MODIFICATION OF CHEMICALLY STABLE POLYMERIC MATERIALS 88. IMPROVEMENT IN THE ADHESION PROPERTY OF POLYOLEFIN, SILICONE RESIN, AND FLUOROCARBON RESIN

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ABSTRACT

Chemically stable polymers and polymer composites of which modification was impossible by a plasma discharge treatment were modified by our original method, DHM-process. Glass-fiber reinforced polypropylene (GFRP) modified by the process could be coated well with water-based paints, and the coating fastness was very high. Poly(tetrafluoroethylene) (PTFE) sheets could be modified well, and the modified PTFE sheets were adhered to aluminum (Al) board with usual water-soluble glues. The modification of an engineering plastic, MC nylon was examined, and the modified MC nylon boards could be adhered strongly to aluminum boards with epoxy resin adhesives. DHM-processed silicone rubber and DHM-processed fluorocarbon resins could be adhered strongly to each other, using silicone resin adhesives. Polymer composites were made using modified PP, poly(ethylene terephthalate) (PET) or poly(phenylenesulfide) (PPS) fibers and epoxy or PP resins. The obtained polymer composites were very strong as compared with those made with non-modified fibers and the same resins.

1 INTRODUCTION

Polyolefins such as polypropylene (PP), polyethylene (PE), ultra-high-molecular-weight polyethylene (UHMPE) and poly(methyl pentene) (PMP), and other many polymers are hydrophobic. They are not adhered easily to each other or to other materials. Many techniques have been carried out to modify these stable polymeric materials [1,2]. At present, a plasma discharge treatment is extensively used to improve the adhesive property. But, plasma discharged materials must be used quickly for the subsequent process because the obtained effect is lost with time. In addition, there are many kinds of polymers of which modification is impossible by the plasma discharge; i.e. polycarbonate (PC), silicone resins, fluorocarbon resins, engineering plastics such as poly(oxymethylene) (POM, polyacetal), poly(butyleneterephthalate) (PBT), polyamides, poly(sulfone) (PS), polyimide (PI), poly(ether ether ketone) (PEEK), etc. We made PP fabrics which absorb water, using a combination of several conventional techniques. In addition, we studied our technique to improve the adhesion property of chemically stable polymeric materials of which modification is impossible by the plasma discharge [3]. We considered that the interface of fibers and resins in usual FRPs is not adhered well to each other in usual polymer-resin composites. Thus, the improvement of the adhesion property of polymer composites such as GFRP (glass fiber reinforced PP), CFRP (CF-epoxy resin) and CFRTP (CF-PEEK resin) boards was investigated. CFRP boards are extensively used for the light-weighting of cars and aircrafts. CFRTP is one of the most expected materials because of the thermoplasticity, but it is no adhesive property. In this article, the adhesion property of modified materials is compared with the materials modified by a plasma discharge treatment or a peel ply method. In addition, the preparation of polymer composites using modified fibers and polymer resin is reported.

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 recieved 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-time modified epoxy resin adhesive (3M AF163-2) are 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 Modification mechansm

Polymeric materials are oxidized by an activation process. The oxidation mechanism was considered by references [4-6]. The oxidized materials are protected by functional or coupling reagents (e.g. silane agents). Table 1 gives the XPS analysis of unmodified PP film, plasma-discharged PP film and DHM-processed PP film. The amount of C-O, C=O and O=C-O groups increased after the two process. It is remarkable that C-O groups were much more included in the DHM-processed PP.

Table 1 Functional groups in PP film observed by XPS

Specimen	observed functional groups (mol%)				ratio, O/C
	C-C, C-H	C-O	C=O	O=C-O	
unmodified PP	100	0	0	0	0.02
plasma-discharged	81.6	8.2	3.58	6.58	0.22
DHM	74.9	17.3	3.23	4.53	0.30

3.2 Adhesion of PP sheets with PSA tapes

Unmodified PP resin sheets were not adhered to each other using PSA tapes. But, DHM-processed PP sheets were adhered strongly to each other. Figure 1 gives specimens after the T-type peel strength test of PP-PP sheets adhered with PSA. Unmodified PP sheets were not adhered to each other using PSA. Plasma treated PP sheets were adhered to each other using PSA, and the specimen showed an interface failure. On the other hand, DHM processed PP sheets were strongly adhered to each other, and the specimen showed a cohesive failure of PSA tape.

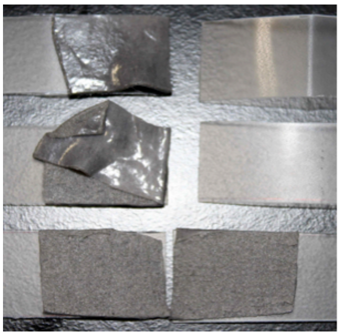

Figure1 Specimens after T-type peel strength test of PP-PP sheets adhered with PSA. Upper: unmodified PP, middle: plasma treated PP, lower: DHM processed PP

3.3 Water-based paint coating of GFRPP

It is known that the water-based paint coating onto GFRPP (grass-fiber/PP resin FRP) is impossible. When plasma-discharge treated GFRP boards were coated with water-based paints, the coated paints were peeled easily. On the other hand, the DHM-processed GFRP was coated well with water-based paint, and the cross-cut test of the coating gave a full mark, 100/100 in the JIS cross-cut test. The water-based paint coating of the other polymeric materials modified by the present method was also possible. Figure 2 gives the water-based paint coating onto unmodified GFRPP and DHM-processed GFRPP boards.

