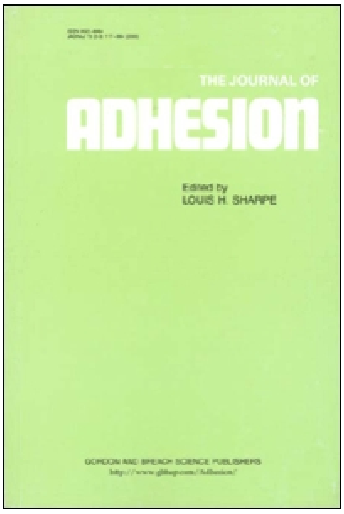

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Effect of Components on Apparent Shear Strength in Oil-Accommodating Adhesive

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Two steel plates were bonded with oil-accommodating adhesives, the components of which are epoxy resin, NBR (nitrile rubber) modified epoxy resin, $CaCO_3$ and silica powder. The effect of components on the apparent shear strength was studied using the plates, which were covered with rust-preventing oil. The shear strength increased most effectively with the silica powder content, as compared with other components. Further, each component was exposed to the vapour of rust-preventing oil. Silica powder absorbed the largest amount of oil among the components per unit weight. We concluded that the performance of the oil-accommodating adhesive was attained by the strong oil absorption ability of silica powder in the adopted adhesive.

Keywords: Oil-accommodating adhesive; epoxy resin; NBR modified epoxy resin; silica powder; oil absorption; rust preventing oil

INTRODUCTION

Adhesives have become more important day by day and their use has increased, especially in the automobile industries [1]. For example, the procedures for bonding a car bonnet with an adhesive are well known and adhesives are used in many other parts of a car.

It is possible to bond different materials with adhesives, and the bonding strength is 30–40% stronger than the corresponding

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spot-welded assembly, because of the more uniform stress distribution [2]. However, the surface of steel plates used for many products is covered with an oil layer to protect the steel from rusting. This oil layer, in general, also prevents optimum bonding of steel plates with an adhesive. Therefore, some degreasing process is required before bonding. If it were possible to attain adhesive bonding without degreasing, there would be a large advantage in car production. An oil-accommodating adhesive was developed in the 1970s for such demands. The effects of curing temperature, curing time, thickness of oil, *etc.*, on the adhesion were already discussed in previous papers [3 – 5]. However, the adhesion mechanism in this adhesive has not been sufficiently clarified.

Adhesives used in industry include various fillers to increase the volume and to control the viscosity [6]. The oil-accommodating adhesive referred to in this study is composed of epoxy resin, NBR (nitrile rubber) modified epoxy resin, $CaCO_3$, silica powder and hardener.

Graham [7], Debski [2, 8] and Nakajima [9] have suggested the following two steps for bonding with an oil-accommodating adhesive. The first step is the displacement of the oil layer by the adhesive. The liquid adhesive reaches the surface of the adherend through the oil layer and the bonding starts. At this time, oil molecules are driven from the adhesion surface. However, this step is neither rational nor meaningful. Any adhesive can be applied as oil-accommodating adhesive, if the displacement of oil by adhesive is an indispensable condition for adhesion. The second step is the absorption of oil into the adhesive layer. This step seems to be reasonable. In this paper, we study the effect of the components in an oil-accommodating adhesive on apparent shear strength and discuss the adhesion mechanism in relation to oil absorption.

EXPERIMENTAL

Materials

The composition of the oil-accommodating adhesive used in this study is shown in Table I. The main component is the epoxy resin D.E.R. 331J, (The Dow Chemical Japan Co., Ltd., Aichi, Japan). A copolymer

TABLE I Composition of adhesive (wt.%)

Sample component	*E*	*N*-10	*N*-20	*N*-30	*C*-5	*C*-15	*C*-25
Epoxy resin	90.7	81.5	72.7	63.6	86.4	77.3	68.3
NBR modified epoxy resin[a]	0	10.2	19.8	30.0	0	0	0
$CaCO_3$[b]	0	0	0	0	5.0	15.0	24.9
Silica powder	0	0	0	0	0	0	0
Hardener[c]	9.3	7.7	7.5	6.4	8.6	7.7	6.8

