

# High-Strength/High-Modulus Fibers of *p*-Phenylene Oxadiazole/*N*-Methyl Hydrazide Copolymers—A New Class of High-Performance Organic Materials

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## Synopsis

*p*-Phenylene oxadiazole/*N*-methyl hydrazide copolymers were prepared by polymerization of terephthalic acid, dimethyl terephthalate, and hydrazine sulfate in fuming sulfuric acid, and coagulation of the polymer was obtained in aqueous sulfuric acid. Fibers spun from these copolymers have unusually high strength and modulus, making these materials attractive for the reinforcement of articles such as tires. Yarn tenacities of 16–21 gpd and moduli of 350–450 gpd were obtained. Yarn of these copolymers showed no significant degradation under conditions to which a tire cord material is subjected in tire building and end use. In their performance in vehicle tires, tire cords were found to be competitive with other reinforcing agents such as fiber glass, steel, and commercial poly(*p*-phenyleneterephthalamide).

## INTRODUCTION

Filamentary materials of superior specific strength and outstanding stiffness are gaining increasing importance in the reinforcement of rigid as well as flexible structures. Among these materials are steel wire, fiber glass, other inorganic filaments, and organic fibrous polymers. Special consideration is given to fibers that exhibit excellent strength and stiffness, good fatigue resistance, low density, and commercially acceptable manufacturing cost. The combination of these requirements appears to be best met by organic polymers and fibers. Attempts at preparing such high-performance organic (HPO) materials are exemplified by X-500,<sup>1</sup> an aromatic *p*-phenylene hydrazide/amide copolymer, and by Kevlar (du Pont registered trade mark),<sup>2</sup> assumed to be poly(*p*-phenyleneterephthalamide) (PPT). Numerous other fibrous HPO materials have been developed; these are adequately reviewed in a recent publication.<sup>3</sup>

The cited polymers are mostly prepared by polymerization of aromatic diacid chlorides with aromatic diamines. For achievement of ultimate fiber properties, rigid aromatic structures are preferred which have a high degree of straight-line connection of units such as found in the *p*-phenylene radical. Most of these polymers and fibers are somewhat disadvantaged in the marketplace due to comparatively high costs of raw materials and/or solvent recovery, e.g., of organic amide solvents or sulfuric acid.

The discovery by Neugebauer<sup>4</sup> that aromatic acids will condense with hydrazine (as its sulfate) in fuming sulfuric acid to yield monomeric oxadiazole compounds provided a seemingly less costly route to the condensation of aromatic units. This reaction was applied by Iwakura<sup>5</sup> and Korshak<sup>6</sup> to the preparation of all-aromatic oxadiazole homopolymers. Such polymers were subsequently

spun from sulfuric acid by Imai,<sup>7</sup> in spite of their relative intractability. In order to make the aromatic oxadiazole homopolymers more tractable and spinnable, Imai employed *m*-/*p*-phenylene oxadiazole copolymers instead of the structurally preferable all-*p*-phenylene polyoxadiazole. In a later paper Iwakura<sup>8</sup> showed that poly(*p*-phenylene-*N*-methyl hydrazide) can be prepared in oleum if dimethyl terephthalate is condensed with hydrazine sulfate. Recently, subsequent to the bulk of our reported investigations, preparation and spinning of aromatic oxadiazole/*N*-methyl hydrazide copolymers was reported by Sekiguchi.<sup>9</sup> Strength of fibers spun was reported to be less than 5 g/den, similar to properties of oxadiazole homopolymers. The comparatively low strength of these fibers might possibly be attributed to the low molecular weight of the polymers obtained.

In our investigations of the cited reactions it became quickly apparent that aromatic polyoxadiazole homopolymers with a high degree of *p*-phenylene content are not practical for the preparation of high-performance organic fibers due to the intractability of the polymer dopes as well as of the spun fibers. The *N*-alkylated aromatic hydrazide polymer of Iwakura was shown to exhibit poor coagulation characteristics.

