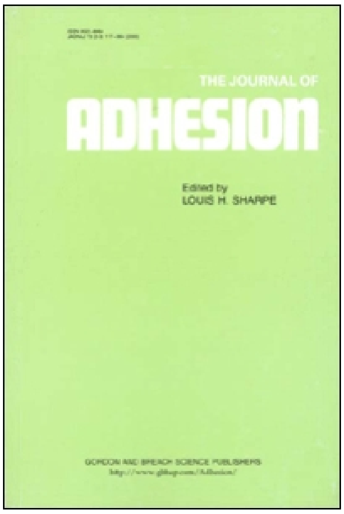

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Adhesion of Polypropylene Sheet with Steel Plates

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Adhesion of polypropylene sheet with steel plate was investigated using a mixed adhesive which was composed of a silane coupling agent with peroxide. This adhesive was applied to both surfaces of polypropylene sheet by brushing or spraying. A steel/polypropylene/steel laminated structure was formed at around 200°C. The effects of the bonding conditions on peel strength were investigated in the laminates. Considerable reduction of the amount of the adhesive used was achieved by adopting a spraying technique, and excellent peel strength was attained.

KEY WORDS Polypropylene sheet; steel plate; adhesion; laminated plate; silane coupling agent; peroxide.

INTRODUCTION

Steel/polypropylene/steel laminates have a great many uses, because of their outstanding properties with respect to vibrational absorbency and reduction of weight. The usual method of bonding of steel plates with polypropylene sheet in this laminate has been as follows. The polypropylene is modified by mixing with adhesive so as to have bonding properties in itself, and then the sheet is bonded to steel plates.[1] However, in this method, it is very difficult to control the quantity of adhesive which takes part in the bonding. Furthermore, the adhesive exists not only on the surface of polypropylene sheet, but also inside the sheet. The adhesive present inside the sheet does not take part in the adhesion, and is wasteful. It is desirable that the adhesive exists only on the surface of the sheet, before bonding.

In this study, the laminate was prepared by brushing or spraying adhesives on the surfaces of the polypropylene sheet. We succeeded in making sandwich laminated steel plates having high peel strength with the use of an extremely small amount of adhesive. Details regarding the laminates will be discussed. The details regarding failure mode in peel tests will be presented elsewhere.[2]

EXPERIMENTAL

Experiments were classified into Experiments A and B according to the method of application of the adhesive. Experiment A corresponds to brushing and Experiment B corresponds to spraying.

Materials

Ethylenepropylene block copolymer ZS-633 (Ube Industries, Ltd., Tokyo, Japan) was used as the core material. The melting point was determined by differential scanning calorimetry (DSC). There was a small melting peak at 121.7°C in addition to the large peak at 162.7°C. It is considered that the melting point of 162.7°C is due to polypropylene (ZS-633), and that the small melting peak shown at 121.7°C is due to the ethylene group present as block-structure, where the ethylene content is estimated to be 15 mol%. The steel plate (supplied by Shin Nippon Steel Co. Ltd., Tokyo, Japan), as shown in Table I, was a special grade and was used as the skin material of the laminate. Liquid silane coupling agent KBM503 (Shinetsu Chem. Co. Ltd., Tokyo, Japan) was used as the adhesive. Silane coupling agents have a hydrolyzable group which reacts with inorganic materials and an organic reactive group which chemically reacts with organic materials. A silane appears to be most appropriate for the bonding of polypropylene sheet with steel plates because it can build cross-linking at the interface between the inorganic and the organic materials. However, polyolefins such as polypropylene have high crystallinity and nonpolarity, and so the surface of polypropylene sheet must be activated by the use of an oxidizing agent. In this study, peroxide Perbutyl Z (Nihon Yushi Co. Ltd., Tokyo, Japan) was used to activate the surfaces. Details of all these materials are shown in Table II. In this study, the mixture of silane coupling agent with peroxide was used and is called the mixed adhesive. Without mixing silane coupling agent with peroxide, the adhesion experiment of polypropylene sheet with steel plate was carried out, but no peel strength was observed. Additionally, when the surface of polypropylene sheet was treated with peroxide alone, the sheet shrank quickly, so that it was very difficult to conduct the adhesion experiment. Therefore, it is desirable that the silane coupling agent and peroxide are used as a mixture.