Sample component	*S*-0.5	*S*-1	*S*-1.5	*S*-2.5	*S*-5	*S*-10
Epoxy resin	90.5	90.0	89.5	88.6	86.4	81.8
NBR modified epoxy resin[a]	0	0	0	0	0	0
$CaCO_3$[b]	0	0	0	0	0	0
Silica powder	0.5	1.0	1.5	2.5	5.0	10.0
Hardener[c]	9.0	9.0	9.0	8.9	7.7	8.2

[a] NBR content is 47 wt.% and actrylonitrile content in NBR component is 14 wt.%.
[b] The average diameter of the $CaCO_3$ powder is 2 μm.
[c] Dicyandiamide.

was formed with the epoxy resin EPICLON TSR-601 (Dainippon Ink and Chemicals, Inc., Tokyo, Japan) by introducing the NBR (nitrile rubber, acrylonitrile–butadiene copolymer) molecular chain; we call it "NBR-modified epoxy resin" hereafter. Other components are $CaCO_3$, silica powder and hardener. The specific surface area of the silica powder was determined by the gas adsorption method (BET one-point adsorption method), and is 109 m^2/g. In Table I, *E* is composed of epoxy resin and hardener, the *N*-series of epoxy resin, hardener and NBR-modified epoxy resin, the *C*-series of epoxy resin, hardener and $CaCO_3$, and the *S*-series of epoxy resin, hardener and silica powder.

Cold strip steel plates having the size of 100 × 25 × 1.6 mm (Taiyu Kizai Co., Osaka, Japan) were degreased with 1,1,1-trichloroethane, followed by cleaning with an ultra-sonic washing machine with the same solvent as in degreasing. These steel plates are hereafter called "degreased plates". Moreover, the oil was applied to the degreased steel plates, which are hereafter called "oily steel plates" in this study. The thickness of the oil layer was determined from the weight increase after dipping the steel plates into the oil. The oil was Metal Guard 831 ®(Mobile Oil Co., Ltd., Tokyo, Japan), the main component of which is liquid paraffin with a small amount of an additive such as Ba or Ca alkyl benzene sulfonate. Actually, the oil is gas oil fraction having a boiling point of 200–350°C.

Apparent Shear Test

The adhesive was applied to the surface of one a steel plate and another steel plate was placed on it. The thickness of the adhesive was fixed at 0.15 mm with two parallel spacers, as shown in Figure 1. These test specimens were cured using a test press at 180°C for 40 min. The apparent shear test (single-lap) was carried out for the specimens in accordance with JIS K 6850 at a speed of 5 mm/min. This test corresponds to ASTM D 1002.

Oil Absorption Test

Each component of the adhesive was placed in a Petri dish and exposed to the oil vapour in a glass container at 20°C. The weight increase of the component was measured by removing the dish from the container after exposure and weighing it. The amount of oil absorption was expressed as the percent weight increase as a function of exposure time.

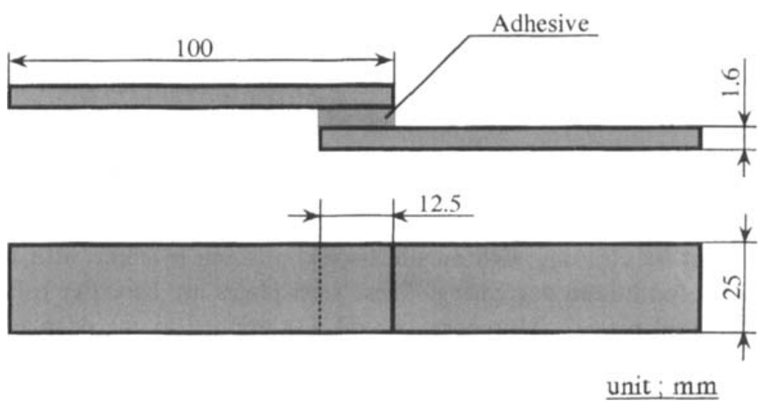

FIGURE 1 Specimen for apparent shear test (JIS K6850); Thickness of adhesive; 0.15 mm.

