

ELECTRODEPOSITION OF POLYMERS ON CARBON FIBERS

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ABSTRACT

Styrene-co-maleic anhydride, vinyl acetate-co-maleic anhydride, methyl methacrylate-co-maleic anhydride copolymers were deposited on the surface of carbon fibers by an electrodeposition technique. The anion-free radical mechanism of this process and the physical adhesion to the surface were preliminarily confirmed. The adhesion at fiber-resin matrix interface in carbon fiber reinforced plastics was improved by the electrodeposited polymer interlayer and the shear failure occurred mainly in the matrix. Interlaminar shear strength of the unidirectional carbon fiber reinforced epoxy composite is increased from about 600 kg/cm² to 1000 kg/cm² by electrodeposition of polymers and the strength loss of the composite which has been immersed in boiling water for 100 hrs is decreased.

The introduction of a polymer interlayer between the carbon fiber and the resin matrix can lead to interface adherence, which is helpful to prevent from the formation and propagation of cracks at the interface of reinforced plastics. The methods for introducing polymer interlayer nowadays are impregnation^[1], electropolymerization^[2] and electrodeposition^[3]. The effectiveness of the polymer layer was evaluated by measuring the interlaminar shear strength, impact strength and water resistance of reinforced plastics. In this paper the electrodeposition mechanism of polymers on carbon fibers along with the effects of polymer interlayer on shear failure and optimum conditions of operating technique are studied.

EXPERIMENTAL METHODS

Materials

The carbon fibers used in our experiments were as follows:

*1100 plies with filament diameter of 9 μm , having strand tensile strength of 14,000 kg/cm² (medium strength) and sizing.

*1000 plies with filament diameter of 6—7 μm , having strand tensile strength of 25,000 kg/cm² (high strength) and without sizing.

Aqueous solutions of amine salts of styrene-co-maleic anhydride (S-MA), vinyl acetate-co-maleic anhydride (VA-MA), methyl methacrylate-co-maleic anhydride (MMA-MA) copolymers were used as the electrodeposition solution. All copolymers were prepared in our laboratory.

Apparatus

Fig. 1 shows a simple set-up, designed for the continuous deposition of carbon fibers. It consists of four parts for fiber feeding, gas regulation, pretreatment and electrodeposition. The third part equipped with gas sources of argon and hydrogen was set up for preparing different surface conditions. The fourth part comprises an electrodeposition cell (Fig. 2), a solvent tank and a DC power supply. In the deposition cell there are two stainless steel plates as the cathode, a steel roller as the anode which is in contact with carbon fiber, and two Teflon rollers as the guides.

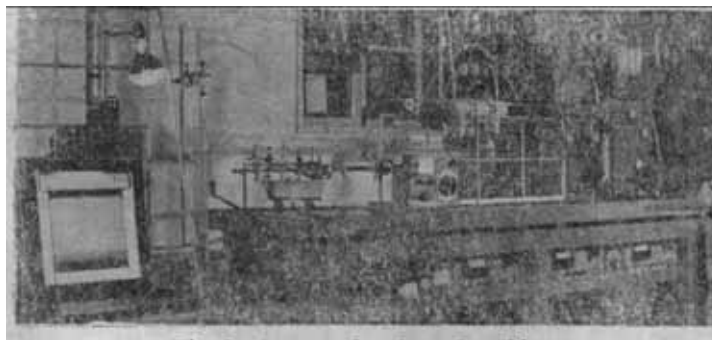


Fig. 1 A set-up for electrodeposition



Fig. 2 An electrodeposition cell

Electrodeposition

The pretreatment of carbon fiber was carried out in three ways: desizing, desizing followed by oxidation, and desizing followed by reduction. During desizing and reduction the carbon fibers were heated by passing electricity through them.

For optimizing the operating conditions a Latin Square was arranged by selecting three factors (the pretreatment of the fiber, the electric current density and the time of electrodeposition) and three levels for each factor. The carbon fibers were electrodeposited continuously as the anode, followed by rinsing in acetone tank.

Analysis of electrodeposited polymer layer

The electrodeposited polymer layer was analysed by using Infrared Spectroscopy (IR), Nuclear Magnetic Resonance Spectroscopy (NMR), Electron Spectroscopy for Chemical Analysis (ESCA) and Scanning Electron Microscopy (SEM).

Preparation and test of reinforced plastics specimens

Using epoxy resin 648 as matrix and $\text{BF}_3\text{-EtNH}_2$ as curing agent, laminated specimens reinforced by carbon fiber unidirectionally were prepared. The interlaminar shear tests were conducted according to a short beam method similar to ASTM D2344-76. The dimensions of the specimens are $6.5 \times 2.2 \times 22$ mm, the span-to-thickness ratio is 5:1. The shear fractures were observed with SEM.