TABLE I
Constituents of steel plate used in this study as determined by use of ESCA

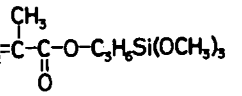
	Constituents[a]/wt.%				
Material	C	Si	Mn	P	S
Steel plate	0.16	0.50	0.14	0.04	0.05

[a] Constituents other than Fe and O.

TABLE II
Materials used in this study

Material (Trade name)	Chemical name	Properties
Polypropylene (ZS-633)	Ethylenepropylene-blockcopolymer	Propyrene : ethylene = 85 : 15 (mol%) M.F.I. = 0.35
Silane coupling agent* (KBM-503)	r-Methacryloxypropyl-trimethoxysilane	M.W. = 248.4 Sp.gr. (25°C) = 1.04 B.p. = 255°C
Peroxide** (Perbutyl Z)	t-Butylperoxybenzoate	Purity = 98% min

*



$CH_2{=}C(CH_3){-}C({=}O){-}O{-}C_3H_6Si(OCH_3)_3$

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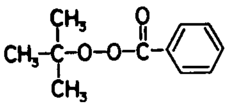

Apparatus

Spraying apparatus A spraying apparatus was designed and made by us for applying the mixed adhesive to polypropylene sheets. The equipment is made of aluminum, except for the body of the spray gun and the belt of the conveyor. This apparatus is schematically illustrated in Figure 2, where the adherend is fixed by the holder and moved in the *X* direction by actuating the conveyor with a motor. The mixed adhesive is sucked up and is sprayed on the adherend. The profile of the spray gun is shown in Table III. The method of application will be explained in detail in the section concerning experimental procedure.

Hot-press A desktop test press SA-302(II)(Tester Industries, Ltd., Tokyo, Japan) was used in order to form the steel/polypropylene/steel bonds.

TABLE III
Specifications of spray gun

Category	Air spray gun
Atomization	Outside mixed type
Supply of adhesive	Suctional type
Narrowest clearance of nozzle for	
compressed gas	ϕ0.84 mm
adhesives	ϕ0.47 mm
Compressed gas for use	N_2
Pressure of compressed gas	2.9×10^5 Pa

Peel testing machine A Shimadzu autograph AG-10TA(Shimadzu Seisakusyo, Ltd., Kyoto, Japan) was used to test the laminate in a T-peel mode.

Surface roughness A Surfcom 304B(Tokyo Seimitsu, Ltd., Tokyo, Japan) was used for measuring surface roughness of the steel plates. This instrument has a contact stylus whose point has a radius of 5 μm and is a 90° conical diamond. In measuring, the cutoff value was 0.8 mm and the undulation was excluded.

Experimental procedure

Experiment A 50 × 150 × 0.25 mm steel plates were degreased with absorbent cotton containing acetone, and 50 × 100 × 0.5 mm polypropylene sheets were also degreased with acetone. The absorbent cotton was repeatedly renewed in order to prevent recontamination.[3] After the mixed adhesive was applied to both surfaces of the degreased polypropylene sheet by brushing, the polypropylene sheet was sandwiched between two degreased steel plates. These were pressed at 1216N at 200°C, as shown in Figure 1. After removal from the press, they were allowed to air cool.

Experiment B In Experiment B, the mixed adhesive was sprayed with the spraying apparatus shown in Figure 2.

To apply the mixed adhesive to both surfaces of the adherend, a holder was used to hold the adherend above the conveyor surface. When the adherend moves in X direction on the belt conveyor, the mixed adhesive is uniformly sprayed on the adherend. The adherend was then turned over on the belt conveyor and the adhesive was sprayed on the reverse side of the polypropylene. The amount of the mixed adhesive on the adherend was controlled by changing the distance between the spray gun and the adherend or changing the moving speed of the adherend in the X direction.