RESULTS AND DISCUSSION

The relationship between apparent shear strength and NBR-modified epoxy resin content is shown in Figure 2. In oily steel plates A having a 3 μm oil layer, the apparent shear strength increased with NBR-modified epoxy resin content. When the content was 20 wt.%, the strength reached 34.5 MPa. The increase in the apparent shear strength with NBR content is due to the improvement of elongation at break rather than the oil-absorbing effect [10–12]. Interfacial and adhesive failures were always observed on the final failure surface. In oily steel plates B having a 6 μm oil layer, the apparent shear strength became low. This means that the adhesive in the *N*-series does not sufficiently absorb oil.

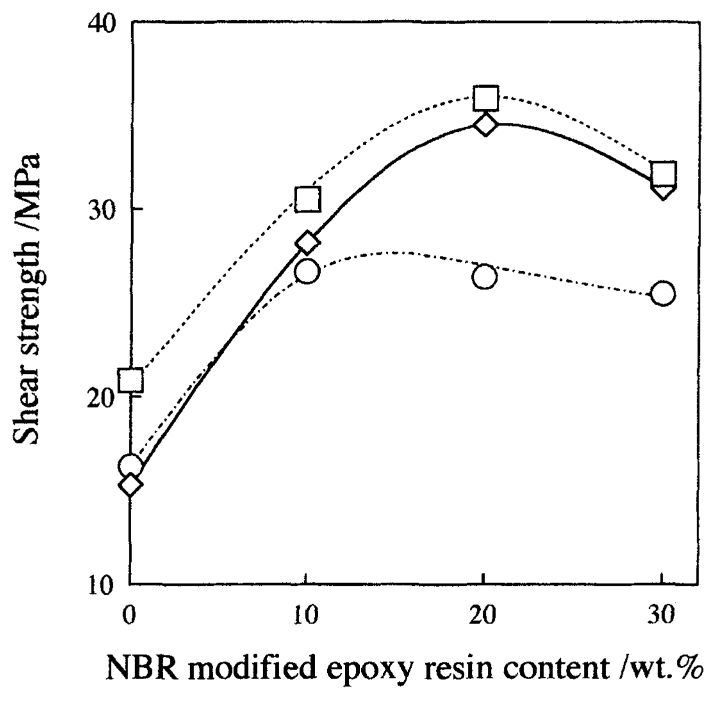

FIGURE 2 Relationship between shear strength and NBR-modified epoxy resin content in *E*- and *N*-series; □: degreased steel plate, ◇: oily steel plate A, oil thickness; 3 μm, ○: oily steel plate B, oil thickness; 6 μm.

Figure 3 shows that the shear strength is not improved even if $CaCO_3$ is added to the adhesive. Moreover, the shear strength with the oily steel plates is always lower than that with degreased plates, and the difference is considerable as compared with the *E*- and *N*-series. This suggests that the $CaCO_3$ does not absorb the oil.

As shown in Figure 4, the shear strength on oily steel plates increased with the silica powder content and leveled off at around 2.5 wt.% of the powder in the adhesive. Finally, the shear strength for that content of the powder coincides with that in degreased plates. It should be regarded that this increase was attained by oil absorption into the adhesive, although the silica powder seems originally to have been added to control the viscosity of the adhesive.

