been found to be useful for the decomposition of silyl peroxides through either a redox type reaction or a radical induced decomposition. Effects of the addition of cobaltic acetylacetonate or benzoyl peroxide to the vinyltris(*t*-butyl peroxy)silane applied as a 50% toluene solution promoted Al—PE—Al joints at 120°C are shown in Table IV.

TABLE IV

Effect of peroxide accelerators.

Accelerator	Loading* %	Peel strength lbs./in.
Control		8
Cobaltic Acetylacetonate	0.1	16
	1	12
Benzoyl peroxide	1	24
	5	12

* Based on Silyl Peroxide.

A substantial improvement in adhesion was realized, although the resulting adhesive strength was still significantly below the optimum value attainable at higher temperatures.

As one would expect, most antioxidants tend to depress the bonding behavior of the silyl peroxides. Being a strong oxidizing agent, silyl peroxides are readily consumed by antioxidants at either ambient or elevated temperatures. While the phenolics or amine type antioxidants exhibit only mild effects at elevated temperatures, sulfur containing antioxidants are deleterious. A proper selection of antioxidants is therefore necessary for a maximum utilization of the silyl peroxides.

POLYMERIZATION OF UNSATURATED SILYL PEROXIDES

Reactivity of the unsaturated silyl peroxides toward organic materials is well demonstrated by their ability to form grafting or random copolymers.

Copolymerization is usually carried out in solution under mild conditions, with or without the presence of a suitable radical initiator, so that decomposition of the silyl peroxide monomers is kept at a minimum.

One of the most reactive silyl peroxides is the gamma-methacryloxypropyltris(*t*-butyl peroxy)silane which can be readily copolymerized with a variety of olefinic or vinyl monomers to impart excellent adhesive properties to the resulting copolymers. Its ability to play the role of not only an initiator but also a comonomer and an adhesion promoter contributes to its outstanding performance in the glass fiber reinforced polyester composites[6].

Vinyltris(*t*-butyl peroxy)silane behaves similarly although less reactive probably as a consequence of steric hindrance and of the deactivating effect of the Si—C bond[7].

Well characterized graft-copolymers have been prepared from the above or other unsaturated silyl peroxides onto polyolefins or other organic polymers with a similar solution process. Efficiency of grafting varies with the nature of silyl peroxides, specifically the reactivity of a particular unsaturated functionality present in a given silyl peroxide. Silyl peroxide grafted copolymers exhibit good bonding characteristics.

Aside from the vinyl polymerization, silyl peroxides having multiple silyl peroxy radicals may also undergo self-condensation through the initial formation of silanols forming either linear or cross-linked polysiloxanes.

CHARACTERIZATION OF INTERFACES

We have already discussed the reactivity of the unsaturated silyl peroxides toward the organic matrices. Such reactions would, conceivably, lead to the formation of new resin compositions at the interfaces. FMIR (Frustrated Multiple Internal Reflectance) infrared spectroscopy was employed to characterize the interfacial chemical compositions in our system.

Experimental work was conducted on surfaces exposed from polyethylene-metal composites bonded with different silyl peroxides. The specimens were cured under mild conditions such that the polyethylene layers were readily separated from the metallic substrates during peel. The freshly exposed surfaces were used immediately for FMIR measurements.

A set of Al—PE—Al composites bonded with vinyltris(*t*-butyl peroxy)silane at 140°C but different cycles was studies. Figure 4 shows two regions in the spectra of the exposed polyethylene surfaces. Upon curing, two groups of new bands, centered at 1100 and 770 cm^{-1} respectively, began to appear. The former group is assigned to Si—O frequencies resulting from the formation of Si—O—Si and Si—O—C linkages[8,9], while the latter group arises from the Si—C absorptions. Figure 5 shows the same regions in the spectra of the exposed aluminum surfaces. The presence of polyethylene