RESULTS AND DISCUSSION

Adhesion of electrodeposited polymer to carbon fiber surface

The adhesion between the deposited polymer layer and the fiber surface is considered principally to be of physical nature owing to the following facts. The original surface of the fiber was revealed again when the deposited fiber was washed by water or ammonia, as in the SEM pictures grooves and other details of the fiber could be seen clearly.

The deposited polymer covers the fiber surface completely and compactly. The fiber surface before and after electrodeposition was detected by ESCA for comparison (Fig. 3). In our experiments the fiber used contains Sn owing to manufacturing process. For deposited fiber the Sn peaks vanish in the ESCA spectrum. In the nearest adjacency of fiber surface the deposited polymer, which in bulk is soluble in acetone, becomes unsolvable in acetone. After being immersed in acetone for a period of 100 hours, the erosive spots and swollen pieces were seen as shown in Fig. 4, and the Sn peaks are absent in the ESCA spectrum.

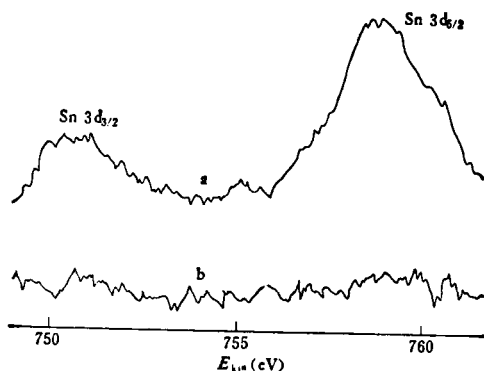


Fig. 3 ESCA spectra of carbon fiber surface
(a) without deposited layer; (b) with deposited layer.

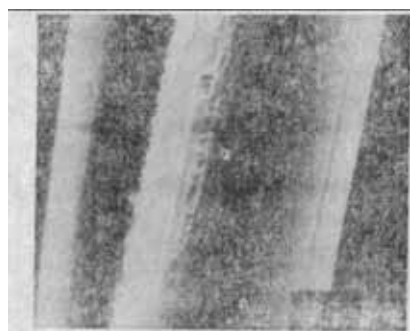


Fig. 4 S-MA electrodeposited layer after being immersed in acetone

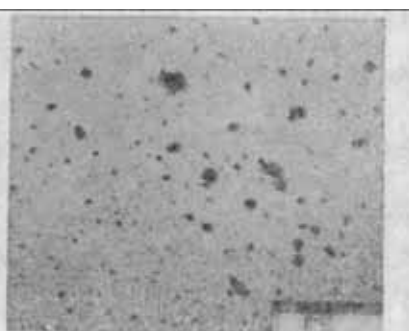


Fig. 5 The erosion of electrodeposited layer on platinum surface

Tiny holes of the fiber surface might be filled by the deposited polymer, because the apparent density of fiber with deposited layer is 1.85–1.90 g/cm³ in comparison with density of 1.72 g/cm³ of the fiber without that layer when they are measured in density gradient column.

Electrodeposited polymer layer can also be formed on inactive platinum and the erosive spots appear similarly after being immersed in acetone (Fig. 5), which shows again that the physical adhesion may exist mainly between the deposited layer and the substrate surface. The physical adhesion can also be seen from the data obtained in optimization of operating conditions. So clean surface without any sizing is enough for deposition of polymers.

Mechanism of electrodeposition

The mechanism of electrodeposition of copolymers with carboxylate groups on zinc and cold-rolled steel was discussed by Rheineck and Usmani^[4]. In our work, the IR and NMR spectra of bulk polymers and deposited polymers, which were extracted by trifluoroacetic acid from fiber, were compared (Figs. 6 and 7). In the IR spectra of deposited polymers, the absorption bands of C—O, C=O stretch vibration in —COOH group appear at 1220, 1690 cm^{-1} , indicating the existence of —COOH group in the deposited layer. The protonation of polyanions occurs and results in the precipitation of polymer with the formation of a film.