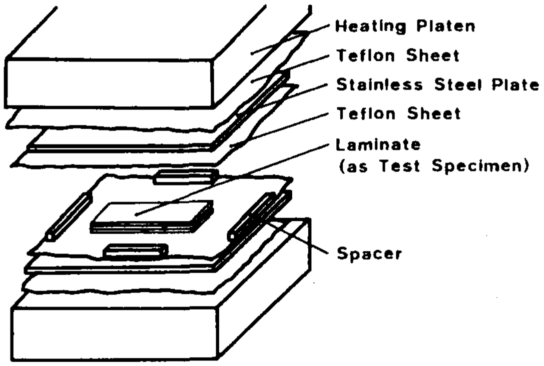

FIGURE 1 Arrangement for adhesion of polypropylene sheet with steel plates.

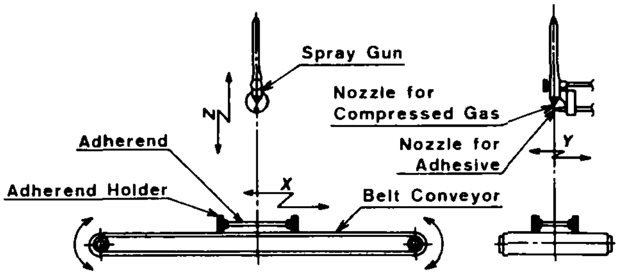

FIGURE 2 Model of adhesive spraying apparatus.

The procedure of lamination in Experiment B was as follows. The surface of the 20 × 150 × 0.25 mm steel plate was polished with a piece of #600 emery paper. The emery paper was used only once to prevent recontamination.[3] Furthermore, since it was considered that the degree of polishing would be dependent on the individual doing the polishing, all steel plates were polished by one person, and each plate was abraded the same number of times. The polished steel plates and 20 × 50 × 0.5 mm polypropylene sheet were degreased with a Kimwipe® tissue L-100 (Jujo Kimberly Co. Ltd., Tokyo, Japan) containing acetone. Each tissue was used only once. The sheet with applied mixed adhesive was sandwiched between the degreased steel plates. The assembly was then pressed at 4905N, as shown in Figure 1. After removal from the press, they were allowed to air cool.

T-peel test The laminates prepared in Experiment A or B were tested in peel within a week after bonding. Peel strength of the laminates was obtained by a T-peel test with an autograph which is a tension tester. The cross head speed of the autograph was 10 mm/min in Experiment A and 100 mm/min in Experiment B. Though Experiment A disagrees with Experiment B on speed, there was no especial reason for the difference. The peel strength at the peel rate of

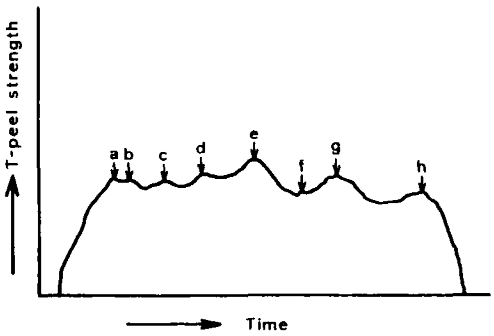

FIGURE 3 Profile of T-peel strength curve: a–h indicate positions picked up for calculation of peel strength.

100 mm/min increased about 23% as compared with that at 10 mm/min in Experiment B. Therefore, this fact must be considered in comparing the result in Experiment A with that in Experiment B.

The averaged value of peaks read off from the curves of three test specimens was adopted for peel strength. This method for peel strength is specified on JIS (Japanese Industrial Standard) K6854-1977.[4] An example of peel strength *vs.* time is shown in Figure 3.

