

Effect of Polymeric Silane Coupling Agents on Adhesion of Polypropylene and Polystyrene to Glass

HIROSHI INOUE and SHIGEMI KOHAMA, *Osaka Municipal Technical Research Institute, Kitaogi-machi, Kita-ku, Osaka, Japan*

Synopsis

The coupling performance of some polymeric silane compounds was compared with that of the monomeric silanes for adhesion of polypropylene (PP) and polystyrene (PS) to glass. A silylated poly-1,2-butadiene was found to be effective for PP and, on the other hand, some copolymers derived from styrenyl triethoxysilane or γ -methacryloxypropyl trimethoxysilane for PS. Benzoyl peroxide also showed a pronounced effect on the adhesion of PP, rather than that of PS. The adhesion strength was approximately correlated with the contact angles of the resin melts on the coated glass, intensively suggesting the dependence of compatibility between resinous matrix and coupling agent on the adhesion. Their critical surface tensions, thermal behavior, and infrared spectra were also measured to discuss the relationship between the surface constitution and the adhesion effect.

INTRODUCTION

As is known very well, silane compounds are often used to improve the reinforcing effect of some inorganic fillers in reinforced plastics (composites). These compounds play an important role in a bonding between an inorganic filler and a resinous matrix, and thus are called silane coupling agents, or adhesion promoters.

A silane coupling agent consists of two functional groups, i.e., an organofunctional group and a siliconfunctional group (alkoxy-, acetoxy-, or halo-silyl group). These groups can react with the resin and the inorganic surface to give strong bonds. On this basis, improvement in the mechanical properties of these composites can be achieved by use of these agents, although a rigid adhesion between them would produce a brittle and a crack-sensitive composite having low strength and resistance to temperature. In addition, it is a characteristic that the mentioned adhesion effect takes place in a wet condition.

Thermoplastic resins such as polyolefins and polystyrene which do not have any functional group to react with the coupling agent are not expected to show high reinforcement like thermosetting resins. However, improved adhesion between resinous matrix and inorganic filler may be obtained by using polymeric coupling agents. In this study, the purpose to use such polymeric compounds is as follows: (1) to increase the number of organofunctional groups per molecule; (2) to enhance the compatibility with resinous matrix,¹ and (3) to use as sizing agents on glass fiber.

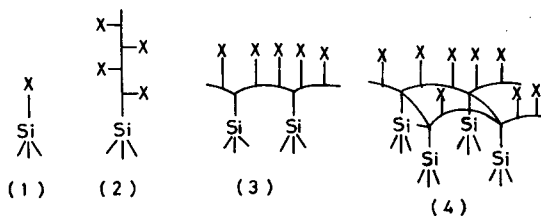


Fig. 1. Types of coupling agents.

Three types of the polymeric coupling agents (from 2 to 4 in Fig. 1) will be considered for the above purpose.

In Figure 1, X stands for an organofunctional group. Type 1 represents an ordinary monomeric coupling agent. In the polymeric ones, many X groups can be attached to a molecule. This does not indicate any superiority of type 2 over 1, because only one silyl group on the glass has to support many X groups under shear stress. In this discussion, it should be emphasized, of course, that the silyl group orients toward the inorganic surface to form a covalent bond or a hydrogen bond, which can withstand a high level of shear stress, although this picture is simplified. Type 4 shows a planar or three-dimensional main structure with both groups. From the practical point of view, however, this type cannot be used because of ready gel formation.

Type 3 is expected to have the highest coupling performance in the three types of the polymeric types, even if some problems still remain about its structure. In the present paper, effectiveness of coupling agents of type 3 will be described with respect to adhesion of inert resins such as polypropylene (PP) and polystyrene (PS) to glass.

The flexural properties as a measure of the coupling performance in the glass fiber-reinforced plastics were generally determined by the use of the following test samples: (a) compression-molded thermoplastic laminate,^{2,3} (b) injection-molded parts.^{4,5} In this study, however, a glass plate method was used instead of the above two methods because of experimental simplicity. The effectiveness of the polymeric coupling agents was discussed in comparison with that of the monomeric ones. Some factors which influence the effectiveness were also investigated, but the effect of moisture on the adhesiveness is not described in this paper.

EXPERIMENTAL

Silane Coupling Agents

Coupling agents used here are shown in Table I, showing both the monomeric and the polymeric ones. Their names are hereafter abbreviated as shown in Table I.

A151, A174, A187, and A1100 were the commercial products (Nippon Unicar Ltd.) and were used as such or after distillation. S and all of the polymeric coupling agents were prepared according to the procedures described in the literature or by means of the ordinary polymerization technique.

S: Manami and Nishizaki's method⁶ was used; bp 107°C/2 mm Hg (lit.⁶ 92–93°C/0.2 mm Hg).

