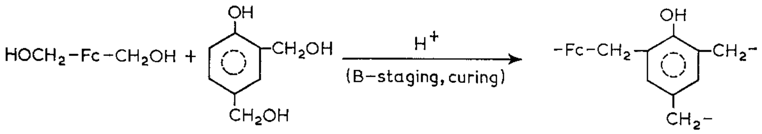
Letters

Transition metal-modified matrix resins for composite materials [1]

In recent years special efforts have been made to develop resin-matrix fibre composites that are modified with metallic particles to impart special electrical or magnetic properties, added abrasion resistance, and opaqueness to certain types of radiation. Such modification may give rise to undesirable interfacial polarization or reduced mechanical strength, in addition to requiring intricate rotation techniques in staging and curing to prevent the build-up of density gradients and metal-depleted resin pockets in the matrix.

To circumvent some of these problems the feasibility of introducing the metal as an organometallic complex rather than in elementary metallic form is being investigated. Provided that such a complex can be substituted with functional groups capable of reacting with matrix-resin intermediates during the staging and curing steps, its use will entail several distinct advantages over that of metallic particulates: (i) the complex may be chemically designed so as to become soluble in the initially liquid-matrix resin, thus providing the necessary homogenization; (ii) the metal will exist as a discrete atomic species surrounded by ligand elements (especially carbon), securing atomic distribution in the matrix; (iii) the chemical bonds established between complex and matrix constituents will add to cross-link density, preventing undue strength reduction. In principle, the choice of suitable complexes is almost limitless. In practice, however, arguments of accessibility, economy, stability, and ease of substitution suggest restriction to compounds in which the transition-metal atom is π-bonded to aromatic ligands, preferably cyclopentadienyl or benzene rings, the metal being selected from groups VI, VII, and VIII of the Periodic Table. Prototype complexes are benzenechromium tricarbonyl [$(\pi\text{-}C_6H_6)Cr(CO)_3$], cyclopentadienylmanganese tricarbonyl [$(\pi\text{-}C_5H_5)Mn(CO)_3$], and ferrocene [$(\pi\text{-}C_5H_5)_2Fe$]. In accord with accepted curing mechanisms*, the functional groups of choice attached to parent complexes of these types include hydroxymethyl for reaction with a phenol/formaldehyde matrix, vinyl or acrylyl for copolymerization with unsaturated polyester resins, and oxirane rings, anhydride functions, or amino groups for incorporation into epoxy matrices.

To demonstrate the feasibility of the proposed approach, the incorporation of iron, via 1,1′-bis(hydroxymethyl)ferrocene [3], into a representative "phenolic" resin, a commercial phenol/formaldehyde condensation product (Monsanto SC 1008) was chosen. The iron complex reacts with the A-stage matrix resin (typically containing bis(hydroxymethyl)phenols) to give, probably through the intermediate formation of dimethyleneoxy-bridged structures, three-dimensionally crosslinked end-products as exemplified by the segment I (Fc = 1,1′-ferrocenylene)*:



1,1′-bis(hydroxymethyl)-ferrocene   2,4-bis(hydroxymethyl)-phenol

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The iron complex was blended at various concentrations into warm (75° C) phenolic varnish previously vacuum-concentrated to 85% resin solids. A portion of the homogenized blend was advanced (80 to 100° C, N_2) to incipient gelling and was cast into neat, i.e. unreinforced resin specimens (Table I).

The remaining portion of the blended resin varnish was allowed to impregnate S-glass fabric (style 181, A-1100 finished) and carbon cloth (Hitco CCA-1) at 80° C. The prepregs, advanced (100° C, N_2) to 7 ± 1% resin flow, were fabricated (12-ply, parallel lay-up) and cured into panels (Table II; properties not necessarily optimized).

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*Polyester, phenolic, and epoxy resin cross-linking mechanisms have been discussed, for example, by Lenz [2].

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TABLE I Iron-modified phenolic resin matrix, unreinforced*

Complex content in matrix, %*	Iron content in matrix, %†	Hardness, Barcol	Poisson's ratio‡	Char yield at 800° C, %§
0	0.0	55	0.36	51
10	2.3	55	—	—
15	3.4	56	0.37	68
20	4.5	57	—	70

*Casting conditions (staging and curing): 10 h at 100° C, 10h at 125° C, 6h at 130° C, 8h at 150° C, 4h at 170° C (all under N_2).

†Nominal, by wt of phenolic resin solids.

‡By ASTM Method E 132.

§By wt of virgin material (predried), in thermogravimetric analysis (Ar; 15° C min^{-1}).

TABLE II Iron-modified phenolic resin matrix, glass- and carbon-fibre-reinforced*

	Reinforcement: 181 S-glass fabric, A-1100‡			Reinforcement: Hitco CCA-1 carbon fabric§		
Complex content in matrix, %†	Flexural strength, GN m^{-2}	Flexural modulus, GN m^{-2}	Compressive strength, GN m^{-2}	Tensile strength, GN m^{-2}	Tensile modulus, GN m^{-2}	Compressive strength, GN m^{-2}
0	0.47	24.2	0.37	0.13	17.0	0.30
10	—	—	0.38	0.11_5	15.5	0.29
15	0.44	23.8	0.38_5	0.12	16.4	0.29
20	0.43	24.7	0.37	0.11_5	15.7	0.28

*Cure cycle: 50 to 150° C, 0.7 to 1.5 MN m^{-2}, in 2h; 2h at 150° C, 7.0 MN m^{-2}; 3h at 160° C, 7.0 MN m^{-2}. Post-cure: 5h at 160° C, 3h at 170° C (under N_2). Tensile (warp), compressive, and flexural (flatwise) strengths by Federal Standard No. 406, Test Methods 1011, 1021, 1031.

†By wt of phenolic resin solids.

‡28 % resin content.

§34 % resin content.

As the tables show, the metal, at the complex concentrations employed, does not significantly affect the mechanical composite properties listed. It is only at concentrations exceeding 20 to 25% that more than marginal strength reduction must be expected. On the other hand, even the moderate 15% concentration level suffices to raise the 800° char yield of the neat matrix by 17%, attesting to the potential of iron-modified matrices of this type in, for example, composite ablative heat shield components.

Iron is incorporated with equal effectiveness into an epoxy matrix. Thus, 1,1′-diglycidylferrocene [4] was found to copolymerize readily with a conventional, benzyldimethylamine-accelerated, methyl nadic anhydride-crosslinked Epon 828/1031 system. Preliminary experiments, furthermore, indicate that 1,2-bis(hydroxymethyl)benzenechromium tricarbonyl [5] lends itself as a vehicle for chromium introduction into a phenolic resin, giving similar matrix processibility to that shown by the ferrocene derivative. The successful incorporation of this chromium complex suggests the use of the high-atomic-number tungsten congener to be equally feasible; a tungsten-modified composite would be of interest in protective systems designed to exhibit absorptive effectiveness in high-energy radiation environments.

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*The susceptibility of ferrocene to electrophilic attack being in the same order as that of phenol, some nuclear substitution on the ferrocene rings can be expected as well.