RESULTS AND DISCUSSION

Experiment A

First, the effect of bonding conditions on peel strength in Experiment A was investigated. The effect of the melting point of the polypropylene sheet and the reactivity of the mixed adhesive should be taken into account in the choice of the pressing temperature. It is desirable that the polypropylene sheet be molten in order to allow the sheet and the steel plate to come into intimate contact. Further, according to the supplier's catalog, the silane coupling agent with the peroxide increases adhesion at 150–250°C. In consideration of this reaction temperature, a pre-experiment for choosing the pressing temperature was carried out. It was determined that the mixture remained in a liquid state in the region of temperature below 150°C and did not show an adhesion reaction. Therefore, it was decided that the pressing temperature should be set over 150°C. Thus, a pressing temperature of 200°C was chosen to satisfy both the requirements. The pressing time was set at 180 s, because the bonding reaction requires some period of time.

Thus, the oxidation of the polypropylene sheet surface and bonding the sheet with the steel plates was carried out at the same time. The effect of the mixing ratio of peroxide to silane coupling agent on peel strength was examined under these conditions. The effect of the mixing ratio on peel strength is shown in Figure 4. The peel strength increased with the proportion of silane coupling agent

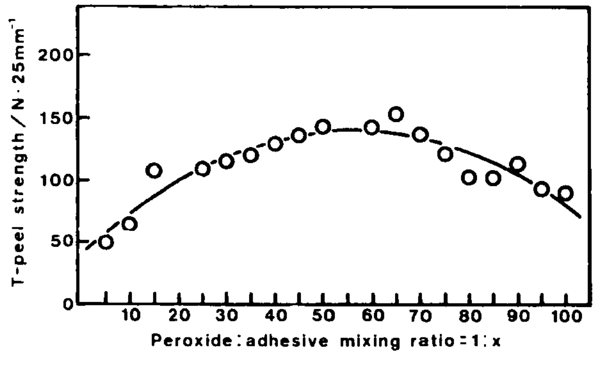

FIGURE 4 Effect of mixing ratio of silane coupling agent to peroxide by volume on peel strength. Pressing temperature, 200°C; pressing time, 180 s; method of application, brushing.

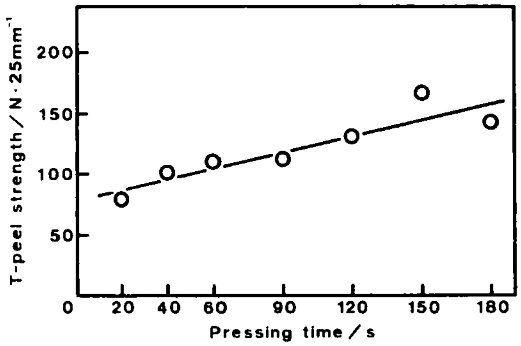

FIGURE 5 Effect of pressing time on peel strength. Mixing ratio of peroxide : silane coupling agent by volume, 1 : 50; pressing temperature, 200°C; method of application, brushing.

in the mixed adhesive in the region of mixing ratio smaller than 1:50 or 55 (peroxide: silane coupling agent). The strength decreased with the increase in the ratio. The peel strength was found to be maximized at a ratio of 1:50. The amount of the mixed adhesive on the polypropylene was around 4 mg/cm^2, though the value was somewhat variable.

The effect of the pressing time on peel strength is shown in Figure 5. The peel strength reached a maximum value at the mixing ratio of 1:50, as described above, and increased linearly with the pressing time. It seems that some period of time is required to attain good adhesion. The reaction period should be decided by taking into account the effect of the quantity of adhesive spread on the polypropylene. In this case, a pressing time of nearly 3 minutes is required in order to complete adhesion. The maximum peel strength was 168N/25 mm in Experiment A. The calculated thickness of the adhesive layer lying between the polypropylene sheet and the steel plate was 38.5 μm.

Experiment B

In Experiment A, the quantitative control of the adhesive and uniform application were very difficult. In Experiment B, the disadvantages in Experiment A were overcome by adopting a spraying method.