In our subsequent studies it was found that a combination of the oxadiazole and *N*-alkyl hydrazide units in an all-*p*-phenylene polymer structure would yield fiber properties superior to either of the homopolymers. As data in this paper demonstrate, fibers of all-aromatic oxadiazole/*N*-methyl hydrazide copolymers provide a new class of high-performance organic (HPO) materials for the reinforcement of passenger car tires. These modified oxadiazole fibers are found to be competitive with other reinforcing agents such as fiber glass, steel, and PPT in their performance.

## EXPERIMENTAL

Polymers reported in this paper were prepared from commercially available (Amoco) terephthalic acid and dimethyl terephthalate by reaction with recrystallized (from aqueous sulfuric acid) hydrazine sulfate which was prepared from dihydrazine sulfate (Olin) by reaction with aqueous sulfuric acid. Reagent-grade oleum used was acquired from Fisher Scientific Co. at the 20% and 30% SO<sub>3</sub> concentration level. Oleum of higher SO<sub>3</sub> concentration was prepared by adding liquid SO<sub>3</sub> (Sulfan, Allied Chemical Co.) to oleum.

A typical polymer preparation was conducted as follows: terephthalic acid (127.82 g, 0.77 mole), dimethyl terephthalate (122.22 g, 0.63 mole), and hydrazine sulfate (184.99 g, 1.42 mole) were charged to 3753 g 20% oleum in a 3-liter resin kettle equipped with a helical ribbon stirrer and protected from moisture by means of a drying tube. After dissolution of the monomers, the temperature was raised to 140°C for 6 hr. Polymer inherent viscosity obtained was 3.3 (0.2 g of calculated oxadiazole/*N*-methyl hydrazide copolymer/100 ml conc. H<sub>2</sub>SO<sub>4</sub>, 30°C, solution obtained by dilution of dope).

The dope was spun to fiber in a standard dry-jet spinning procedure by coagulating the extruded filaments in water at 20°C, washing the fibers in water after neutralization with aqueous sodium carbonate, drying, and hot-drawing the yarn bundle.

Commercial Kevlar tire cord was used as PPT.

## RESULTS AND DISCUSSION

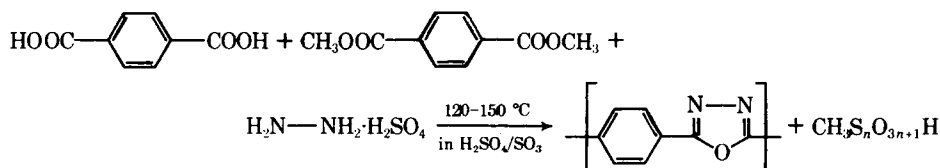
## Polymerization

Fibers of *p*-phenylene oxadiazole/*N*-methyl hydrazide copolymers are prepared by polymerization at elevated temperatures of terephthalic acid, dimethyl terephthalate, and hydrazine (as its sulfate) in fuming sulfuric acid (oleum). Oleum serves in this polymerization as a condensing (dehydrating) agent as well as a polymer solvent. Polymer solutions obtained are directly spinnable into aqueous sulfuric acid to yield the oxadiazole/*N*-methyl hydrazide copolymer fibers.

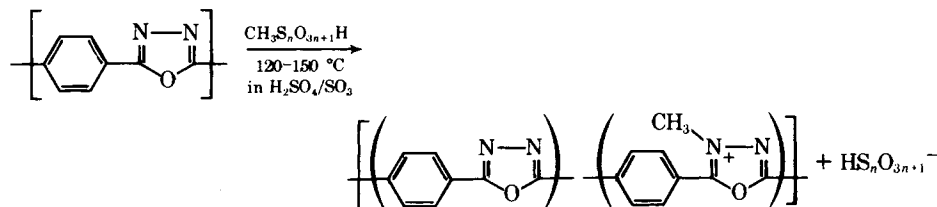
Investigations reported in this paper were mostly conducted with polymer compositions obtainable from equimolar mixtures of terephthalic acid and dimethyl terephthalate. Other polymer compositions with higher oxadiazole-to-hydrazide ratios were also found to produce excellent fibers. These compositions and corresponding evaluations will be reported in forthcoming papers.