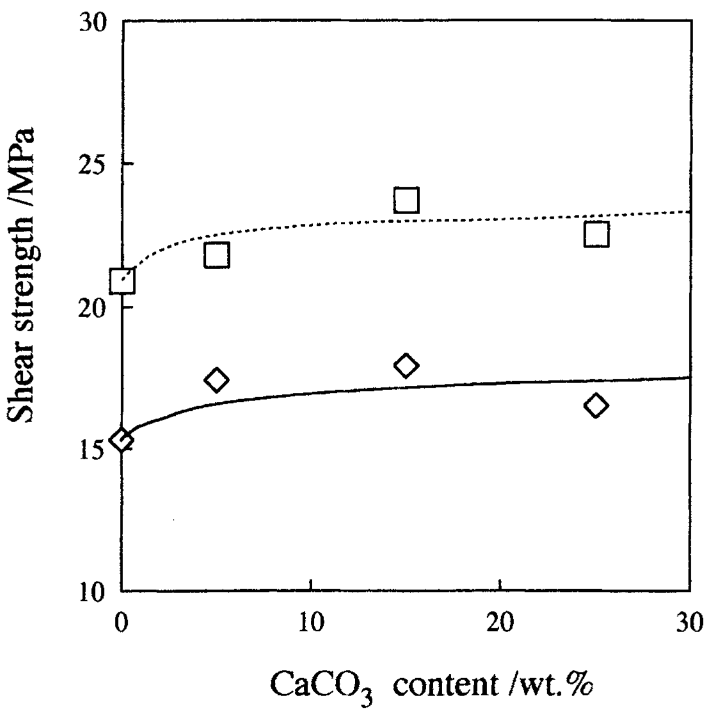

FIGURE 3 Relationship between shear strength and $CaCO_3$ content in adhesive; Thickness of adhesive; 0.15 mm, oil thickness; 3 µm □: degreased steel plate, ◇: oily steel plate.

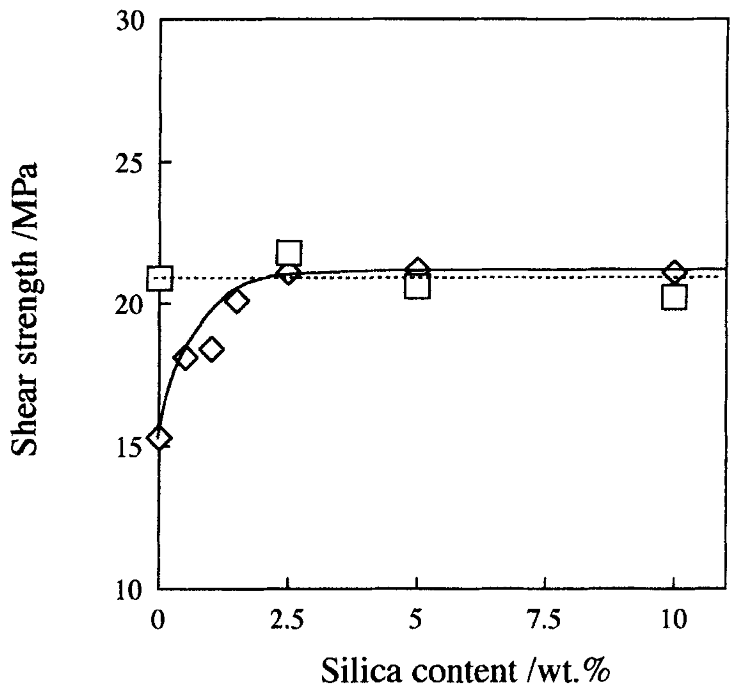

FIGURE 4 Relationship between shear strength and silica powder content; □: degreased steel plate, ◇: oily steel plate.

The increase of oil content in the component materials was measured as a function of exposure time and is shown in Figure 5. The amount of oil absorption for the NBR-modified epoxy resin and the epoxy resin were 3.8 wt.% and 3.4 wt.%, respectively, at equilibrium. No large difference was observed in the amount of oil absorption between the NBR-modified epoxy resin and the epoxy resin, although we estimated in our earlier paper [5] that the NBR-modified epoxy would absorb the most oil.

On the other hand, the silica powder absorbed 9.51 wt.% of oil, giving the highest value among the tested components.

Oil of 6.02 ml/m^2 quantity is present on the two sides of the steel plate surface when the oil thickness is 3 μm. In the case of sample S-2.5, the epoxy resin absorbs 5.66 ml/m^2 of oil when the adhesive has the thickness of 0.15 mm. Silica powder should absorb 0.51 ml/m^2 of oil, taking into account its content in the adhesive. Thus, the adhesive