The optimum mixing ratio was examined when a small amount of the adhesive was applied. The effect of the mixing ratio on peel strength is shown in Figure 6. The amount of the mixed adhesive was set at 0.1 mg/cm^2 because one of the purposes of Experiment B was that the adhesive had to be applied as small as possible in an amount. The pressing temperature was 200°C in Experiment B as well as in A. The pressing time in Experiment B was set at 90 s, shorter than that in Experiment A, because the amount of adhesive in Experiment B decreased by approximately one order as compared with that in Experiment A. This selection was based on the consideration that the smaller amount of adhesive requires a shorter bonding time.

As compared with the same experiment in Experiment A, the maximum in the

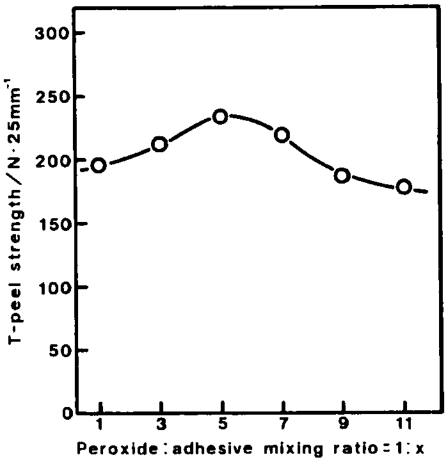

FIGURE 6 Effect of mixing ratio of silane coupling agent to peroxide by volume on peel strength. Amount of mixed adhesive, 0.1 mg/cm^2; pressing temperature, 200°C; pressing time, 90 s; method of application, spraying.

peel strength shifted to a lower level of the mixing ratio of silane coupling agent and peroxide, as shown in Figure 6. It seems that this shift was caused by the change in absolute quantity of peroxide in the mixed adhesive, as follows. When the amount of the mixed adhesive at the mixing ratio of 1:50 decreases from 4 mg/cm^2 to 0.1 mg/cm^2, the absolute quantity of peroxide decreases from 7.84×10^{-2} mg/cm^2 to 1.96×10^{-3} mg/cm^2. In Experiment B, 0.1 mg/cm^2 adhesive was used. In this case, however, the mixing ratio showing the maximum strength was at 1:5, so that 1.67×10^{-2} mg/cm^2 of peroxide was included in the

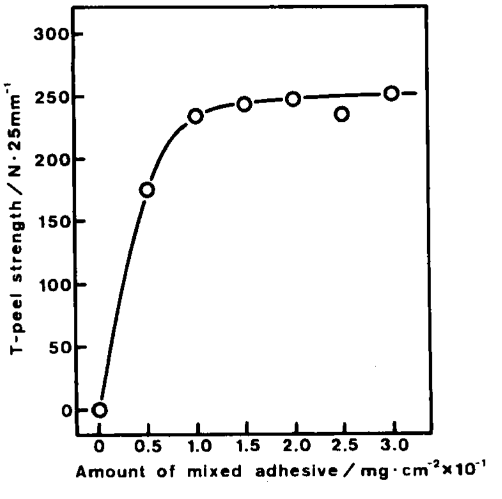

FIGURE 7 Effect of amount of mixed adhesive on peel strength. Mixing ratio of peroxide:silane coupling agent by volume, 1:5; pressing temperature, 200°C; pressing time, 90 s; method of application, spraying.

mixed adhesive. Therefore, the shift in the mixing ratio to a lower level leads to an increase in the absolute quantity of peroxide. Sufficient oxidization of the surface of the sheet is therefore attained, even though the amount of the mixed adhesive decreases. Thus, the position showing maximum strength shifted from higher to lower mixing ratio, as shown in Figures 4 and 6.

The effect of amount of the mixed adhesive on peel strength is shown in Figure 7, where the mixing ratio is 1:5. The peel strength rapidly decreased in the region of less than 0.1 mg/cm^2. Additionally, when the amount is zero, the adhesion by the anchoring effect[5] will occur without the adhesive. However, this bonding force is very weak, and such a laminate was easily peeled.

