Organometallic Polymers. II. Crosslinking of Ferrocenylene–Methylene-Type Polymers

ALON GAL, MICHAEL CAIS, and DAVID H. KOHN, *Department of Chemistry, Technion—Israel Institute of Technology, Haifa*

Synopsis

Poly(ferrocenylene-methylmethylene) (PFMM) was prepared and subsequently crosslinked by the aid of either 1,1'-bis(α-hydroxyethyl)ferrocene or polyfunctional ferrocene polymers, containing reactive -CH_2OH or -$CH(CH_3)OH$ groups. The thermal behavior of both the primary polymer and the thermoset was investigated. The solubility parameter of PFMM was determined and the degree of crosslinking was studied by solvent swelling and sol fraction measurements. Various thermosetting structural composites were prepared and subjected to mechanical testing.

INTRODUCTION

In a previous paper[1] we reported that solution polymerization of α-ferrocenylmethylcarbonium fluoborate produced branched, polydispersed products having number-average molecular weights up to 20,000. The structure proposed for these polymers can be depicted schematically as follows:

$$\text{-----}\overset{\text{CH}_3}{\underset{|}{\underset{\text{CH}}{\boxed{\text{Fe}}}}}\text{-----} \tag{1}$$
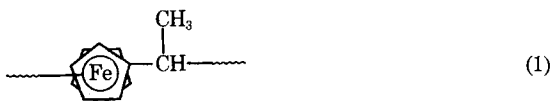
In this formula, the line stemming from the center of the "ferrocene sandwich" represents one or more C–C bonds linking one or both aromatic cyclopentadienyl rings to other recurring units.

Poly(ferrocenylene–methylmethylene) (PFMM) is a brown, glasslike, brittle polymer, which softens below 120°C and is soluble in a number of chlorinated and aromatic solvents. In order to convert it to a product of improved dimensional, thermal, and chemical stability and thus rendering it suitable for the fabrication of structural composites, it was interesting to study the crosslinking of PFMM.

As shown by Phillips,[2] functionless aromatic polymers can be crosslinked by reactions between aromatic moieties of the "prepolymer" and suitable difunctional curing agents in the presence of a Friedel-Crafts catalyst. This method has already been applied to the crosslinking of low molecular weight polybenzyls,[3,4] silicone- and phosphorus-containing compounds with pendant phenyl groups,[3,5] polyphenylene,[6] and polyferrocenylene.[7,8]

This paper presents results of the crosslinking experiments of PFMM by means of either a ferrocenedicarbinol or resol-type ferrocene polymers. It also includes the characterization of PFMM in both its thermoplastic and crosslinked forms.

EXPERIMENTAL

Materials

Both α-hydroxyethylferrocene and 1,1′-bis(α-hydroxyethyl)ferrocene were prepared from the corresponding ketones by $NaBH_4$ reduction[9] and were purified by recrystallization from petrol ether (40–60°C), to yield products melting at 78.5°C and 67–69°C, respectively.

As filler in the thermosetting mixtures, Long Fiber Asbestos, Fluka, was employed. The reinforcements used in laminations were Glass Cloth No. 181 (vinylsilane finish), Owens-Corning Fiberglass Co., and Asbestos Paper 1-470, Fisher.

Polymerization Reactions

Low Molecular Weight PFMM. α-Hydroxyethylferrocene (424 g, 1.83 mole) was dissolved in a mixture of hydrobromic acid (30% in acetic acid; 362 ml, 1.83 mole) and nitroethane (400 ml). An exothermic reaction ensued, the solution reaching a maximum temperature of 75°C after 20 min. After 85 min from the start of the reaction, methylene chloride was added (2.8 liters) and the product was poured into a well-stirred aqueous solution of sodium carbonate (850 g/3 l. H_2O). Stirring was continued for another 45 min, water (3 liters) was added, and the phases were allowed to separate. The organic layer was washed with two portions of water (6 liters each) and then methanol (4 liters) was added. The dark-brown precipitate formed was dried at 50°C under reduced pressure (390 g; yield 93%). A portion of this product (204 g) was dissolved in methylene chloride (1 liter) and reprecipitated with methanol (1 liter). This operation was repeated twice. The purified polymer (170 g, yield 83%) had an intrinsic viscosity [η] of 0.033 dl/g and a molecular weight M_n of 3200.