TABLE I
Coupling Agents

Notation	Structure (composition)	Solvent
A151	$\text{CH}_2=\text{CHSi}(\text{OC}_2\text{H}_5)_3$	pH 3.1 H_2O + ethanol (20%)
A174	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{CCOOCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \end{array}$	pH 3.1 H_2O + ethanol (20%)
A187	$\begin{array}{c} \text{CH}_2\text{CHCH}_2\text{OCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3 \\ \diagdown \quad \diagup \\ \text{O} \end{array}$	H_2O
A1100	$\text{H}_2\text{NCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OC}_2\text{H}_5)_3$	H_2O
S	$\text{CH}_2=\text{CH} \begin{array}{c} \diagup \quad \diagdown \\ \text{C}_6\text{H}_4 \\ \diagdown \quad \diagup \end{array} \text{Si}(\text{OC}_2\text{H}_5)_3$	H_2O + ethanol (60%)
Mc	methyl methacrylate (92%)–A174 (8%)	toluene
BAc	Butyl acrylate (89%)–A174 (11%)	toluene
Gc	glycidyl methacrylate (88%)–A174 (12%)	THF
Vc	vinyl acetate (90%)–A174 (10%)	toluene
Sc	styrene (82%)–A174 (18%)	toluene
SSc	styrene (88%)–S (12%)	toluene
MMc	maleic anhydride (61%)–A151 (39%)	acetone
ANt	acrylonitrile (37%)–styrene (57%)–A174 (6%)	acetone
AAt	acrylamide (55%)–styrene (40%)–A174 (5%)	DMF
MAt	methylolacrylamide (38%)–styrene (49%)–A174 (13%)	DMF
Cr	crotonaldehyde (2%)–styrene (77%)–A151 (21%)	toluene
Bu	$\begin{array}{c} \text{Si}(\text{OC}_2\text{H}_5)_3 \qquad \qquad \qquad \text{Si}(\text{OC}_2\text{H}_5)_3 \\ \qquad \qquad \qquad \\ (\text{CH}_2)_3 \qquad \qquad \text{CH}=\text{CH}_2(\text{CH}_2)_3 \\ \qquad \qquad \qquad \\ \text{NHCO}-(\text{CH}_2\text{CH})- \dots -\text{CONH} \end{array}$	toluene

Random co- and terpolymers: Some monomers were polymerized in sealed tube by initiating with α, α' -azobisisobutyronitrile or benzoyl peroxide at 60° or 80°C. The contents of silyl monomer in these polymers were calculated to be about 10 mole-% by means of elemental analyses of C, N, and Si.

Bu: An end-carboxylated poly-1,2-butadiene (MW 2000) was converted to the end-acid chlorinated one with thionyl chloride, followed by reaction with A1100. Si content in polymer: Found 2.80%, calcd. 2.59%.

Glass Plates Coated with Coupling Agents

The glass plates (microslide glass, JIS 1st grade, 76 × 26 × 1 mm) were cleaned by immersing in nitric-sulfuric acid or sodium hydroxide-methanol-water solution, followed by rinsing with distilled water, and drying at 70–90°C for half a day. The solvents shown in Table I were used to apply the coupling agents to the glass plates. After immersing in the 1.0% solution, the glass plate was dried at room temperature and then at 50–60°C, 1 mm Hg or 80–90°C, atmospheric pressure for 5 hr. In the deposition of benzoyl peroxide (BPO), the glass plate was dried under reduced pressure at room temperature after immersing in the 0.5% ethanol solution.

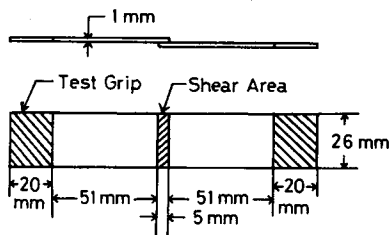


Fig. 2. Test specimen.

Evaluation of Adhesion Force

The following glass plate method was used to estimate the coupling performance.

PP and PS films (thickness, 40 and 20 μ , respectively) were interposed between two coated glass plates as shown in Figure 2. They were attached with the same glass plates as spacers, then lapped in aluminum foil, and put between two thin tin plates, followed by hot press at 2 kg/cm². After 10 min, the specimen was taken out from the press and allowed to be pressed under a 5-kg steelblock till it cooled. The tensile test was performed by the use of an Instron testing machine, Shimazu Autograph IS-5000, at 20°C and 65% relative humidity (R.H.).

Contact Angles (θ_m) of Resin Melts

The contact angles (θ_m) of the resin melts on the glass plate were measured by means of an Erma contact anglemeter (Goniometer type, Model G-II). Some disk chips (diameter 1 mm, height 0.5 mm) of the resins PS and poly(methyl methacrylate) (PMMA) as a reference resin, were placed on the glass surface under constant conditions of 200°C and 65% R.H. As they melted, the change in θ_m was followed as a function of time. The measurement was continued till θ_m became constant. The mean θ_m value was obtained by averaging after elimination of the maximum and the minimum values.

Critical Surface Tension (γ_c)

The sessile drop method was employed for the measurement of the advancing contact angles (θ) of some wetting liquids on the coated glass in order to estimate the critical surface tension (γ_c) at 20°C and 65% R.H. The contact angle was equilibrated after 2 min to give a constant value, i.e., not showing any change even after 20 min. The contact angles of at least five drops were measured and

TABLE II
Surface Tensions of Wetting Liquids at 20°C

Wetting liquid	Surface tension, dynes/cm	Reference
Water	72.8	7
Glycerol	63.3	8
Formamide	58.2	7
Ethylene glycol	49.0	8
Polyethylene glycol (P-300)	46.0	8
Dipropylene glycol	34.6	8

averaged except for the maximum and the minimum values. In these cases, the errors due to the reading and the heterogeneity of the surface were of the order of a few degrees.