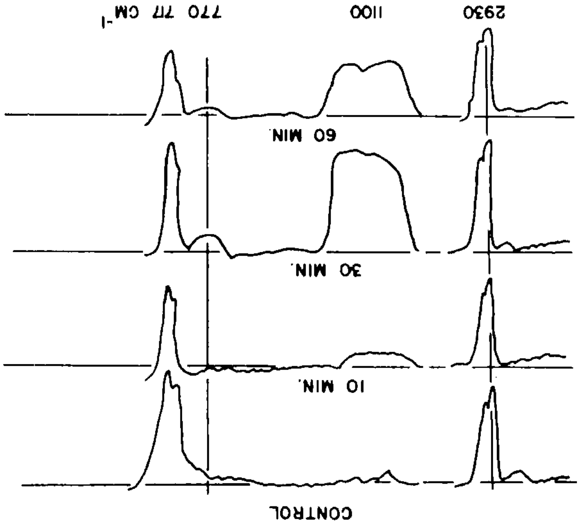


FIGURE 4 FMIR of exposed polyethylene surfaces of Aluminum-polyethylene-aluminum composites bonded with vinyltris(*t*-butylperoxy)silane at 140°C.

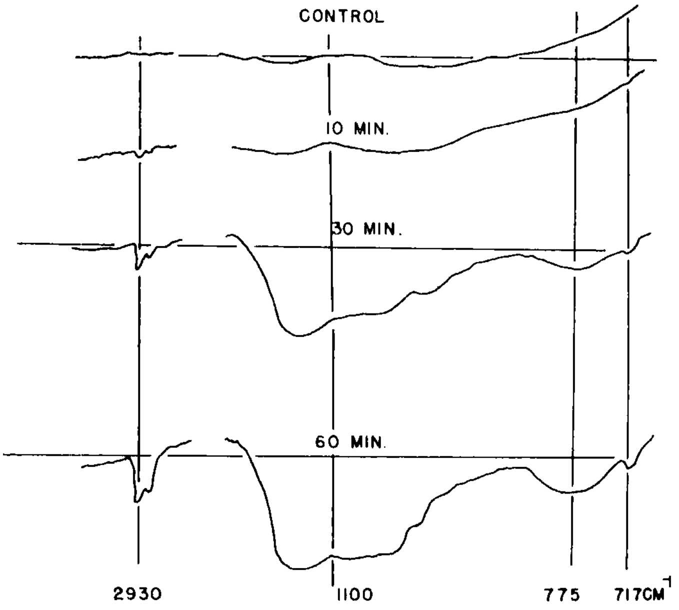


FIGURE 5 FMIR of exposed aluminum surfaces of aluminum-polyethylene-aluminum composites bonded with vinyltris(*t*-butylperoxy)silane at 140°C.

absorptions at 2930 and 717 cm^{-1}, and Si—O and Si—C absorptions centered at 1100 and 770 cm^{-1} respectively are quite apparent. These results suggest that, first, failure occurred in regions where new chemical compositions were formed due to reactions of the silyl peroxide molecules among themselves and with the substrates; and, second, the extents of reactions increased with increasing silyl peroxide decomposition which is consistent with our data shown in Figures 1 and 2.

Similar findings were also obtained with vinyldimethylbis(*t*-butyl peroxy)-silane or dimethylbis(*t*-butyl peroxy)silane in both Al—PE—Al composites and copper-polyethylene-copper composites.

FMIR spectra of tetrakis(*t*-butyl peroxy)silane promoted joints are interesting because they also exhibited Si—C absorptions around the 800 cm^{-1} region indicating the possible formation of silyl radicals through an induced cleavage at the silicon-oxygen bond. Our preliminary mass spectroscopic data seems to support such a hypothesis.

EFFECT OF QUENCHING

Although we have suggested that the improvement in adhesion at elevated temperatures results from the increasing extents of decomposition of the silyl peroxides, any significant property changes in the polyethylene interlayer would undoubtedly also influence the adhesive strength of the resulted composites, because a cohesive failure in the polyethylene phase is usually encountered during the peel test.