In the region of adhesive quantity from 0.1 mg/cm^2 to 0.3 mg/cm^2 the peel strength became constant, with a value of 245N/25 mm. The quantity of 0.1 mg/cm^2 corresponds to an adhesive layer of 0.96 μm in thickness. In general, peel strength is believed to increase with adhesive thickness.[6–8] However, in this case, it is noteworthy that the peel strength in Experiment B increased about 46% over that in Experiment A in spite of the reduction of the amount of adhesive from 4 mg/cm^2 to 0.1 mg/cm^2, though there is a difference due to the variation in peel rate between Experiment A and B. Siloxanes are inherently weak materials and a greater thickness of the adhesive could lead to cohesive failure in the siloxane. This provides an explanation as to why the smaller amount of adhesive led to higher peel strength.

The effect of the pressing time on peel strength, shown in Figure 8, is similar to the result in Experiment A: the peel strength increased linearly with the pressing time. However, the slope of the line in Experiment B is smaller than that in Experiment A. Therefore, good peel strength is obtained in Experiment B even at a short pressing time. This fact shows that good peel strength is obtainable with

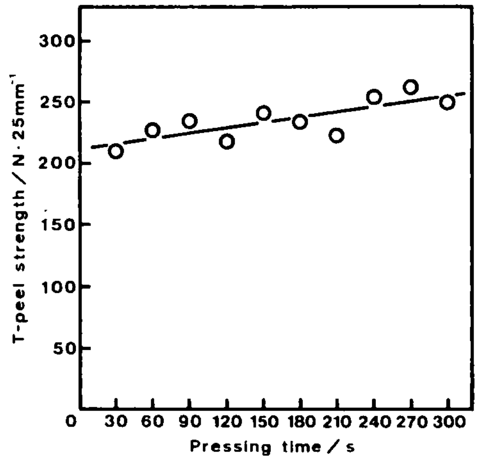

FIGURE 8 Effect of pressing time on peel strength. Mixing ratio of peroxide:silane coupling agent by volume, 1:5; amount of mixed adhesive, 0.1 mg/cm^2; pressing temperature, 200°C; method of application, spraying.

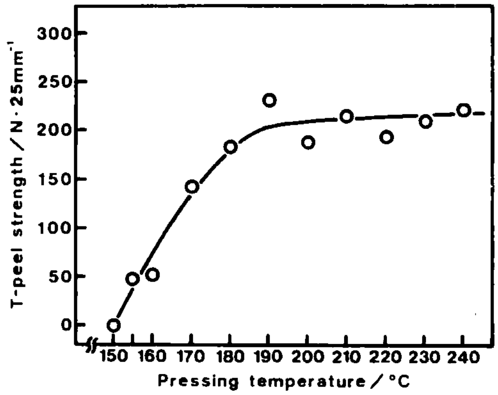

FIGURE 9 Effect of pressing temperature on peel strength. Mixing ratio of peroxide:silane coupling agent by volume, 1:5; amount of mixed adhesive, 0.1 mg/cm^2; pressing time, 90 s; method of application, spraying.

short bonding time when the amount of the adhesive is small. Short pressing time will lead to a large advantage in production of the laminates in industry.

The effect of the pressing temperature on peel strength is shown in Figure 9. Good peel strength was obtained at 190°C and the value was constant at higher temperatures. Consequently, the pressing temperature of 200°C is high enough to bond polypropylene sheet with steel plates. In the region of the temperature from 170°C to 180°C, the peel strength tends to decrease with decreasing temperature. It is considered, at the lower temperatures, that the reaction rate of the mixed adhesive is not high enough to attain sufficient peel strength. Peel strength decreased markedly for pressing at 160°C, and adhesion was not realized at 150°C.