The wetting liquids used here and their surface tensions are shown in Table II.

Infrared Spectra of Coupling Agents

The infrared spectra of the films and KBr disks of the polymeric coupling agents were measured by means of a Shimadzu infrared spectrophotometer IR-27G.

Thermal Analyses of Coupling Agents

Thermogravimetry (TG) and differential thermal analysis (DTA) were done with a Shimadzu Thermal Analyzer DT-2B.

RESULTS

Tensile Shear Strength of Test Specimens (Coupling Performance)

Not all the noncoated glass plates could form satisfactory test specimens in this experiment. The failure in most of the specimens occurred between the plastic film and the glass plate. Strong adhesion sometimes led to failure in the glass plate itself. Although it was difficult to obtain reproducible tensile shear strengths (abbreviated as TSS hereafter), the data could be regarded as a measure of the coupling performance. In Figures 3 and 4, the effect of the amount of the coupling agent and BPO on the TSS is shown in a case for the adhesion of PP to glass plate.

The TSS increased with increase in the amount of BPO, while the amount of coupling agent did not significantly affect the TSS. However, the amount of the agents is not especially considered from the following description. It should be noted in these results that the coupling agents with a TSS below 20 kg/cm² were considered as poor and those above 40 kg/cm², as very effective.

Figure 5 shows the effect of press temperature and BPO on the TSS. From Figure 5, BPO proved to have a pronounced effect on the TSS, while Gc itself was

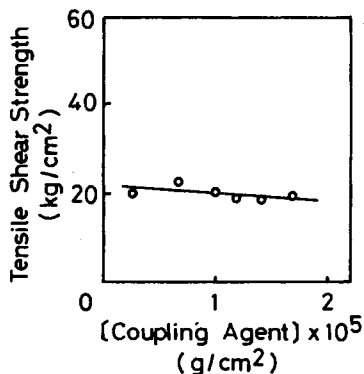


Fig. 3. Effect of amount of coupling agent on TSS in adhesion of PP to glass plate coated with Gc. Press temp., 250°C.

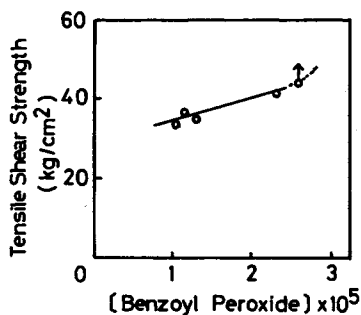


Fig. 4. Effect of amount of BPO on TSS in adhesion of PP to glass plate coated with GC. [Coupling agent] = 1×10^{-6} g/cm²; press temp., 225°C.

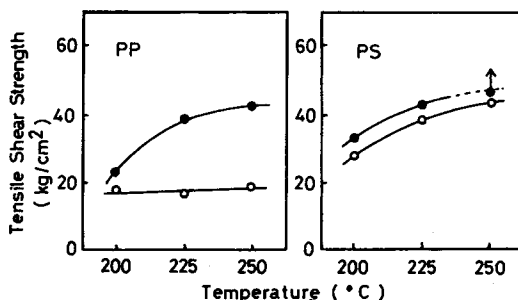


Fig. 5. Effect of press temperature and BPO on adhesion of PP (left) and PS (right) to glass plate coated with Gc: (○) in the absence of BPO; (●) in the presence of BPO.

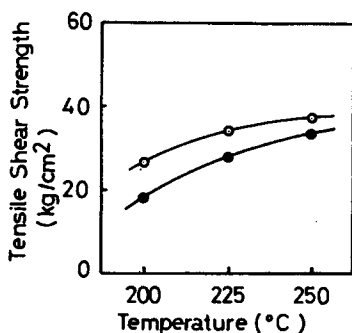


Fig. 6. TSS in adhesion of PP and PS to glass plate coated with Bu: (○) PP; (●) PS.

not satisfactory for strong adhesion between PP and glass. Some examples for evaluation of the effectiveness of the other coupling agents are illustrated in Figures 6 and 7.

Table III summarizes the effectiveness of these coupling agents in the absence and in the presence of BPO for PP and PS, in which the press temperature was maintained at 225°C as standard condition.

In the absence of BPO, outstanding activity for PP was not observed in these polymeric coupling agents, except for Bu. However, most monomeric ones were relatively effective, especially in A1100, as is known well. For the adhesion of PS to glass, some polymeric coupling agents such as Mc, Gc, SSc, Sc, ANt, and Cr exhibited good effectiveness, suggesting the importance of compatibility

TABLE III
Effectiveness of Coupling Agents^a

Coupling agent	Tensile shear strength, kg/cm ²	
	PP	PS
A151	39 (>47)	27 (41)
A174	39 (>66)	28 (>56)
A187	23 (29)	37 (42)
A1100	>46 (53)	>53 (>53)
S	>35 (>57)	>54 (47)
Mc	14 (21)	42 (56)
BAc	— (—)	24 (21)
Gc	16 (41)	38 (43)
Vc	17 (41)	22 (23)
Sc	12 (32)	>50 (36)
SSc	14 (52)	>59 (38)
MMc	30 (41)	34 (40)
ANt	22 (52)	>36 (35)
AAt	19 (24)	33 (30)
MAt	19 (26)	32 (39)
Cr	18 (>40)	46 (40)
Bu	34 (41)	25 (>29)

^a Values in parentheses represent those obtained in the presence of BPO.