ANAL. Calcd for $(C_{12}H_{12}Fe)_n$: C, 67.96%; H, 5.70%. Found: C, 66.93%; H, 5.81%.

The mother liquors were poured into water (8 liters) and after separation of the phases, the organic solution was dried over anhydrous magnesium sulfate and the solvent was evaporated. The dry product (30 g) had a molecular weight M_n of 750 and the following elemental analysis: C, 65.55%; H, 5.76%.

High Molecular Weight PFMM. The procedure was described in a previous paper.[1]

Polyfunctional PFMM

Two kinds of polyfunctional polymers were prepared from PFMM: "Polyol F," containing -CH$_2$OH groups, and "Polyol A," having -CH-(CH$_3$)OH groups.

"Polyol F." In the first step, PFMM was formylated by the Vilsmeyer reaction similar to the synthesis of ferrocene aldehyde.[10] N-Methylformanilide (6.2 g, 0.046 mole) was mixed with phosphorus oxychloride (7.05 g, 0.046 mole). After 1 hr, a solution of PFMM (M_n 3200; 10 g, 0.046 mole based on the recurring unit) in methylene chloride (25 ml) was added. The mixture was stirred for 3 hr, and subsequently more methylene chloride (50 ml) and water (200 ml) were added. Stirring was continued overnight, the organic layer was separated and washed with water, aqueous sodium carbonate solution, and again water, and then the polymer was precipitated with methanol (800 ml). The product exhibited in the infrared spectrum in addition to the bands characteristic to PFMM, a very strong carbonyl peak at about 1660 cm^{-1}.

ANAL. Calcd for a polymer containing one -CHO group per every second recurring unit, Fe$_2$C$_{25}$H$_{24}$O: C, 66.40%; H, 5.31%; O, 3.54%. Found: C, 66.45%; H, 5.55%; O, 3.33%.

In the second step, the carbonyl groups of the intermediary product were reduced to carbinol groups by the addition of sodium borohydride (2 g, 0.052 mole) to a solution of the formylated polymer in a mixture of methylene chloride (75 ml) and methanol (25 ml) and stirring for 1.5 hr. The mixture was then shaken with a threefold volume of water, the CH$_2$Cl$_2$ layer was dried over anhydrous MgSO$_4$, and the solvent was evaporated, yielding a dry product (7.8 g).

"Polyol A." PFMM (M_n 800; 38 g, 0.179 mole based on the recurring units) was acetylated by dissolving the polymer in methylene chloride (200 ml). Acetic anhydride (36.5 g, 0.358 mole) was added to the stirred solution, followed by boron trifluoride etherate (51.5 g, 0.358 mole), which was introduced dropwise during 100 min at room temperature. Stirring was continued for another 75 min, and then the violet liquid was poured into an aqueous solution of sodium carbonate (1.5 liters). The organic layer was washed three times with water, dried over MgSO$_4$, and concentrated to about 80 ml. Petrol ether (40–60°C; 300 ml) was added, and the precipitated product was separated and dried (yield 30 g). The infrared spectrum of this product was similar to that of the formylated polymer.

ANAL. Calcd for a polymer containing two acetylated recurring units out of three, Fe$_3$C$_{40}$H$_{40}$O$_2$: C, 66.65%; H, 5.56%; O, 4.45%. Found: C, 65.91%; H, 5.52%; O, 4.19%.

The reduction of the ketone to the corresponding alcohol was accomplished by the same method as employed for the preparation of "Polyol F," yielding 28.5 g of product.

Curing of Thermosetting Mixtures

In order to obtain crosslinked products, the thermoplastic polymer (PFMM in the M_n range of 1.0–7.2 × 10⁴), the curing agent (1,1'-bis(α-hydroxyethyl)ferrocene, "Polyol F," or "Polyol A"), and the catalyst (boron trifluoride etherate) were mixed together in a methylene chloride solution. The catalyst was added in all experiments in a proportion of 2.5 parts per 100 parts polymer–curing agent mixture.

The unfilled molding powders were prepared by evaporating the solvent under reduced pressure and grinding the dry mixture.

For the preparation of asbestos-filled composites or reinforced laminates, the fibers or reinforcements were impregnated with the previously mentioned solution and dried at room temperature.

