MODIFICATION OF CHEMICALLY STABLE POLYMERIC MATERIALS 87. IMPROVEMENT IN THE ADHESION PROPERTY OF FRP, CFRP, AND CFRTP FOR CAR/AIRCRAFT-USE.

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ABSTRACT

Chemically stable polymeric materials of which modification was impossible by a plasma discharge treatment were modified by our original combination method, DHM-process. Modified materials had a high adhesion property, and the property was not changed for several years as compared with the plasma discharge treatment. The modification of polymer composites such as GFRPP (glass fiber reinforced polypropylene) and CFRP (carbon fiber reinforced plastics) used for cars, aircrafts and other machines was studied. The adhesion shear strength of modified CFRP boards increased over twice (50MPa) of that of unmodified CFRP boards (21MPa). In addition, the adhesion property of CFRTP (carbon fiber reinforced thermoplastics) (CF- PEEK resin) boards could be improved well by the DHM process, although the modification of CFRTP is known to be very difficult. The uniformity of the adhesion property was seen throughout the modified materials. The obtained modification effect gave a durability, as compared with the effects modified by a plasma discharge treatment or a peel-ply method.

1 INTRODUCTION

Many techniques were investigated to modify chemically stable polymeric materials such as polyethylene (PE), polypropylene (PP), polycarbonate (PC) etc. [1,2]. At present, a plasma discharge treatment is extensively carried out to improve the adhesion property of chemically stable polymeric materials. Plasma-discharged materials have to be used quickly for the subsequent process, because the modified property is lost with time. In addition, it is known that a process inhomogeneity is caused in plasma discharge treated materials with big size. The plasma-discharge is not effective for some polymers such as poly(methyl pentene) (PMP resin), silicone resin and fluorocarbon resin. We studied a modification of polyolefins and other chemically stable polymeric materials, and found that the combination of several conventional methods was effective for the improvement of the adhesive property. The technique was named as "DHM-process". We found that engineering plastics such as poly(oxymethylene) (POM, polyacetal), poly(butylene terephthalate) (PBT) and polyamides could be also modified well by the DHM process. The adhesion property obtained by the DHM-process is not decreased with time for several years. The modified polymeric materials were useful for the preparation of new base materials for pressure-sensitive tapes (PSA tapes) [3]. Recently, carbon fiber reinforced plastics (CFRP) with epoxy resin are extensively used for the light-weighting of cars and aircrafts. In general, CFRP materials are modified by a plasma discharge or a peel-ply method to improve the adhesion property. But, there are some problems in the CFRP boards modified by these techniques. In addition, industries are trying to use carbon fiber reinforced thermoplastics (CFRTP) because they are easily formed by heating. But, CFRTP has no adhesion property. We considered that the interface of fibers and resins in usual FRPs is not adhered well to each other. In this article, the modification of fiber-reinforced plastics such as GFRP (glass fiber reinforced PP), CFRP (CF-epoxy resin) and CFRTP (CF-PEEK resin) boards was investigated. The adhesion property of modified materials was compared with the materials modified by a plasma discharge treatment or a peel-ply method.

2 EXPERIMENTAL

2.1 Materials

Polymeric materials (forms: films, sheets, fibers, boards, rods and tubes) were used after washing with methanol. Commercial chemical reagents were used as received or after a simple purification.

2.2 Adhesives

Polyvinylpyrrolidone (PVP), starch, a woodwork bond, PVAC-water mixture: Konishi Co.), cyanoacrylate adhesive (CA; Aron alpha: Toa Gosei Kagaku Co.), epoxy resin adhesive (Quick 5; mixture of epoxy resin and polythiol, a product of Konishi Co. Ltd.), a cyanoacrylate-primer set (PPX of Cemedine Co. Ltd.; primer: organic amine 1% and heptane 99%), etc. were used. Film-type epoxy resin adhesive (3M:AF163-2) was used for the adhesion of CFRP boards for aircrafts.

2.3 Modification

Polymeric materials were activated by energy irradiations such as an UV-irradiation and chemical oxidations. The activated polymeric materials were treated with monomers, coupling reagents or other chemical reagents in the presence of catalysts. The treatment conditions were considered for each material. These techniques were named as “DHM processes”.