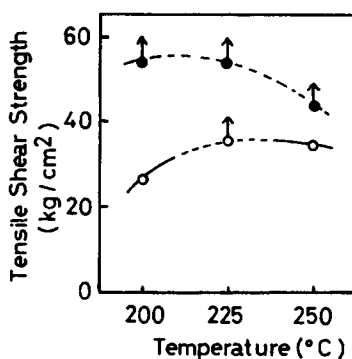


Fig. 7. TSS in adhesion of PP and PS to glass plate coated with S: (○) PP; (●) PS.

between the resin (PS) and the coupling agent. In the monomeric coupling agents, A1100 and S, in particular, appeared to be the most effective.

In the presence of BPO, besides A151, A174, S and Bu containing unsaturated groups, A1100, ANt and SSc were also very effective for PP, suggesting the formation of a covalent bond with crosslinking. The effect of BPO for PS was less significant than that for PP, probably due to easy oxidation of PP through a reaction with benzoyloxy radical.

It is necessary for the coupling agent to hydrolyze the silicon-functional group completely and to perform polycondensation of themselves together with the bond formation on the glass surface. From these points of view, the monomeric coupling agents would be favorable because they can be treated with aqueous or alcoholic solution. For the polymeric ones, on the other hand, aprotic solvents such as toluene and acetone used here were difficult to hydrolyze the group completely, even though the coated glass plates were subsequently immersed in

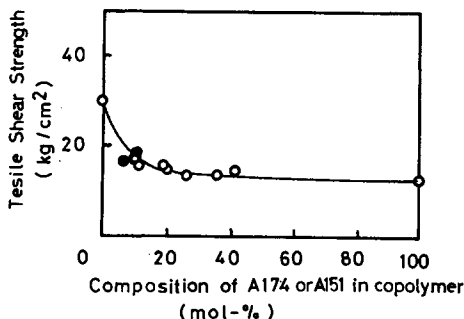


Fig. 8. Effect of copolymer composition in adhesion of PP to glass plate. Press temp., 225°C: (O) copolymers of A174 with glycidyl methacrylate; (●) copolymers of A151 with glycidyl methacrylate.

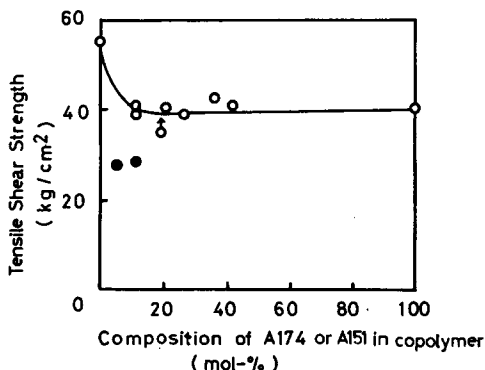


Fig. 9. Effect of copolymer composition in adhesion of PS to glass plate. Press temp., 225°C: (O) copolymers of A174 with glycidyl methacrylate; (●) copolymers of A151 with glycidyl methacrylate.

water. The following procedures were adopted for the polymeric ones in order to hydrolyze them fully: (a) The coated glass plate was boiled in 20% aqueous HCl solution for 20–30 min. (b) Dibutyltin dilaurate was added to the solution as a curing catalyst. (c) The emulsion was prepared with the copolymerization technique accompanied by hydrolysis to apply the glass plate.

The tensile tests of these specimens revealed the following. Procedure (a) gave somewhat better results, for instance, from 34 and 16 to 46 and 25 kg/cm² for Bu and Gc, respectively, in the adhesion of PP. Nevertheless, no special variation was observed in the case of PS. Dibutyltin dilaurate in procedure (b) gave the mentioned effect only for PP. In procedure (c), finally the TSS; for both resins were inferior to those in the controlled experiment because of the gel formation prior to treatment.

Copolymers with various compositions were tested with regard to TSS in order to see the effect of the trialkylsilyl group on the adhesion force. Figures 8 and 9 show the effect of the composition on the adhesion of PP and PS, respectively, on the glass plate coated with Gc.

It became apparent from Figures 8 and 9 that the TSS decreased with an increase of the content of silylmonomer (A174) for both PP and PS. These results indicate less importance of the silyl group on the adhesion. This also suggests

that the silyl group does not work specifically on the glass surface, probably implying the burying of most of the silyl group in the copolymer itself.

Contact Angles of Resin Melts

The contact angles (θ_m) of the resin melts on the coated glass plate were determined in terms of the wettability of the resins. It was difficult to get reproducible data owing to traces of void and water contained in the resin chip and heterogeneity of the glass surface. Therefore, if possible, many measurements (at least 5 points) were done to get improved precision. In the case of PP, the viscosity dropped down abruptly when it melted, quite different from the cases of amorphous polymers such as PS and PMMA. In addition, θ_m for PP was too small to be measured accurately.

The θ_m for PS and PMMA decreased with elapse of time, as shown in Figure 10. In Table IV, their θ_m values are summarized.

As shown in Table IV, the polymeric coupling agents containing the same monomer units (styrene and methyl methacrylate) as the resinous matrix exhibited low θ_m values as compared with the others, thus suggesting good wettability of the resins on the coated glass.