All curing processes were performed under pressure, at elevated temperature, according to the curing program given in Figure 1. The maximal pressure applied during the compression, P_f, was 68 atm for laminations and 1000 atm for molding of powders. The cured samples were allowed to cool gradually under pressure.
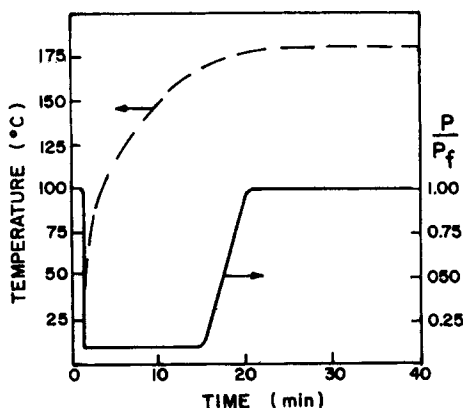

Fig. 1. Curing program for thermosetting systems.

Physical Test Methods

The methods for determination of infrared spectra, intrinsic viscosities, and number-average molecular weights were described previously.[1]

Solubility Parameter. The solubility parameter of PFMM (M_n 3200) was determined by turbidimetric titration[11] of 3 g/l. solutions. Experimental data and results are compiled in Table I.

Solvent-Swelling and Sol Fraction Determinations. Crosslinked polymer pellets were prepared by pressing unfilled thermosetting mixtures (0.8 g per pellet) in a heated, cylindrical mold (cross section 1 cm²). The curing was performed according to the standard procedure (Fig. 1), P_f being 1000 atm. The cured pellets were placed in vials containing 20 ml 1,2-dichloro-

TABLE ?
Determination of Solubility Parameter of PFMM by Turbidimetric Titration[a]

Solvent	δ_1	Lower non-solvent	δ_2	V_m'	δ_n'	Higher non-solvent	δ_2	V_m''	δ_m''	Polymer δ_3
Benzene	9.15	n-heptane	7.45	6.75	8.71	cyclohexanol	11.4	11.0	10.37	9.65
1,2-Dichloro-ethane	9.8	n-heptane	7.45	9.0	8.75	cyclohexanol	11.4	16.5	10.92	9.98
Chlorobenzene	9.5	n-heptane	7.45	8.5	8.66	cyclohexanol	11.4	14.0	10.72	9.80
										9.81[b]

[a] The values for the solubility parameters δ_1 and δ_2 ($cal^{0.5}/cm^{1.5}$) were taken from the literature.[12]

[b] Average value.

ethane and allowed to swell for 30 days (after 20 days, no further sorption was observed).

The equilibrium-swollen specimens were weighed, vacuum dried, and weighed again.

Thermal Characterization

Softening Point. The softening point of polymers was determined by means of an automatic penetrometer according to the method of Edgar.[13] The powdered polymer samples were cold-pressed[14] at 5000 atm in a cylindrical sample holder (ID 7 mm, depth 5 mm). For measurements, the temperature of the silicone oil bath was raised at a rate of 2°C/min. The penetration rod had a circular cross section of 1 mm² and carried a load of 250 g.

Thermogravimetric Analysis (TGA). A modified helical spring microbalance[15] was used for thermogravimetric analysis, the heating rate being 5°C/min. Powdered samples with an initial weight of 100 mg were used, and the determinations were performed both in air and in nitrogen.

Pyrolysis. The polymer was pyrolyzed in a glass tube placed in an electric furnace and connected to a vacuum pump through an ice-cooled receiver. PFMM (M_n 10,000; 0.47 g) was heated at 0.5 mm Hg at a rate of 10°C/min up to 300°C, and kept at this temperature for 50 min. The final material balance was as follows: residue, 61.3%; condensed pyrolysis products, 33.4%; volatile pyrolysis products (by difference), 5.3%. Pyrolyzing the same polymer for 7 hr at 500°C under nitrogen, a residue (37%) of the following elemental composition was obtained: C, 57.79%; H, 0.88%.

The residue was a dark-grey ferromagnetic material. The condensed pyrolysis product appeared as a light-brown soft mass, having a number-average molecular weight of 560. It could be separated chromatographically on neutral alumina into three distinct fractions. The first fraction, eluted with petrol ether (40–60°C), was yellow, while the second and the third, both eluted with methylene chloride, were reddish and brown, respectively. Qualitative chemical analysis (potassium ferricyanide test in chloroform–acetic acid solution[16]) showed that all the three fractions were ferrocene derivatives. The main absorptions exhibited by the fractions in their infrared spectra were the bands of the unsubstituted cyclopentadienyl rings (1000 cm⁻¹ and 1100 cm⁻¹) and those characteristic for methinyl and methyl groups, in the 2850–3000 cm⁻¹ range.