The surface of the steel plates was polished with emery paper, and the effect of grain size[9] of emery paper on peel strength was investigated. This effect was examined as a function of grain size from #46 to #1500.

The results are shown in Figure 10, where the relationship between the grain size G and the average diameter of the grain r(mm) is given as[10]

$$G = (45/r)^{1/1.28} \tag{1}$$

That is to say, the decrease in the surface roughness of the polished steel plate should correspond to the increase in G if the polishing pressure for each polishing and the number of polishing cycles are kept constant. However, #1500 emery paper clogged easily, so that polishing with this paper was not practical. The surface roughness of the steel plates is represented by an arithmetical mean deviation R_a, defined as follows;[11]

$$R_a(\mu m) = \frac{1}{l} \int_0^l |f(x)|\, dx \tag{2}$$

The profile of the roughness curve is shown in Figure 11.

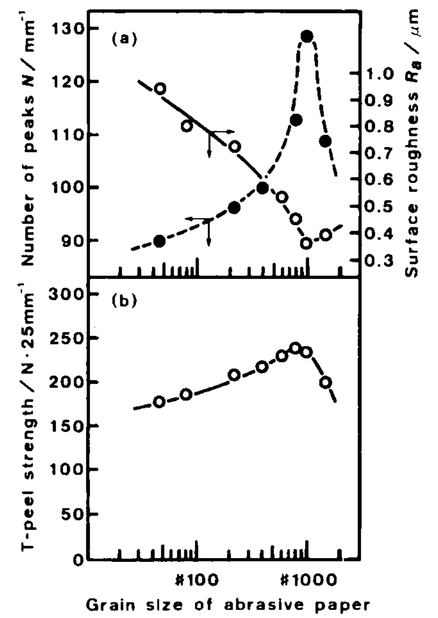

FIGURE 10 Effect of surface roughness of steel plate on peel strength: a) ———, surface roughness (arithmetical mean deviation); – – – – – –, number of peaks on surface roughness curves; b) ———, T-peel strength. Mixing ratio of peroxide:silane coupling agent by volume, 1:5; amount of mixed adhesive, 0.1 mg/cm^2; pressing temperature, 200°C; pressing time, 90 s; method of application, spraying.

As shown in Figure 10(b), the peel strength increased with the decrease in the surface roughness R_a and reached the maximum in the vicinity of the minimum surface roughness. After that, the peel strength decreased with the increase in the surface roughness. Thus, the behavior of the peel strength can not be explained by the surface roughness. Next, the number of peaks N in the traversing length l of 1 mm was counted on the profile curve of the roughness. The number of peaks N increased with the grain size in the region below #1000, and then decreased in the region above #1000. This tendency is completely contrary to the

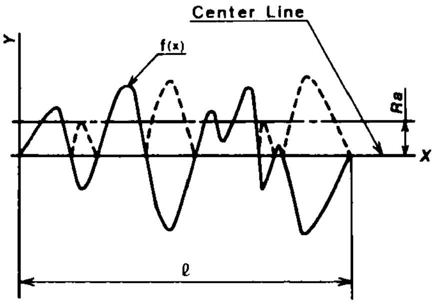

FIGURE 11 Profile of roughness curve for arithmetical mean deviation.

relation between the grain size and the surface roughness R_a, but is quite consistent with the variation of the peel strength. Thus, the peel strength in this case is influenced, not by the dimension of the surface roughness, but by the number of peaks N in the cross section of the polished steel.

Therefore, we can conclude that the increase in peel strength comes from the anchoring effect between the adhesive and the steel adherend. In addition, it is not always desirable simply to roughen the surface of the adherend,[5] because there is an optimum condition in the shape of the cross section of the roughened surface.

The durability of adhesion of polypropylene sheet with steel plates is shown in Figure 12. The laminates were left in a dark place where they were only influenced by atmospheric temperature and humidity. In general, the durability of adhesion may be evaluated under circumstances of high temperature and humidity in a chamber. However, in this study, the durability was investigated under natural atmospheric conditions, as shown in Figure 12.