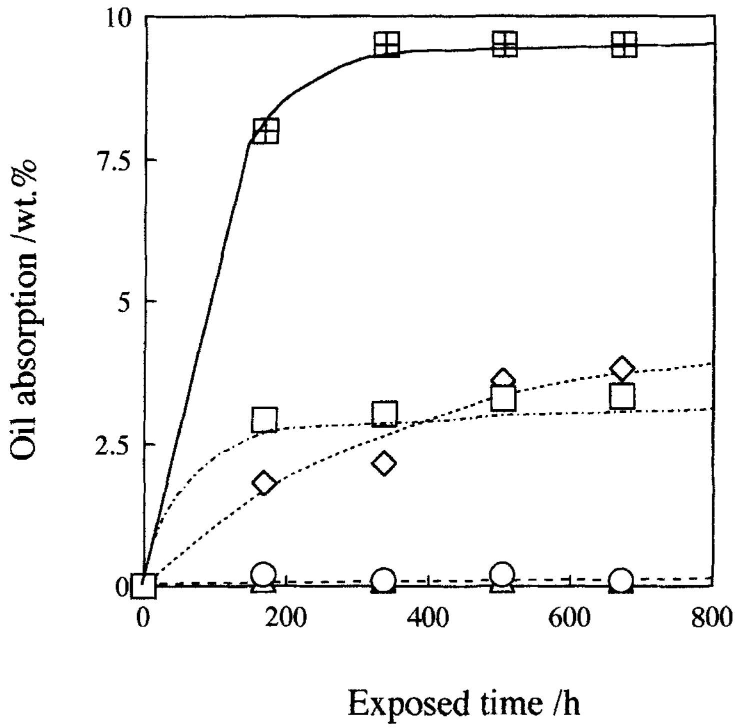

FIGURE 5 Oil absorption by component materials as a function of exposure time. □: Epoxy resin, ◇: NBR-modified epoxy resin, Δ: Hardener, ⊞: Silica powder.

is able to absorb 6.17 ml/m^2 of the oil. Therefore, it is reasonable that the shear strength in this case shows almost the same value as that for degreased steel plates, as shown in Figure 4.

The high absorption ability of silica powder is considered to be due to its large surface area of 109 m^2/g, as mentioned previously. Next, we estimated the amount of oil adsorption on silica powder surface from the molecular volume of oil. Since the main component of rust-preventing oil is a gas oil fraction, we assumed *n*-hexadecane, $C_{16}H_{34}$, as the typical molecule. Its molecular volume was calculated by using a computer program based on the molecular orbital method (ANCHOR) which was supplied by Fujitsu Co. Ltd. (Japan). In this program, the molecular configuration is optimized. The calculated result is shown in Figure 6. Three different adsorptions are considered. The largest amount of oil molecules is absorbed on silica surface when S_3

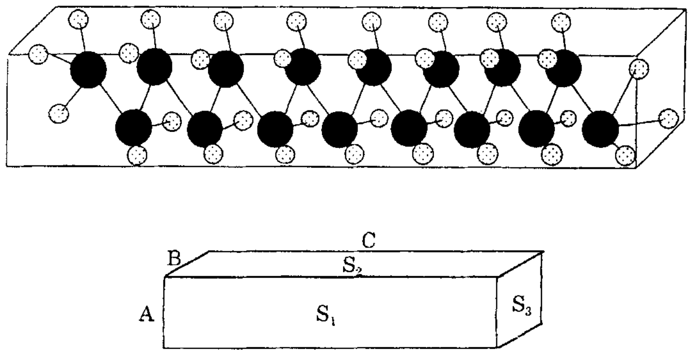

FIGURE 6 Molecular shape of *n*-hexadecane A: 3.09×10^{-10} m, B: 1.77×10^{-10} m, C: 1.73×10^{-9} m, S_i: Surface area. ●: Carbon, ⊙: Hydrogen.

becomes the bottom face. However, even in this case, two molecular layers must be present on the silica surface to absorb all the oil from the steel plates. In other words, we can not explain the large amount of oil adsorption by the simple assumption of monolayer adsorption on the silica surface. Probably, some amount of oil is present as liquid in cavities on the silica surface or on the steel plates.

CONCLUSIONS

The apparent shear strength and oil-absorption performance were examined in detail for an oil-accommodating adhesive. The apparent shear strength of the adhesive increased largely with silica powder content and leveled off at a powder content of 2.5 wt.%. Silica powder absorbed oil more than any other of the components per unit weight. Thus, it was concluded that silica powder in the adhesive plays the most important role in improving the strength of adhesive joints made with oily steel plate.

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