Torsional Braid Analysis (TBA). For the thermomechanical characterization of the polymer, a torsional braid apparatus[17,18] was employed. The test specimens consisted of 34-cm-long glass braid substrates, impregnated with about 100 mg polymer. The substrate was obtained by braiding, by hand, three yarns from Glass Cloth No. 388 (Pierre Genin), each consisting of about 1000 filaments. After impregnation with the polymer solution in dichloroethane, the braids were air dried in an extended state. The experiments were performed in air or in nitrogen at a heating

rate of 5°C/min.   The relative rigidity was calculated as the square of the ratio between the periods of free oscillations at the initial temperature (usually 25°C) and at the measured conditions.

Mechanical Tests of Filled and Reinforced Polymers

Both compressive and flexural strengths were measured with a Hounsfield Tensometer.

Compressive Strength.   Cylindrical   specimens   (diameter   12   mm, height 24 mm[19]), prepared from asbestos fibers impregnated with PFMM (M_n 20,000)–curing agent–catalyst mixture, were cured by compression molding according to the standard procedure (Fig. 1), P_f being 1000 atm.

The relative velocity of approach of the two cross heads of the testing machine was 1.6 mm/min.

Flexural Strength.   The laminates (12 cm long, 7 cm wide, and about 0.1 cm thick) were made from impregnated glass cloth (4 layers) or asbestos paper (3 layers).   The curing conditions were those illustrated by Figure 1, P_f being 68 atm.   The cured sheets were cut to 2 in. × $1/_2$ in. rectangular test specimens.[20]

Four specimens were tested from each laminate;   the span was 1 in. and the rate of cross-head motion, $1/_2$ in./min.

RESULTS AND DISCUSSION

Thermal Behavior of the Primary Polymer

The glass transition temperature of PFMM in the lower molecular weight range is strongly dependent on the degree of polymerization, as indicated by the values of a number of coarsely fractionated polymers (Fig. 2).   At values exceeding 30,000, the softening point of the polymer tends asymptotically to about 120°C.   (The softening point of a polymeric fraction whose M_n was presumably larger than 72,000[1] was found to be also 120°C.)

The behavior of PFMM upon thermal and thermo-oxidative exposure was investigated by means of a penetrometric softening point apparatus, a
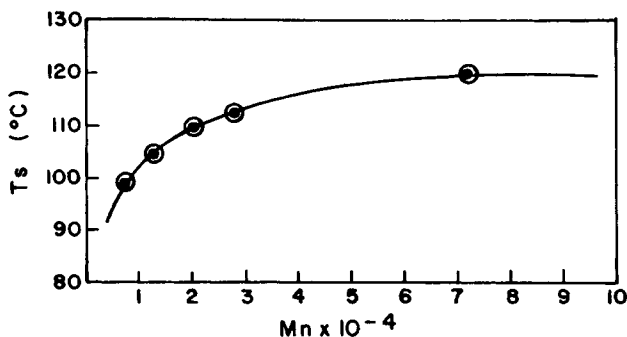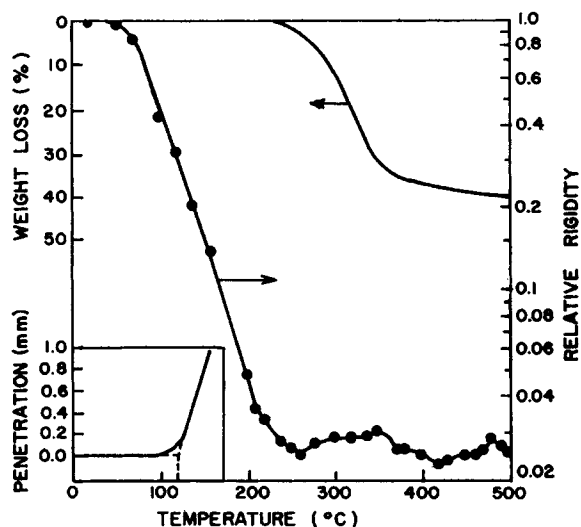

Fig. 2. Dependence of softening point on M_n.