In the reaction of the aromatic diacid and diester with hydrazine in oleum and the subsequent polymer coagulation during spinning, three principal stages can be distinguished as shown in the following scheme:

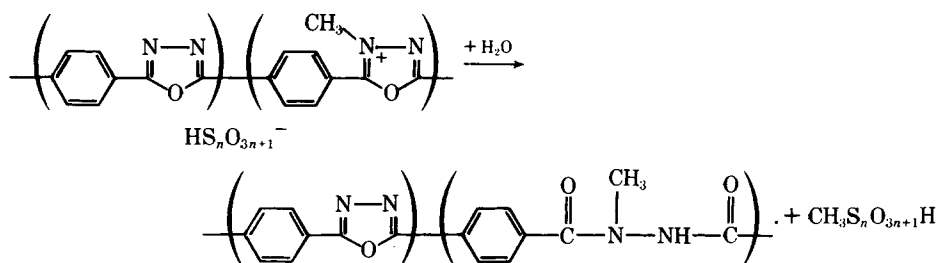
## A. Polymerization



## B. Methylation



## C. Hydrolysis



Details of this sequence of reactions as well as the pertinent chemistry of reactions in oleum will be discussed in a forthcoming paper. During this polymerization, polymer inherent viscosities of 3 to 5 are easily obtained if a slight excess of hydrazine sulfate is employed.

### Yarn Properties

Fibers of *p*-phenylene oxadiazole/*N*-methyl hydrazide copolymers reported in this paper exhibited a high degree of strength (tenacity) and stiffness (modulus) combined with an unusually high—for an all *p*-phenylene polymer—elongation. Maximum as well as typical tensile properties obtained are shown in Table I. Data are for a 50/50 TA/DMT composition.

Tensile data shown demonstrate the potential of these modified oxadiazole copolymers as high-strength, high-modulus fibrous materials. A few other physical data are given in Table II. Density and moisture regain are in the range to be expected for an aromatic condensation polymer. The chemical transition of *N*-methyl hydrazide to oxadiazole units at temperatures above 300°C would preclude use of these fibers as materials in the area where long-term high-temperature stability is required. For the intended end uses in the moderately elevated temperature range no difficulties were expected or encountered.

### Yarn Evaluation

Prior to fabrication and testing of tires made from the reported fibers, yarn of the oxadiazole/*N*-methyl hydrazide copolymers was evaluated very extensively in regard to its stability under tire processing and end use conditions. This test series was aimed at discovering any "fatal flaw" that could absolutely preclude use of these polymers and fibers in the intended end use.

Some selected test data are given in Table III. As these results show, no substantial deficiencies for in-tire use of *p*-phenylene oxadiazole/*N*-methyl hydrazide copolymeric fibers were found. Data shown were substantiated by further tests, which will be described in a later paper.

Accelerated evaluation of retention of tensile properties upon light exposure revealed a low degree of light stability as shown by data given in Table IV.

The low degree of light stability was not unexpected for a polymer containing

TABLE I  
Tensile Properties<sup>a</sup> of Aromatic Oxadiazole/*N*-Methyl Hydrazide Copolymer Yarns

	Best Sample <sup>b</sup>	Typical Sample <sup>c</sup>
Tenacity, gpd (psi × 10 <sup>-3</sup> )	21.2 (369)	16–18 (278–313)
Elongation, %	5.5	5.5–6.5
Modulus, gpd (psi × 10 <sup>-6</sup> )	449 (7.81)	350–420 (6.09–7.31)
Work to break, g-cm/den-cm	0.57	0.45–0.60
Denier per filament	0.3	0.5–1.0

<sup>a</sup> Average of five bundle breaks, Instron, 10 cm gauge length, 10% extension/min.

<sup>b</sup> Average shown, best individual break (Ten/Elong/Mod): 28.0 gpd/5.3%/519 gpd.

<sup>c</sup> Representative range of properties of series of polymerization and spin runs.