The effect of the copolymer composition on the θ_m is also shown in Figure 11.

An increase of the silyl group in the copolymer tends to correlate to an increase in θ_m , that is, poor wettability. The relationship between θ_m and TSS will also be described in the discussion.

TABLE IV
Contact Angles of Resin Melts on Coated Glass Plates at 200°C

Coupling agent	Contact angle, deg	
	PS	PMMA
Untreated glass		
NaOH-methanol-H ₂ O	21.7	23.5
HNO ₃ -H ₂ SO ₄	30.0	23.7
Treated glass		
A151	27.4	38.1
A174	28.3	24.7
A187	40.0	22.0
A1100	39.4 ^a	22.5 ^a
S	24.6	21.0
Mc	26.8	28.4
BAc	27.8 ^b	29.3 ^b
Gc	23.6	17.3
Vc	42.0	30.6
Sc	19.0	24.5
SSc	31.8	31.5
MMc	20.0	31.5
ANt	17.8	26.5
AAt	62.9	55.4
MAt	41.5	37.5
Cr	26.5	26.3
Bu	28.5	26.9
	48.5	39.8
	41.6	22.0

^a Methyl ethyl ketone was used for the solvent.

^b Not followed by immersion in water.

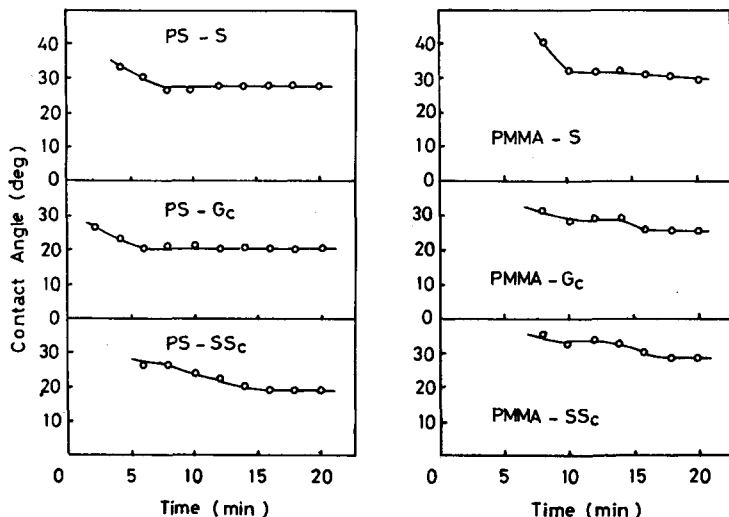


Fig. 10. Time dependence of contact angles for PS (left) and PMMA (right) at 200°C.

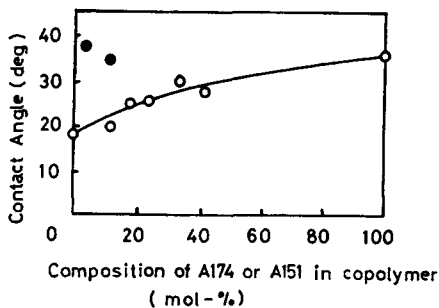


Fig. 11. Effect of copolymer composition on contact angles of PS melts on glass plate: (O) copolymers of A174 with glycidyl methacrylate; (●) copolymers of A151 with glycidyl methacrylate.

Critical Surface Tensions of Films Formed from Coupling Agents

The critical surface tensions (γ_c) of the coated glasses were determined by a Zisman method to determine the wettability of the surface by some liquids. The Zisman plots ($\cos \theta$ versus surface tension of wetting liquid) are illustrated in Figures 12 and 13.

In these measurements, all of the wetting liquids did not show any remarkable contact angle hysteresis, suggesting the absence of swelling and dissolution of the surface film by the wetting liquids. A satisfactory linear relationship evidently exists in both figures. The critical surface tension (γ_c) refers to the intercept of a horizontal line $\cos \theta = 1$ with the extrapolated line of the plots. The results are summarized in Table V.

The γ_c values of the polymeric coupling agents derived from styrene and methyl methacrylate were found to resemble closely those of their homopolymers (PS, 33, and PMMA, 38 dynes/cm),⁹ indicating that the wetting properties of the surface depend on their bulk composition. End-silylated poly-1,2-butadiene (BU), which gave the smallest γ_c in the polymeric coupling agents, also had a close value to randomly silylated poly-1,2-butadiene (30 dynes/cm).¹⁰ It can

TABLE V
Critical Surface Tensions (γ_c) of the Coupling Agent Films

Coupling agent	γ_c , dynes/cm
A1100	31
A174	32
A187	34
S	34
A151	35
Bu	28
Sc	32
SSc	32
AAAt	33
MAt	34
Vc	35
Mc	37
Gc	37
PA174*	38

* Homopolymer of A174.

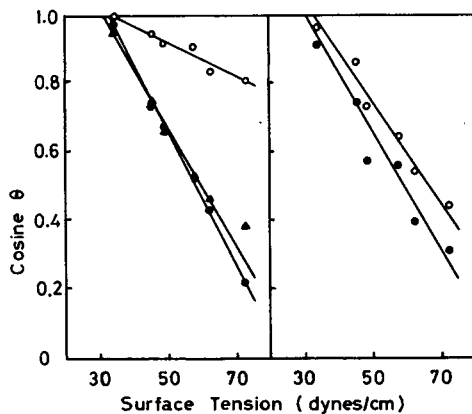


Fig. 12. Zisman plots for monomeric coupling agents. Left: (○) A151; (●) S; (▲) A174. Right: (○) A187; (●) A1100.