Fig. 3. Thermal behavior of PFMM (M_n 72,000) in nitrogen.

thermobalance, and a torsional braid apparatus. The changes in weight and in rigidity of a polymeric fraction (M_n 72,000), heated up to 500°C during about 100 min, are presented in Figures 3 and 4. These figures contain also the penetration-versus-temperature curve outlining the range in which the glass transition of the polymer occurs.

Examination of Figure 3 reveals that in nitrogen atmosphere, up to 230°C, the relative rigidity of the glass braid–PFMM composite decreased to about 3% from its initial value (determined at 25°C). Since the penetrometric softening point of the polymer was found to be 120°C, the
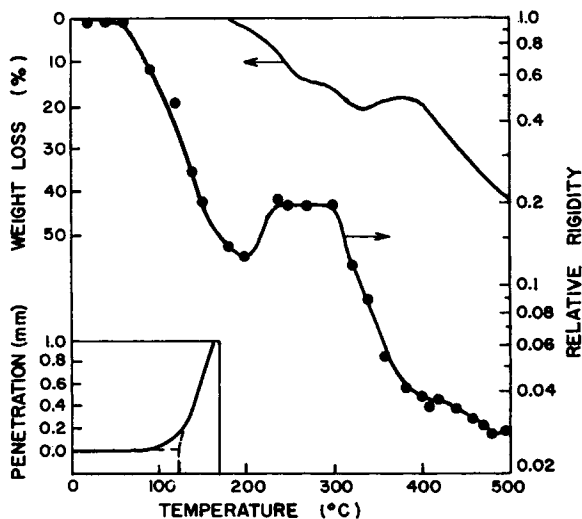

Fig. 4. Thermal behavior of PFMM (M_n 72,000) in air.

abrupt decrease in rigidity can be correlated to the glass transition. The onset of weight loss was observed at 230°C; from this point on, the rigidity did not change significantly.

From the analysis of the pyrolysis products of PFMM, one can conclude that the thermal decomposition proceeds in two ways: by chain fragmentation, yielding as major fraction of the evolving vapors oligomeric ferrocene compounds; and also by total degradation of the metallocene moieties, as indicated by the ferromagnetic properties of the residual char.

From Figure 4 it is apparent that up to a temperature of 180°C, which marks the start of the weight loss, the thermomechanical behavior of the polymer exposed to air is almost identical to that shown in Figure 3. At 200°C, the polymer reached 13% of its initial relative rigidity. On further heating, there occured an increase in rigidity, as evidenced by a plateau in the TBA plot between 200° and 300°C. This plateau could be attributed either to oxidative crosslinking or to the formation of a pyrolyzed continuum. Eventually, above 300°C, this structure seemed to break down, presumably as a result of the oxidation of iron atoms. This is suggested by a peak (about 4% weight gain) in the TGA curve between 330 and 410°C, paralleled by a drastic decrease in rigidity.

Crosslinking

The crosslinking of PFMM was accomplished by means of ferrocene compounds containing two or more α-carbinol groups, in the presence of catalytic amounts of boron fluoride etherate.