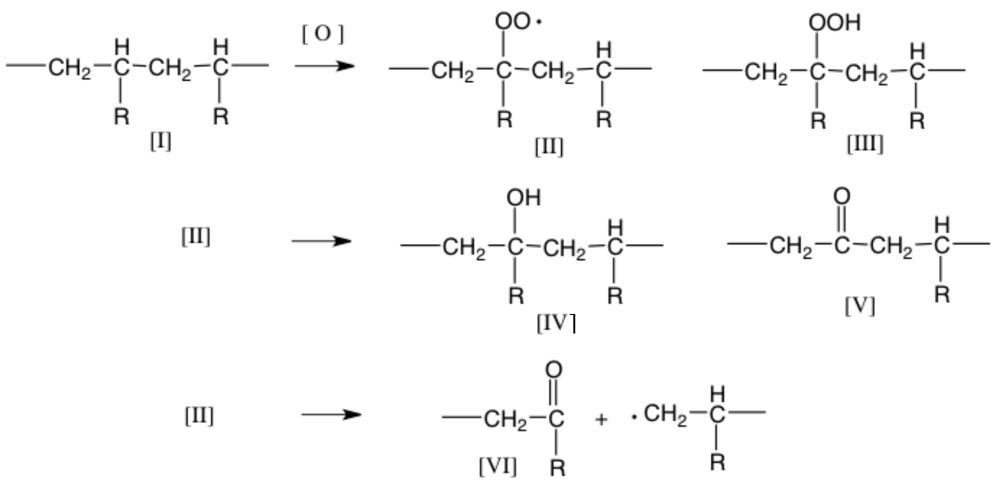
2.4 Adhesion strength and analysis

Adhesion shear strength and three-points bending strength of materials were estimated by a tensile tester, Shimadzu AGS-H5KN. The modified materials were analyzed by IR spectroscopy or XPS. The IR spectra were observed by a Shimadzu IR Prestige-21 equipped with an ATR accessory. The XPS of materials was observed by an Ulvac PHI 5000 VersaProbe II.

3 RESULTS AND DISCUSSION

3.1 Mechanism of modification

Polymeric materials are oxidized in each activation process. The oxidation mechanism is speculated as given in Scheme 1 with reference to the old researches [4-6]. Polymers are changed to several oxidized polymers given by III, IV, V and VI in Scheme 1. The oxidized polymers are protected by a chemical coating with monomers or silane coupling reagents, etc., in the next process.



Scheme 1 Oxidation mechanism of polymer

3.2 Improvement of adhesive property of CFRP boards

3.2.1 Adhesion of CFRP board and CFRP board

CFRP (epoxy resin matrix) boards are modified by a plasma discharge treatment or a peel-ply method in order to increase the adhesion property. They are used for airplanes such as "Boeing 787". But, it is known that the materials obtained by these methods cause an adhesion inhomogeneity. We investigated the modification of CFRP boards, and examined the adhesion of CFRP board and CFRP board to each other. A film epoxy adhesive, 3M-AF163-2 was used for the adhesion. The adhesion shear strengths of adhered unmodified CFRP/unmodified CFRP boards, plasma-discharge treated CFRP/plasma-discharge treated CFRP boards, peel-ply treated CFRP/peel-ply treated CFRP boards and DHM processed CFRP/DHM processed CFRP boards, and the failure style are given in Table 1. The highest shear strength was obtained in the adhesion of DHM-processed CFRP boards; 50-51 MPa. In addition, the present method gives adhesion homogeneity throughout the materials. It is remarkable that adhesive was left on each DHM-processed CFRP board, and both of material and cohesive failures was observed. On the other hand, adhesive was left only one CFRP board, and only cohesive failure was observed in the adhesion of unmodified CFRP boards.

Table 1 Adhesion shear strength and failure style of CFRP-CFRP adhesion

Specimen	Shear strength (MPa)	Failure style
Unmodified	24-25	Interface
Plasma	34-36	Cohesive
Peel-ply	35-36	Cohesive
DHM-process	50-51	Material & cohesive

3.2.2 Adhesion of CFRP board to aluminum alloy board

The adhesion of CFRP boards (Unmodified or DHM-processed) to aluminum (Al) alloy boards (unmodified or nano-size porous process) were examined. Table 2 gives the adhesion shear strength of each adhesion. The adhesion of unmodified CFRP and unmodified Al alloy boards gave shear strength 11MPa, and an interface failure was observed in the test. When one of CFRP or Al alloy boards are modified, their adhesion strength is increased. The effect of modified CFRP board is larger than the porous modification of Al alloy board. A combination of DHM-processed CFRP and porous Al alloy boards gave a maximum adhesion shear strength, 53MPa.

Figure 1 gives the specimens after the adhesion shear strength test. It is remarkable that the adhesive is left on each board in the adhesion of DHM-processed CFRP and porous Al-alloy boards. The combination of DHM processed composites and finely porous metal boards are applicable for the machine manufacturing of many fields.