A series of quenching experiments were carried out in a similar manner as described by Tordella[10]. Our results are shown in Table V. Besides the dry-ice quenched specimens which showed substantially higher peel strength, no apparent effect was found, within experimental error, with a 25-fold change in cooling rate.

Cohesive failure in the polyethylene phase occurred for all specimens. However, the dry-ice quenched specimens showed dense formations of fine strands during the peel. Formation of such fine strands became less prolonged with decreasing cooling rate. We suspect that the higher peel strength of the

TABLE V
Effect of cooling rate

Cooling rate °C/min.	Peel strength lbs./in.	% thickness retention of PE interlayer
0.93	43.0	68
18	43.3	65
24	42.7	65
Dry ice quench	54.0	74

dry-ice quenched specimens is probably due to the additional energy required in the formation and separation of such a complex geometry in the polyethylene interlayer.

Retention in thickness of the polyethylene interlayers was fairly consistent for all the cooling rates. This can be attributed, at least in part, to the dimensional stability resulted from the silyl peroxide promoted cross-linking[6].

HYDROLYTIC STABILITY

It is well known that the application of organo-functional silanes in composite materials provides good retention in wet strength[11]. This phenomenon has been attributed by Plueddemann[12] to a favorable equilibrium toward bonding via polar groups in the polymer phase at the interface.

Silyl peroxide promoted bonds exhibit excellent hydrolytic stability when properly prepared. In fact, Al—PE—Al composites, adhered with vinyltris(*t*-butyl peroxy)silane, endured a 700 hr. boiling water test without any apparent loss in bond strength. When a high density polyethylene (Union Carbide DMD-7000) interlayer was employed, adhesion improved with increasing length of test which was presumably due to an annealing effect that resulted in a higher cohesive strength of the polyethylene interlayer.

However, when the above composites were bonded under conditions such that not all the silyl peroxide molecules were reacted in the system, they behaved differently. Adhesion of these composites declined gradually during the course of the test, but regained their initial strength upon drying[13], which is similar to the behavior of the organo-functional silanes[11,12].

A MECHANISTIC CONSIDERATION OF SILYL PEROXIDE PROMOTED ADHESION

The most striking difference between the silyl peroxides and the more conventional organo-functional silanes is that with the silyl peroxides bonding is effected thermally rather than via hydrolysis. On the basis of our findings described in this paper, we may draw the following conclusions:

(1) Adhesion is achieved primarily through chemical bonding rather than pure physical interactions.

(2) A silyl peroxide molecule must provide two or more reactive sites for reaction with either other silyl peroxide molecules and/or molecules of the substrates.

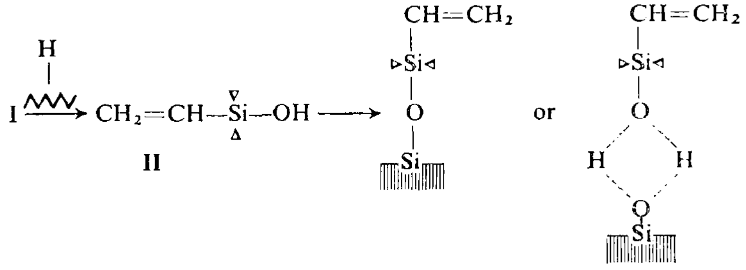
(3) Silyl peroxides are capable of grafting to the backbone of organic polymers through either their unsaturated functionalities or via their radical fragments.

(4) Upon thermal decomposition, the silicon moieties of silyl peroxides are linked together through siloxane bonds.