The difunctional curing agent employed was 1,1'-bis(α-hydroxyethyl)-ferrocene (BHEF), and crosslink formation is believed to proceed according to the following scheme:
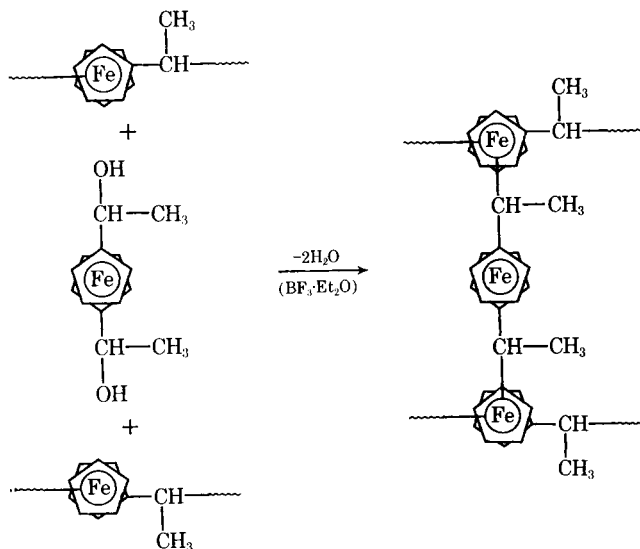
Another crosslinking method involved resol-type ferrocene polymers, designated "Polyol F" and "Polyol A." These polyfunctional macromolecules were obtained by substituting PFMM with the reactive hydroxymethyl and α-hydroxyethyl groups, respectively. During the curing process, the carbinol groups are able to react with ferrocene units belonging to other PFMM chains, in a manner illustrated schematically as follows, when R represent H ("Polyol F") or CH_3 ("Polyol A"):
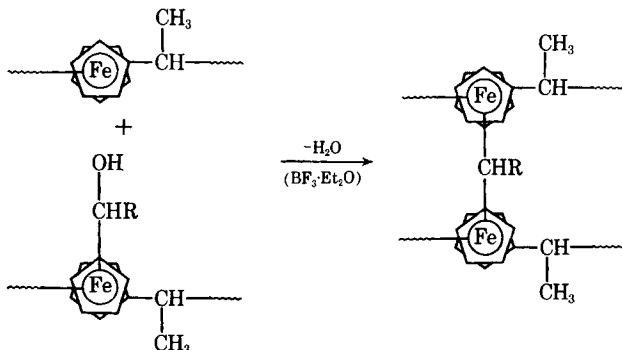
The curing of the various thermosetting mixtures was conducted according to a preestablished program (Fig. 1). At first, the air trapped either in the molding powders or in the impregnated laminates was forced out by cold pressing (at P_f) for several seconds. During the first stage of heating, the samples were subjected to a moderate pressure only, in order to minimize losses due to leaking out of the melted curing agent and/or polymer. After the polymer had hardened sufficiently, curing was completed under a pressure equal to P_f.

The maximum curing temperature (175°C) lies well above the softening range of the polymer, yet sufficiently low to avoid thermal degradation. A preliminary test performed by the aid of the torsional braid apparatus
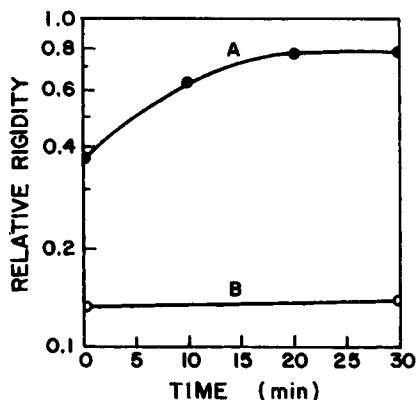

Fig. 5. Isothermal torsional braid analysis of PFMM (M_n 72,000) at 160°C, in nitrogen: (A) with curing agent (30% BHEF); (B) without curing agent.

(Fig. 5) indicated that the curing process with BHEF at 160°C took about 20 min to reach completion.

Characterization of the Crosslinked Polymer

The thermal and thermo-oxidative behavior of crosslinked PFMM is presented in Figures 6 and 7. In this connection, it should be noted that while the crosslinked polymer samples subjected to the penetrometric and thermogravimetric measurements were prepared in closed molds under standard curing conditions (Fig. 1), the curing of the impregnated glass braids for the TBA experiments were carried out at atmospheric pressure, in nitrogen. Considering that during the heating of the TBA specimen part of the curing agent was lost by vaporization, one can assume that the cured polymer had only a low degree of crosslinking. This assumption is supported by the fact that above 100°C the TBA curves indicate a decrease in rigidity (Fig. 6), while by the penetrometric method no softening could be detected up to 200°C (Fig. 7). In nitrogen, the softening of the cured test specimen reached a minimum at the same temperature that marked the onset of degradation (230°C). Between 380
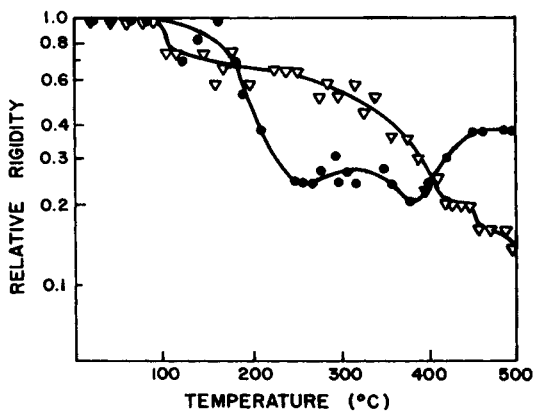
Fig. 6. Torsional braid analysis of crosslinked PFMM (primary M_n, 20,000; curing agent, 30% BHEF): (●) in nitrogen; (∇) in air.
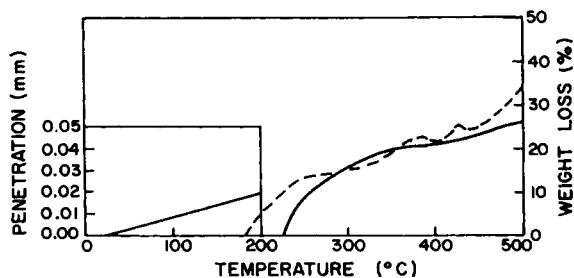
Fig. 7. Penetrometric and thermogravimetric analysis of crosslinked PFMM (primary M_n, 20,000; curing agent, 30% BHEF): (———) in nitrogen; (– – –) in air.