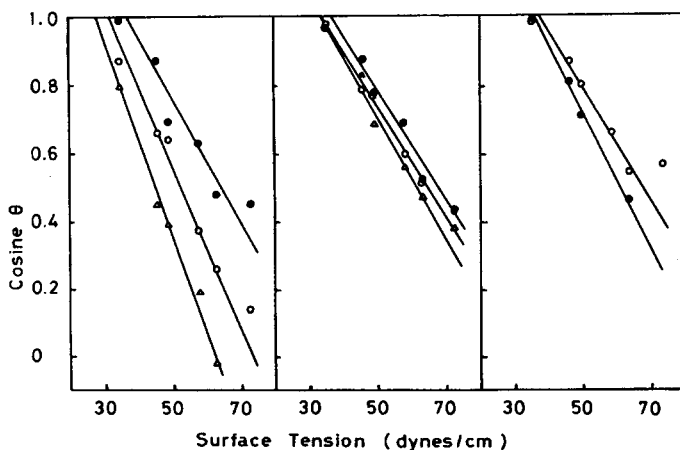


Fig. 13. Zisman plots for polymeric coupling agents. Left: (●) Mc; (○) SSc; (Δ) Bu. Center: (●) Gc; (○) MAt; (Δ) AAAt. Right: (○) PA174; (●) Vc.

be understood readily that Bu was an effective coupling agent for PP ($\gamma_c = 22$ dynes/cm) because of its low γ_c . In the monomeric coupling agents, A1100 film with a low γ_c is subject to wetting by these liquids forming hydrogen bond, due to its hydrophobic character.

Infrared Spectra of Polymeric Coupling Agents

The infrared spectra are a good means following the progress of the hydrolysis-polycondensation process of the silicon-functional group in the agent. Attenuated total reflection spectroscopy (ATR) should yield such information about the surface and the interface structure of coupling agent. The attempt, however, failed because the intensity was too weak to identify. Therefore, the usual transmission spectra of films or KBr disks were measured. In these measurements, severe hydrolysis conditions, such as immersion in a 20% HCl aqueous solution or reflux in the same solution, were necessary to make clear the intensity change of the stretching frequencies of the alkoxy silyl $\nu_{\text{Si-O-C}}$, and of the polysiloxane $\nu_{\text{Si-O-Si}}$. This is due to low content of the silyl group in the copolymers and to the overlap with the other bands in the spectra.

The spectra from 1200 to 950 cm^{-1} are illustrated in Figure 14. In these infrared spectra, a characteristic band $\nu_{\text{Si-O-C}}$ at 1080 cm^{-1} showed decreased intensity with progress of the hydrolysis, while the $\nu_{\text{Si-O-Si}}$ at nearly 1060 cm^{-1} tended to show increased intensity. Of course, O—H stretching frequency due to hydrogen-bonded hydroxyls appeared broadly in the vicinity of 3400 cm^{-1} . Any intensity change was not observed in the other bands. The spectra for Gc showed a typical change from the unhydrolyzed copolymer to the emulsion, as apparent in Figure 14. Such coexistence of both the hydrolysis and the polycondensation properly indicates occurrence of a reaction of the silanol group in the hydrolyzate with the glass surface, or the formation of a hydrogen bond between them.

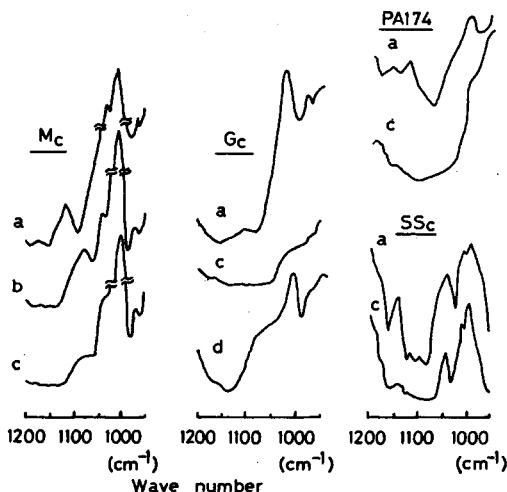


Fig. 14. Infrared spectra of the polymeric coupling agents and their hydrolyzates: (a) unhydrolyzed; (b) hydrolyzed in 20% HCl aq. soln. at room temp. for 1 day; (c) hydrolyzed in 20% HCl aq. soln. at 100°C for 1 hr; (d) emulsion copolymer.

Thermal Analyses of Polymeric Coupling Agents

The TG and DTA afford some information about thermal change of the coupling agents on adhesion. Their thermograms are illustrated in Figures 15, 16, and 17.

In the case of MAT in Figure 15, the first drop in weight loss at 120°C represents the breaking of both methoxy in the silicon-functional group and methylol in the methylolamide group,¹¹ reaching 17% loss at 310°C. Just above that temperature, the main chain completely degraded with a residue of silica or silicon carbide. On actual adhesion conditions (200–250°C), the generation of the radical species must occur together with loss of the functional groups to induce a reaction with the resinous matrix and to form a covalent bond. In fact, MAT was not as effective in the adhesion of both PP and PS. Thus, it should be considered that a problem still remains unsolved with respect to a defect of adhesion due to the evolved gases.