Let us now take the vinyltrist(*t*-butyl peroxy)silane as an example to illustrate the proposed mechanism of bonding. Upon heating, it undergoes primarily a homolytic cleavage to produce a siloxy radical (I) and an alkoxy radical:

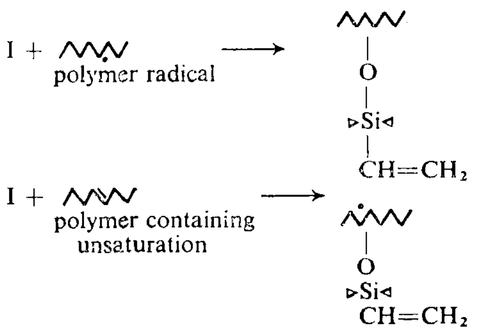
$$CH_2 = CH{-}Si(OO{-}CH_4H_9{-}t)_3 \longrightarrow \underset{\mathbf{I}}{CH_2 = CH{-}\overset{\nabla}{\underset{\Delta}{Si}}O\cdot} + t{-}C_4H_9O\cdot$$

where ∇ represents an undecomposed *t*-butyl peroxy group. Subsequent reactions of the siloxy radical depends on the nature of the surrounding molecules. When the reaction takes place at a polymer-glass interface, it presumably proceeds via hydrogen abstraction from the polymer molecule to form a silanol which may react with the silanol present on the glass surface forming either a disiloxane bond or a hydrogen bond[11]. A similar sequence of

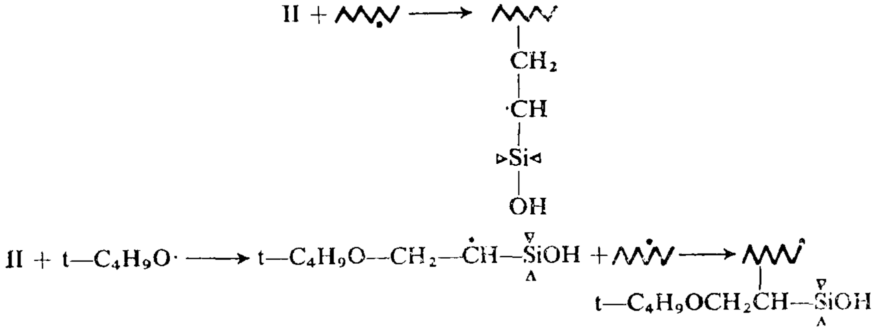


of reactions may also take place in systems where the glass is replaced by another inorganic material or metal.

The primary radicals, such as I, may bond to the polymeric matrix through either chain transfer reactions or couplings. For example:

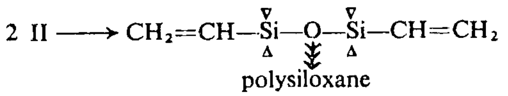


On the other hand, the undecomposed silyl peroxide molecules and species derived from the primary radicals, such as II, may undergo similar reactions through vinyl functionality either directly or indirectly as illustrated by the following examples:



$$\mathrm{II} + t\text{—}C_4H_9O\cdot \longrightarrow t\text{—}C_4H_9O\text{—}CH_2\text{—}\dot{C}H\text{—}\overset{\triangledown}{\underset{\vartriangle}{Si}}OH$$

If we disregard the occurrence of induced decomposition among certain silyl peroxides, the primary reaction taking place between two silyl peroxide molecules is believed to be condensation. The reaction would eventually result in the formation of either siloxane oligomers or polysiloxanes.



$$2\ \mathrm{II} \longrightarrow CH_2{=}CH\text{—}\overset{\triangledown}{\underset{\vartriangle}{Si}}\text{—}O\text{—}\overset{\triangledown}{\underset{\vartriangle}{Si}}\text{—}CH{=}CH_2$$

polysiloxane

Because of the excellent wettability and compatibility of the silyl peroxides with most inorganic and organic materials, formation of siloxane bonds would be expected to extend within the substrate matrices across the interface as a result of diffusion of the silyl peroxide molecules. This is consistent with the results of our FMIR study.

In summary, adhesion promotion with the silyl peroxides is primarily a chemical phenomenon. Formation of covalent bonds, including perhaps hydrogen bonding, through siloxane linkages extending across the interface, is believed to be chiefly responsible for the observed adhesion. Adhesion due to surface oxidation is not considered to be a major contributing factor with the silyl peroxide systems.

Acknowledgement

A sizable portion of results discussed in this paper is drawn from previous work collaborated with Dr. R. G. Shaw of this Research Department.

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