The decrease in the bond strength with time has been explained in a number of ways. One of these ways is by breaking of the bonding due to the difference in linear expansion coefficient.[12] These coefficients for polypropylene sheet and steel plate α_P, α_S were individually determined in a thermomechanical analyzer

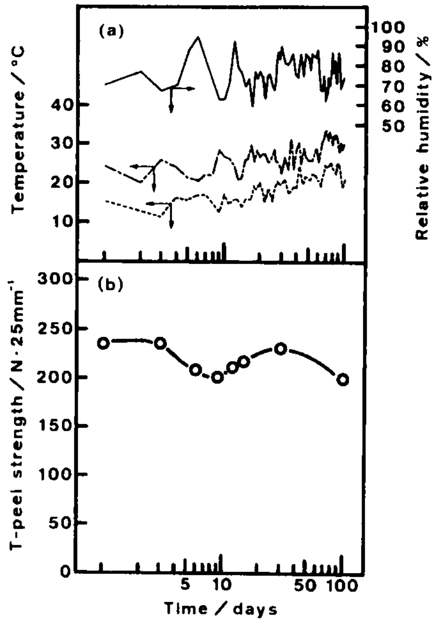

FIGURE 12 Durability of adhesion of polypropylene sheet with steel plate: a) ———, average relative humidity; — — —, maximum atmospheric temperature; - - - - - -, minimum atmospheric temperature; b) ———, T-peel strength. Mixing ratio of peroxide : silane coupling agent by volume, 1:5; amount of mixed adhesive, 0.1 mg/cm^2; pressing temperature, 200°C; pressing time, 90 s; method of application, spraying.

(TMA) under the load of 9.8×10^{-3}N, where both coefficients were averaged in the temperature range from 20°C to 40°C. The result shows that $\alpha_P = 145.98 \times 10^{-6}$ and $\alpha_S = 12.45 \times 10^{-6}$ for polypropylene sheet and steel plate, respectively. The expansion coefficient of polypropylene sheet is approximately ten times as large as that of steel plate. Such a large difference in expansion coefficient causes an increase in thermally-induced internal stress in the adhesive layer and consequently a decrease in bond strength. Shigeki[13] has reported that the bond strength decreases with the increase in difference in expansion coefficient between foreign materials joined with an adhesive. As shown by the solid line in Figure 12(a), in this experimental period, the test specimens were left in the region of 60–95% in relative humidity. It has been reported by Walker[14] for a long time that the bond strength decreases under the effects of high humidity. This is also considered to be a factor for the decrease in peel strength. DeLollis[15,16] suggests that the moisture in air gradually permeates into the interface, and then the adhesive is replaced by water on the surface of the adherend; therefore the bond strength decreases, particularly when the adhesive has hydrophilicity and the adherend is a metal.

Our experimental result demonstrates that the stress induced by variation in temperature and high humidity leads to only a small decrease (39N/25 mm) in peel strength, as shown in Figure 12(b). Such a decrease in peel strength will not interfere with the use of the laminate, and the adhesion of polypropylene sheet with steel plates has sufficient durability even under high humidity.

CONCLUSIONS

The bonding characteristics of polypropylene sheet with steel plates and its peel strength were studied using brushing and spraying as methods for application of adhesives. The results are as follows.

1) Both the activation of the surface of polypropylene sheet and the adhesion of polypropylene sheet with steel plates were carried out at the same time by using a mixed adhesive which was composed of silane coupling agent with peroxide. Adequate peel strength was obtained by both brushing and spraying.

2) The optimum value of the mixing ratio of silane coupling agent with peroxide was found to depend upon the thickness of adhesive spread on the polypropylene.

3) Generally peel strength increased with pressing time.

4) Peel strength increased with pressing temperature and leveled off after 190°C.

5) Peel strength depended upon the number of peaks N on surface roughness curves determined for steel plates. This further demonstrates the effect of surface roughness on peel strength.

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