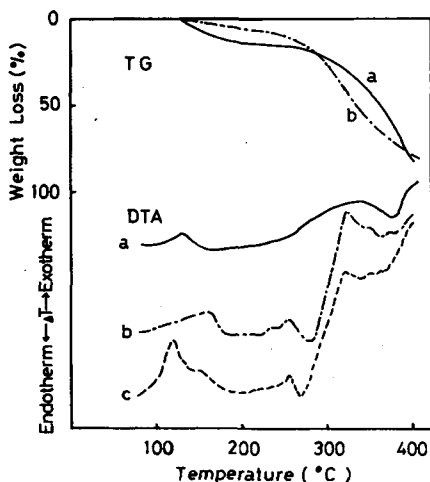


Fig. 15. Thermograms of MAT and Gc: (a) MAT; (b) hydrolyzate of Gc; (c) hydrolyzate of Gc + 5 wt-% of BPO.

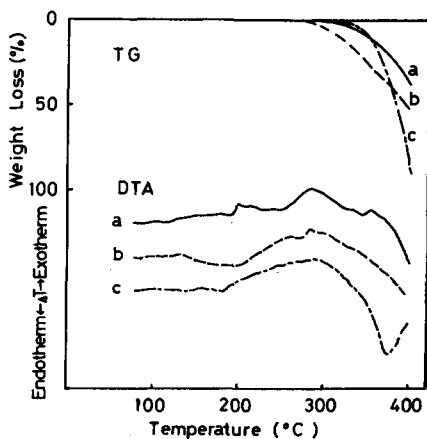


Fig. 16. Thermograms of SSc: (a) SSc; (b) hydrolyzate of SSc; (c) PS.

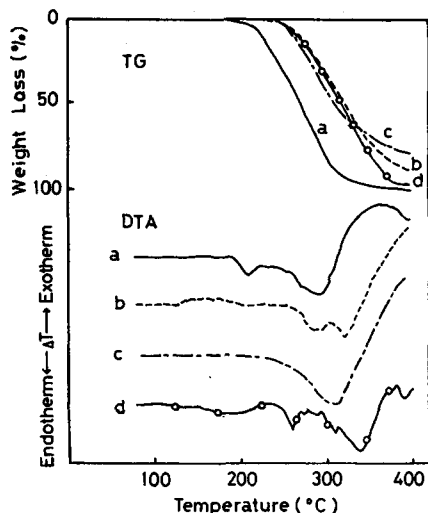


Fig. 17. Thermograms of Mc: (a) Mc; (b) hydrolyzate of Mc; (c) hydrolyzate of Mc + 10 wt-% of SiO_2 ; (d) PMMA.

Meanwhile, addition of BPO gave a sharp exothermic peak at 120°C in the DTA curve of Gc, as shown in Figure 15, attributed to the decomposition of BPO and the induced crosslinking. The crosslinking seems to start with hydrogen abstraction at the glycidoxy group of Gc and the methyl group of PP, followed by coupling in the PP-Gc-glass system. It is probable on this basis that the marked effect of BPO was observed in PP superior to PS.

In Figure 16, the thermograms of SSc and its hydrolyzate did not significantly differ from those of PS. The first drop of weight loss was not observed as that of MAT, although the weight loss due to the degradation of the ethoxy group should reach 10% on complete elimination of the same group. In the polymethacrylates, as shown in Figure 17, the hydrolyzate and silica hydrolyzate had heat stabilities slightly superior to that of the unhydrolyzed copolymer. Complex endothermic patterns of the degradation in their DTA's cannot explain the difference between them.

From these thermal analyses, their heat stabilities turned out not to be improved even by crosslinking with hydrolysis polycondensation and, in addition, filling of silica in spite of their good mechanical properties.

DISCUSSION

The test method used here proved to be useful for determination of the adhesion force. Results with the monomeric coupling agents sufficiently correspond to those of the flexural properties described in the literature.⁴ Therefore, the data of the tests could be used as an index of coupling performance, although the stress in the tensile test of the lap joint was said to concentrate at the adhesion edge because of maldistribution of the load.¹²

Now, generally speaking, the polymeric coupling agents were not as effective as the monomeric ones. This may be attributed to the following two reasons. One is the absence of the active functional group in the polymeric ones to give the covalent bond with the resin, except for the case of Bu. And the other is

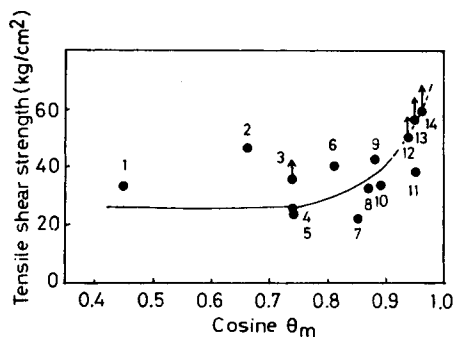


Fig. 18. Relationship between TSS and $\cos \theta_m$ for PS: (1) MMc; (2) Cr; (3) ANt; (4) BAc; (5) Bu; (6) PA174; (7) Vc; (8) MAT; (9) Mc; (10) AAt; (11) Gc; (12) Sc; (13) poly(glycidyl methacrylate); (14) SSc.

the burying of the functional groups in the copolymer. On the contrary, S, Sc, and SSc are apparently favorable in the adhesion of PS. This is attributed to the good compatibility with the resin (PS). In this way, The TSS's of such inert resins as PP and PS intensively depend on the compatibility.