TABLE II
Properties of PFMM[a] Thermosets

| Sample no. | Curing agent | | Potential crosslinks per 100 ferrocene units[b] | S | Q | Q^{-2} |
	Type	Weight, %				
T-1	BHEF	7.5	6.5	0.210	0.694	2.08
T-2	BHEF	10	8.75	0.045	0.594	2.85
T-3	BHEF	15	13.3	0.052	0.570	3.08
T-4	BHEF	20	17.8	0.005	0.489	4.18
T-5	BHEF	30	27.0	0.000	0.453	4.88
T-6	BHEF	40	36.5	0.000	0.308	10.05
T-7	Polyol F	100	32.1	0.000	0.252	15.70
T-8	Polyol A	50	22.5	0.044	0.566	3.12

[a] M_n 10,000.

[b] BHEF: Moles per 100 ferrocene units; "Polyol F" and "Polyol A": atom-grams oxygen per 100 atom-grams Fe (based on elemental analyses).

and 450°C, the value of the relative rigidity increased almost twofold, at 500°C being 0.4, against 0.025 for the noncrosslinked specimen (Fig. 3). The beneficial influence of the crosslinking is evident also from the fact that at 500°C, 75% of the polymer remained as a char, versus 60% for the noncrosslinked one (Fig. 3). In all probability, the hardening of the braid specimen around 400°C can be attributed to the char residue, which acts as binder for the reinforcements (glass yarns). Also in an oxidative atmosphere (air), the stability of the polymer appeared to be improved by crosslinking, as shown both by the weight loss and the loss in rigidity being slowed down to a significant extent (Fig. 6).

Information on the structure of crosslinked PFMM was obtained from solvent swelling and sol fraction measurements. As solvent, 1,2-dichloroethane was chosen because of its relatively low polarity and its solubility parameter (9.8 cal$^{0.5}$/cm$^{1.5}$),[12] which is nearly identical to that found for PFMM by turbidimetric titrations (9.81 cal$^{0.5}$/cm$^{1.5}$).

In Table II, S represents the sol fraction, i.e., the weight of polymer that is not incorporated into the network structure related to the initial weight of the polymer, and Q is the weight fraction of the solvent in the swollen polymer, at equilibrium. The values of Q^{-2} are also given, since for a number of crosslinked polymers a linear relationship was observed between these values and the respective crosslink densities.[21,22]

Thus, more than 20% BHEF is necessary to obtain a material free of solvent-extractable polymer. Yet, one has also to consider that in the presence of Lewis acid catalysts, BHEF undergoes self-condensation to the corresponding polyether, with subsequent crosslinking.[23] The occurrence of such a reaction could diminish considerably the efficiency of BHEF as a curing agent.

TABLE III
Composition and Mechanical Properties of Structural Composites[a]

Sample no.	Type	Weight, %	Potential crosslinks per 100 ferrocene units[b]	Resin content, %	Reinforcement (filler)	Flexural strength, kg/cm²	Compressive strength, kg/cm²
T-17	BHEF	20	17.8	35	glass cloth	620	
T-18	BHEF	20	17.8	42	asbestos paper	330	
T-19	BHEF	5	4.0	48	(asbestos fiber)		1060
T-20	BHEF	15	13.3	46.5	(asbestos fiber)		1340
T-21	BHEF	45	38.9	40.5	(asbestos fiber)		1590
T-22	Polyol F	50	18.6	48	(asbestos fiber)		1350
T-23	Polyol A	50	22.5	44.5	(asbestos fiber)		1250

[a] M_n of PFMM, 20,000.
[b] BHEF: Moles per 100 ferrocene units; "Polyol F" and "Polyol A": atom-grams oxygen per 100 atom-grams Fe (based on elemental analyses).