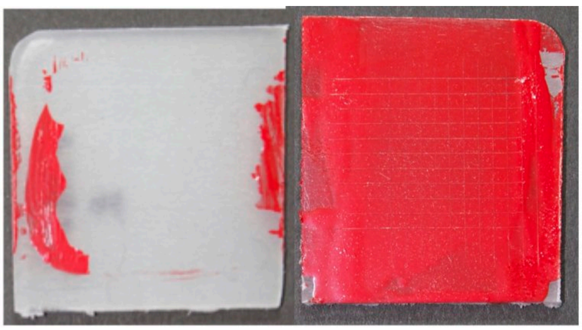

Figure 2: Water-based paint coating on GFRPP (glass fiber-PP) boards; left: unmodified material, right: modified material.

3.3 Adhesion of PTFE resin sheet to Al board

The modification of PTFE by usual techniques is very difficult. The DHM processed PTFE sheet was adhered to aluminum (Al) board with usual PVA glue (see Figure 3). This property makes widely the application of PTFE materials.

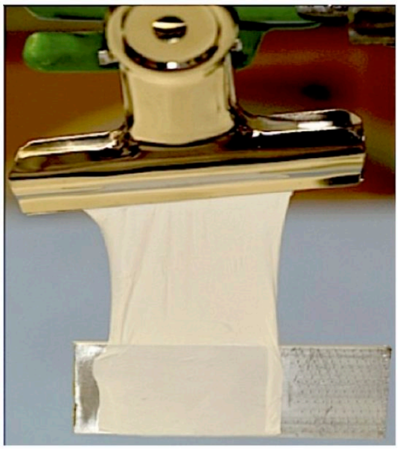

Figure 3: Modified PTFE sheet glued to an Al-board with PVP glue.

3.4 Adhesion of MC nylon boards to Al boards

MC nylon boards were modified by a plasma discharge process or the DHM process. Figure 4 gives the adhesion of unmodified, plasma-processed, and DHM-processed MC nylon boards with CA or CA-primer adhesives. Although the use of CA-primer adhesive gave an adhesion shear strength, 2.86 MPa, the nylon board was broken by the primer. On the other hand, the DHM-processed MC nylon board was adhered to Al board strongly with CA adhesive; the adhesion shear strength was 3.04 MPa and the cohesive failure of adhesive was observed. This property makes the use of MC nylon widely.

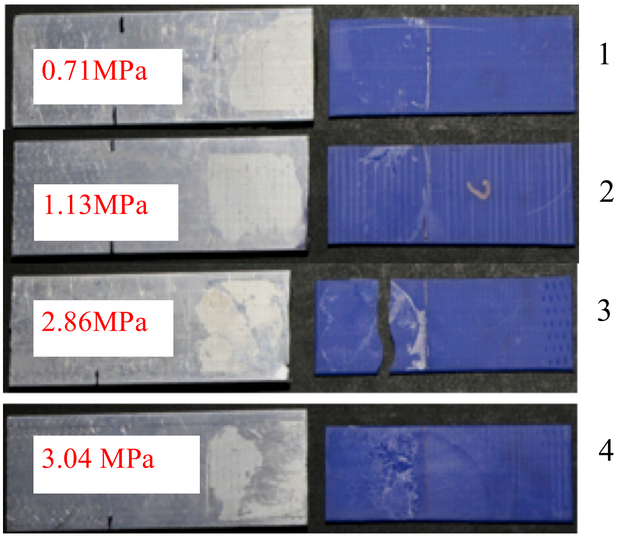

Figure 4: MC nylon-Al boards adhesion specimens after the strength test. Numbers give adhesion shear strength.
1.Unmodified MC nylon board-Al board glued with CA.
2. Plasma-discharge treated MC nylon board-Al board glued with CA.
3. Unmodified MC nylon board-Al board glued with primer-CA.
4. DHM-processed MC nylon board-Al board glued with CA.

3.5 Adhesion of silicone resin and ETFE resin

The adhesion of fluorocarbon resin and silicone resin is one of the most difficult subjects. The DHM-processed ETFE resin materials (ethylene-tetrafluoroethylene copolymer) could be adhered well to silicone resins with silicone resin adhesives. A modified ETFE resin tube covered with silicone rubber tube was made. This tube is useful for the medical or food-industry application, because ETFE resin has less stain adherence.

3.6 Preparation of strong polymer composites using modified fibers and polymer resins

New polymer composites were made, using the DHM-processed PET fibers and epoxy resin. The three-point bending strength of the obtained FRP was much higher than the FRP made by unmodified PET fiber and epoxy resin. In addition, the new FRP showed a unique stress-strain behavior. The FRP board made with unmodified PET fiber and epoxy resin was broken separately in the three-point bending strength test. But, the DHM-processed PET fiber-epoxy resin composite board was bended but showed no separation in the test, as given in Figure 5.

The other non-adhesive synthetic fibers are also useful for the preparation of new stronng polymer composites.

Figure5: Three-point bending strength tests of unmodified PET-epoxy resin FRP (left), and DHM-processed PET-

4 CONCLUSION

The present process is useful for the modification of stable polymeric materials. The modified materials are applicable for many fields since the obtained modification effect has a durable property. 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 automobile, aircrafts and other machines. Strong polymer composites could be made by using modified fibers and polymeric resins. This suggests the possibility of reasonable, strong and light-weight polymer composites.

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