Compatibility factor can be discussed in terms of wettability of the resin melts on the glass surface, giving a measure of adhesiveness. The dependence of the θ_m (represented as $\cos \theta_m$ in the plotting) at 200°C on the TSS is illustrated in Figure 18 for the polymeric coupling agents.

Increasing the $\cos \theta_m$ tends to increase the TSS, with some scatter. This suggests that the compatibility between the resin and the coupling agent plays an important role in the adhesion. Such scatter is not only due to the reading errors, but also to the other factors, that is formation of covalent bond between them. A1100 and S with small θ_m values also resulted in high adhesive effect.

A151, A174, S, and Bu, containing unsaturated double bonds, can induce the generation of some radical species followed by the addition to the double bond, giving crosslinking during heating. The amino group in A1100 is especially subject to oxidation to form covalent bonds. In these cases, peroxide has a remarkable effect on the adhesion force, also suggesting the formation of a covalent bond between the resin and the coupling agent.

The critical surface tension (γ_c) of the films closely correlates to the wetting properties characteristic of the surface constitution. The results of the polymeric coupling agent shown in Table V evidently indicate that most of the silyl groups may not appear on the surface, but may be buried in the copolymer, because the γ_c values of the copolymer films are close to those of the homopolymers formed from the main components of the copolymers. Thus, the surface constitution is nearly equal to the bulk constitution.¹³ These γ_c values can be approximately correlated with the TSS. This means that the coupling agents with γ_c values close to those of the resinous matrix give good adhesiveness, for example, Bu for PP, and SSc and Sc for PS. A linear relationship between γ_c and adhesion strength was reported already for the adhesion with epoxy resin (surface tension, 50 dynes/cm) by Levine et al.¹⁴ However, it should be considered that the smaller $|\gamma_c - \gamma_r|$ (where γ_r stands for the γ_c of the resinous matrix), the stronger the adhesion becomes. This correlation was found to hold approximately for PP ($\gamma_c = 22$ dynes/cm) and PS ($\gamma_c = 33$ dynes/cm). This can be explained

on the basis of good correlations between the γ_c and solubility parameter¹⁵ and, furthermore, between the solubility parameter and the flexural strength in PS laminate.²

The interaction of the silicon-functional group with the glass surface has been intensively studied by many investigators mainly by means of infrared spectroscopy. No direct evidence was obtained with regard to the formation of the covalent bond between glass surface and coupling agent in this study. The infrared transmission spectra evidently showed the formation of O—H and Si—O—Si bonds. The copolymer emulsion, nevertheless, could not give good adhesion, because of gel formation prior to the treatment on the glass plate.

Besides coupling between resin and inorganic filler, the resin itself can be improved in its mechanical properties by the crosslinking itself, accompanied by hydrolysis polycondensation. An example was given in the copolymer of vinylsilane with vinyl chloride.¹⁶ The coupling agent layer with a crosslinked structure on a adherened should be able to bear sufficiently against tensile shear.

References

1. E. P. Plueddemann, *Appl. Polym. Symposia*, **19**, 75 (1972).
2. E. D. Plueddemann, S. P. I., 20th Ann. Tech. Conf. Reinforced Plastics Div., Chicago, Feb. 1965.
3. S. Sterman and J. C. Marsdem, S. P. I., 21st Ann. Tech. Conf. Reinforced Plastics Div., Chicago, Feb. 1966.
4. R. V. Viletti, H. T. Plant, and R. T. Maher, *Mod. Plast.*, **45**(5), 12 (1968).
5. J. T. Engelhardt, F. G. Krantz, T. E. Phillips, J. A. Preston, and R. P. Wood, S. P. I., 22nd Ann. Tech. Conf. Reinforced Plastic Div., Washington, Jan. 1967.
6. H. Manami and S. Nishizaki, *Kogyo Kagaku Zasshi* (Japan), **63**, 366 (1960).
7. W. D. Bascom, *Macromolecules*, **5**, 729 (1972).
8. K. Kamagata and M. Toyama, *J. Appl. Polym. Sci.*, **18**, 167 (1974).
9. W. A. Zisman, *Ind. Eng. Chem.*, **55**(10), 18 (1963).
10. J. Miron, B. Bhatt, and I. Skeist, *J. Adhesion*, **4**, 275 (1972).
11. H. Kamogawa and T. Sekiya, *Kogyo Kagaku Zasshi* (Japan), **63**, 1636 (1960).
12. M. Golanand and E. Reissner, *J. Appl. Mech.*, **11**, 417 (1944).
13. L. H. Lee, *J. Polym. Sci. A-2*, **5**, 1103 (1967).
14. M. Levine, G. Ilkka, and P. Weiss, *J. Polym. Sci.*, **B2**, 915 (1964).
15. J. L. Gardon, *J. Phys. Chem.*, **67**, 1935 (1963).
16. R. Bunig and S. Frick, *Angew. Makromol. Chem.*, **21**, 1 (1972).

Received December 5, 1974

Revised December 12, 1974