Table 2 Adhesion shear strength and failure style of CFRP board adhered to aluminum alloy board

CFRP board	Aluminum alloy board	Shear strength (MPa)	Failure style
unmodified	unmodified	11	Interface
DHM-processed	unmodified	21	Cohesive
unmodified	nano-size porous	36	Cohesive
DHM-processed	nano-size porous	**53**	Cohesive

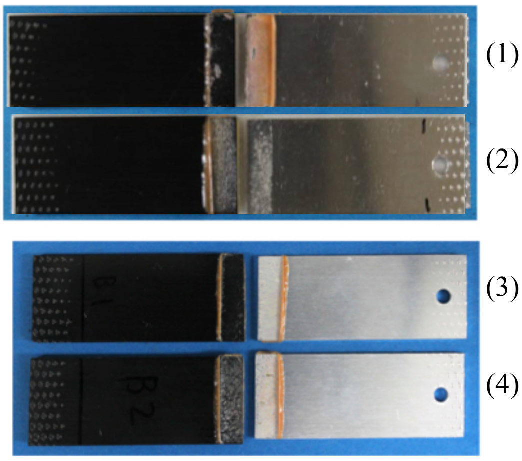


Figure 1: Specimens after the adhesion shear strength test; (1) unmodified CFRP/unmodified Al alloy board, (2) DHM-processed CFRP/unmodified Al alloy board, (3) unmodified CFRP/porous Al alloy board, (4) DHM-processed CFRP/porous Al alloy board.

3.2.3 Heat and cold resistances of CFRP-CFRP board adhesion

Unmodified CFRP board adhered to unmodified CFRP boards (1) and DHM-processed CFRP board adhered to DHM-processed CFRP (2) were maintained at -72˚C for two weeks, or maintained at 85˚C. These adhesion shear strengths are summarized in Table 3, together with the values at room temperature. It was observed that the adhesion of DHM-processed CFRP/DHM-processed CFRP boards have high heat and cold resistances.

Table 3 Heat and cold resistance test of CFRP/CFRP boards adhesion; shear strength (MPa) of CFRP-CFRP boards adhesion and temperature.

Temperature	R.T.	85˚C	-72˚C
unmodified CFRP	25.4	26.4	27.1
DHM-processed CFRP	46.4	45.0	45.6

3.3 Improvement of adhesive property of CFRTP (PEEK resin matrix)

It is known that CFRTP has a poor adhesion property and its modification by usual techniques is very difficult. We tried the modification of CFRP by a combination of activation processes and chemical coatings, and obtained good results. Table 4 gives adhesion shear strength. The adhesion shear strength of modified CFRTP-modified CFRTP boards was 25MPa. Fig.2 shows specimens after the adhesion shear strength test. It is remarkable that the adhesive is separated on each CFRP board in the adhesion of DHM-processed CFRTP to DHM-processed CFRTP boards. On the other hand, the adhesive is pealed from CFRTP boards in the adhesion of unmodified DHM-processed CFRTP to unmodified DHM-processed CFRTP boards.

Table 4 Adhesion shear strength and failure style of CFRTP(PEEK resin)-CFRTP (PEEK resin) adhesion

Specimen	Shear strength (MPa)	Failure style
Unmodified	4.8	Interface
Plasma	8.7	Interface
DHM-process	25.0	Cohesive

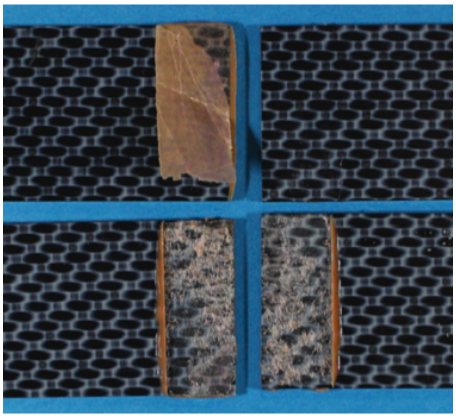


Figure 2: Specimens after the adhesion shear strength test;
(1) unmodified CFRTP/unmodified CFRTP boards,
(2) DHM-processed CFRTP/DHM-processed CFRTP boards.

4 CONCLUSIONS

CFRP and CFRTP boards were modified well by the DHM-process. The modified property was not changed for several years, as compared with plasma-discharge treated materials. The modified materials are useful for the light-weighting and reinforcement of automobiles, aircrafts and other machines. New strong and light-weight polymer composites could be considered using modified fibers and polymer resins.

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