The comparatively high sol content of the polymer crosslinked by means of "Polyol A" may be due to the low molecular weight of the latter. From the swelling data, it is apparent that the highest degree of crosslinking could be achieved by the curing of a "Polyol F"—catalyst mixture.

Data on the composition and mechanical properties of a series of crosslinked PFMM-based structural composites are presented in Table III. The very limited data on the flexural strength of laminates do not allow conclusions to be drawn. Regarding the compressive strength of asbestos fiber-filled samples, it appears to increase with increasing proportions of molecules or meric units capable of forming crosslinks. It is interesting to note parenthetically that the compressive strength of these samples are of the same order of magnitude as those reported for similar composites based on phenol–formaldehyde resins.[24]

References

1. A. Gal, M. Cais, and D. H. Kohn, *J. Polym. Sci. A-1*, to be published.
2. N. Phillips, *Plast. Inst. Trans. J.*, **32**, 298 (1964).
3. N. Phillips and B. Nixon, French Pat. 1,455,821 (Sept. 12, 1966).
4. B. J. C. Moore, *Sci. Tech. Aerospace Rept.*, **3**, 1688 (1965); *C.A.*, **65**, 9098 (1966).
5. F. Long, B. B. Millward, and R. J. Roberts, Advances in Polymer Science and Technology, S.C.I. Monograph No. 26, Soc. of Chemical Ind. (London), 1967, p. 248.
6. N. Billow and L. J. Miller, *J. Macromol. Sci., Chem.*, **A3**, 501 (1969).
7. N. Billow and H. Rosenberg, *J. Polym. Sci. A-1*, **7**, 2689 (1969).

8. N. Billow, A. L. Landis, and H. Rosenberg, *J. Polym. Sci. A-1*, **7**, 2719 (1969).

9. J. K. Lindsey and C. R. Hauser, *J. Org. Chem.*, **22**, 355 (1957).

10. G. D. Broadhead, J. M. Osgerby, and P. L. Pauson, *J. Chem. Soc.*, 650 (1958).

11. K. W. Suh and D. H. Clarke, *J. Polym. Sci. A-1*, **5**, 1671 (1967).

12. J. L. Gardon, in *Encyclopedia of Polymer Science and Technology*, Vol. 3, H. F. Mark, N. G. Gaylord, and M. Bikales, Eds., Interscience, New York, 1965, p. 383.

13. O. B. Edgar, *J. Chem. Soc.*, 2638 (1952).

14. B. Y. Teitelbaum, V. G. Gizatullena, and T. A. Yagfarov, *Polym. Sci. USSR*, **6**, 324 (1964).

15. S. L. Madorski, *J. Polym. Sci.*, **9**, 133 (1953).

16. J. D. Behun, *Talanta*, **9**, 83 (1962).

17. A. F. Lewis and J. K. Gillham, *J. Appl. Polym. Sci.*, **6**, 422 (1962).

18. J. K. Gillham and A. F. Lewis, *J. Appl. Polym. Sci.*, **7**, 2293 (1963).

19. ASTM D 695-61 T, in *ASTM Standards on Plastics*, 13th ed., Amer. Soc. Testing Mater., Philadelphia, Pa., 1962, p. 301.

20. ASTM D 790-61, in *ASTM Standards on Plastics*, 13th ed., Amer. Soc. Testing Mater., Philadelphia, Pa., 1962, p. 469.

21. O. Lorenz and C. R. Parks, *J. Polym. Sci.*, **50**, 299 (1961).

22. N. Ashikari, I. Kawashima, and T. Kawashima, *Bull. Chem. Soc. Japan*, **40**, 2597 (1967).

23. E. W. Neuse, in *Encyclopedia of Polymer Science and Technology*, Vol. 8, H. F. Mark, N. G. Gaylord, and N. M. Bikales, Eds., Interscience, New York, pp. 675 and 676.

24. Plastics Properties Charts, in *Modern Plastics Encyclopedia*, S. Gross, Ed., McGraw Hill, New York, 1969, p. 977.