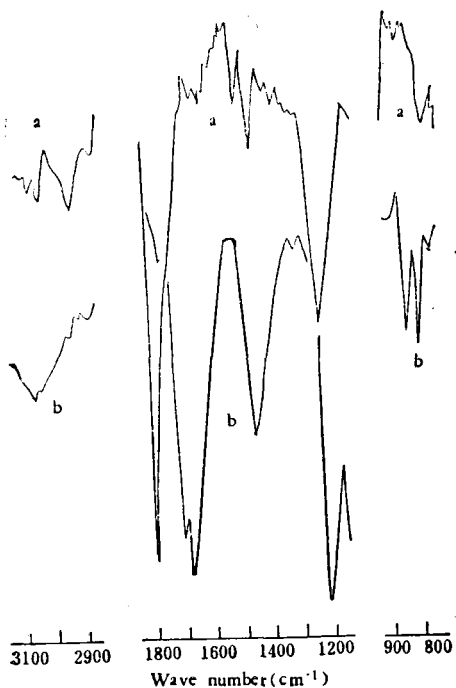


Fig. 6 IR spectra of S-MA
(a) bulk polymer; (b) deposited layer.

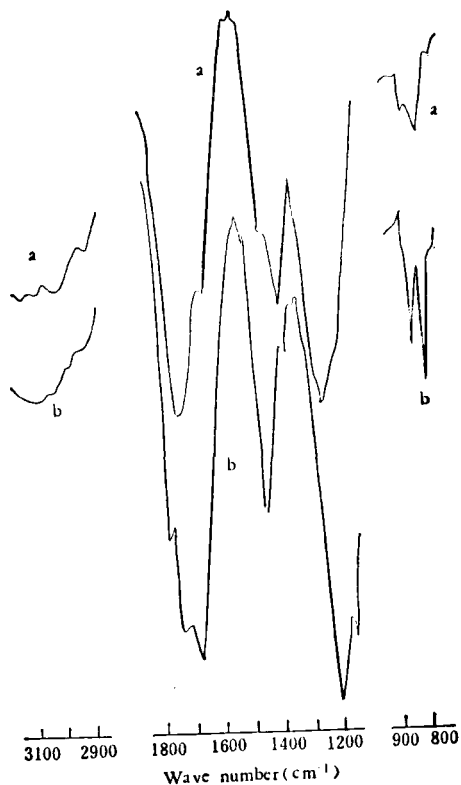
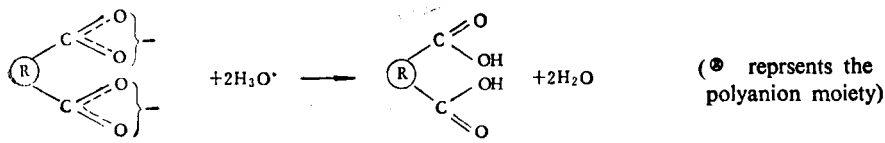
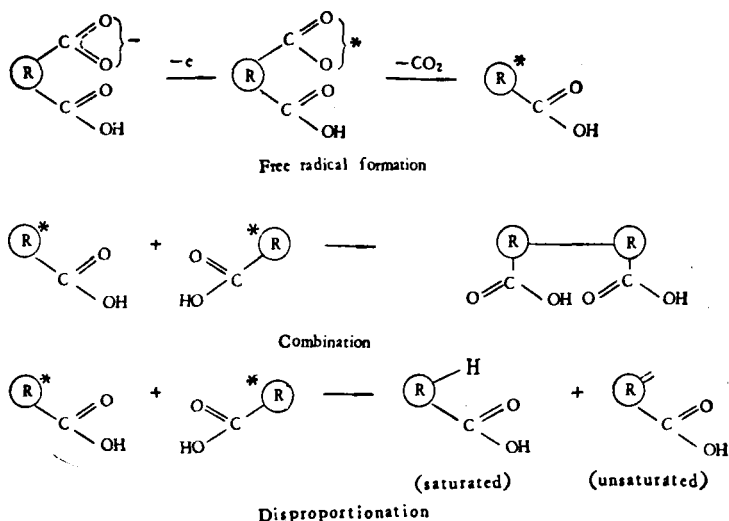


Fig. 7 IR spectra of VA-MA
(a) bulk polymer; (b) deposited layer.



Meanwhile, the absorption bands of C—H stretch and C—H distortion vibrations in $CR_1R_2=CHR_3$ at 3060, 830 cm^{-1} show that the structure of $CR_1R_2=CHR_3$ emerges in the deposited layer. The NMR spectra, in which three peaks appear in the range of 5.6—6.2 ppm, also show the existence of hydrogen atoms attached to C=C double bond.

The reactions which could lead to such product were pointed out in the reference [4]: anodic oxidation of polyanions may yield carboxyl radicals, these may undergo decarboxylation to macroradicals, the macroradicals may combine or disproportionate to give the deposit. These results show that polyanions with carboxyl groups deposit on the carbon fiber by way of an anion-free radical mechanism.



The improvement of properties of reinforced epoxy by polymer interlayer

In Tables 1 and 2 the influence of polymer interlayer on shear strengths of CFRP is listed. The specimens reinforced by bare carbon fiber have strengths in the range of 500—650 kg/cm^2 , and fail in the mode of multiple shear. As for the specimens reinforced by deposited fiber, the adhesion at the fiber-resin matrix interface is improved to such an extent that the tensile failure of fiber takes place in advance of the shear failure of interface for medium strength carbon fiber. The nearly real shear strengths of specimens, up to 1000 kg/cm^2 , were obtained for high strength fiber only.

The changes of shear strengths for specimens after being immersed in boiling water are given in Table 3. For specimens reinforced by bare fiber, the shear strengths decrease sharply for a period of 10 hours only, and they are less than 400 kg/cm^2 after 100 hours immersion, that means 40% and more of strength is lost. In contrast to this, for specimens reinforced by deposited fiber, the shear strengths show no decrease after 10 hours immersion, and the strength loss is small, maintained at about 600 kg/cm^2 , after 100 hours immersion.

It is evident that the electrodeposited polymer interlayer on carbon fiber results in significant improvement of shear strength and water resistance of reinforced epoxy resin.

Table 1 Shear properties of epoxy resin reinforced by medium strength carbon fiber*

Carbon fiber	ILSS (kg/cm ²)	Mode of failure
Without deposited layer:		
As-received	586	4 multiple shear, 1 tension
	648	5 multiple shear
Desized	565	3 multiple shear, 2 shear and tension
	640	1 shear and tension, 4 tension
Desized and reduced	488	5 multiple shear
Desized and oxidized	594	5 multiple shear
With deposited layer:		
VA-MA, washed in acetone	711	5 tension
MMA-MA, washed in acetone	762	6 tension
S-MA, washed in acetone	735	5 tension

* having strand tensile strength of 14,000 kg/cm².

Table 2 Shear properties of epoxy resin reinforced by high strength carbon fiber*

Carbon fiber	ILSS (kg/cm ²)	Mode of failure
Without deposited layer:		
As-received	649	5 multiple shear
With deposited layer:		
VA-MA, washed in acetone	818	4 multiple shear, 1 single shear
MMA-MA, washed in acetone	1038	3 multiple shear, 2 single shear
S-MA, washed in acetone	1043	2 multiple shear, 3 single shear
not washed in acetone	927	5 multiple shear

* having strand tensile strength of 25,000 kg/cm².

Table 3 Water resistance of epoxy resin reinforced by medium strength carbon fiber

Carbon fiber	Duration of im- mersion in boiling water (hrs)	Take-up of water (%)	ILSS (kg/cm ²)	Strength loss (%)	Mode of failure
Without deposited layer:					
As-received	0	0	648		
	10	1.2	581		
	100	2.5	383	40.9	shear and delaminated
Desized	0	0	640		
	10	1.0	560		
	100	1.7	356	44.4	shear and delaminated
With deposited layer:					
S-MA	0	0	735		
	10	1.2	704		
	100	3.1	463	37.0	multiple shear
VA-MA	0	0	711		
	10	2.0	743		
	100	3.0	482	32.2	shear and tension
MMA-MA	0	0	762		
	10	1.2	800		
	100	2.7	598	21.5	tension

The influence of polymer interlayer on the shear failure

Different shear fractures of specimens reinforced by fiber with and without polymer layer are shown in Fig. 8. The fact that the specimen reinforced by bare fiber, so-called fiber-resin structure, appears irregular fracture where many fibers are pulled out and little matrix resin sticks on the fiber surface, shows poor interface adhesion. On the contrary, specimen reinforced by deposited fiber, so-called fiber-polymer interlayer-resin structure, appears "stair-case" fracture where fibers are bound to bundles and much matrix resin sticks on the fiber surface.



Fig. 8 The influence of polymer interlayer on the shear failure
(a) fiber-resin structure, ILSS: 525 kg/cm²;
(b) and (c) fiber-S-MA polymer layer-resin structure, ILSS: 1134 kg/cm².

The possible chemical interaction of the carboxyl groups on the deposited polymer with the epoxy groups on the epoxy matrix results in the transformation of F-R structure into F-I-R structure and the fiber-deposited layer interface becomes the key problem. The polymer interlayer, which covers the grooves and holes of the fiber surface uniformly, completely and compactly, brings physical adhesion of fiber surface into full play and increases the so-called "anchor" effect. The mode of formation and development of cracks are altered and the passages of water penetration at the interface confined. All these effects change the occurrence of the shear failure from at the interface basically to at the matrix mainly, i.e. they result in significant improvement in shear strength and water resistance of reinforced plastics.

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