TABLE II  
Physical Properties of Aromatic Oxadiazole/*N*-Methyl Hydrazide Copolymer Fibers

Density, g/cc	1.36
Moisture regain, % (65% R.H., 25°C)	6.1–6.2
Decomposition temperature, °C (DTA, 10°C/min, in nitrogen)	460 (at > 300°C chemical transition of hydrazide ring closure is observed also)
Color	white to pale yellow

TABLE III  
Stability Evaluation of Aromatic Oxadiazole/N-Methyl Hydrazide Copolymer Yarn

Dry heat shrinkage at 180°C, %	0.6
Dry heat shrinkage, at 220°C, %	0.8
Tenacity, % of R.T. Ten at 100°C	78
Tenacity, % of R.T. Ten at 150°C	61
Tenacity, % of R.T. Ten at 200°C	43
% Retention of Ten/Elon/Mod after exposure in air to elevated temperatures at 150°C, seven days	100/105/104
Creep, <sup>a</sup> load at 20% of breaking strength, 25°C	
Short-term (10 min), %	1.0
Long-term (21 days), %	1.3
Hydrolytic stability, % retention of Ten/Elon/Mod after exposure to boiling water for seven days	90/96/96

<sup>a</sup> Fiber prepared from 75/25 ratio of terephthalic acid/dimethyl terephthalate.

TABLE IV  
Light Stability of Aromatic Oxadiazole/Hydrazide Fibers

Light stability, Fade-O-Meter, <sup>a</sup> % retention of tenacity after exposure for	
30 hr	35%
60 hr	22%
90 hr	20%

<sup>a</sup> Xenon arc lamp, Pyrex filters, AATCC Test Method 16E-1974.

aromatic heterocyclic units. A similar sensitivity to light had been shown earlier for fibers of an all-oxadiazole<sup>10</sup> and a bithiazole-amide<sup>11</sup> polymer. Light exposure is not a problem for the reported *p*-phenylene oxadiazole/N-methyl hydrazide copolymeric fibers in the end uses contemplated. The yarn was shown to be stable to fluorescent light exposure under warehousing conditions.

### Tire Evaluation

Fibers of these copolymers were designed to be used primarily as reinforcing materials for the carcass and belt of bias-belted and radial tires. A series of tire tests was conducted to prove the suitability of these yarns for tire reinforcement and to compare them against materials currently in use, e.g., steel, fiber glass, and PPT. A few illustrative test results are given in Tables V and VI. Most of these tests were conducted earlier in the program when yarn tenacities were only 10–14 gpd and yarn moduli were 300–350 gpd. An expanded series of tire tests and data as well as detailed data on polymerization and spinning are planned for separate papers.

TABLE V  
Treadwear (Bias-Belted Tires, Equal Strength Belts)<sup>a</sup>

Belt cord	Left shoulder	Center	Right shoulder
Oxadiazole fiber	52	94	59
Glass	56	101	60
Steel	65	100	59

<sup>a</sup> Treadwear in miles/mil, with averages normalized for 100 miles/mil for drawn-steel belts.

TABLE VI  
Durability Test (Radial Tires, Equal Weight Basis)

Carcass cord	Failure miles <sup>a</sup>	% Cord strength retained <sup>b</sup>
Oxadiazole fiber (1500/2 11 × 11)	13,300 <sup>c</sup>	90
Oxadiazole fiber (1500/2 11 × 11)	21,600 <sup>d</sup>	47
PPT (1500/2 11 × 11)	6,000 <sup>d</sup>	—
PPT (1500/2 11 × 11)	12,500 <sup>d</sup>	75

<sup>a</sup> Failures were not related to cord breakage.

<sup>b</sup> Original breaking strength of cords used: PPT, 106 lb; oxadiazole, 64 lb.

<sup>c</sup> Failure perhaps related to loss of adhesion.

<sup>d</sup> Failed due to severe tread chunk-out.

In the primary evaluation of tire performance, three main criteria are important: (a) the resistance of the tire to failure due to road hazards or rough road conditions, (b) the mileage obtainable from a given tire until the tread has been worn off, and (c) failure resistance under overload conditions. All of these performance characteristics are strongly influenced by the cord material used in the carcass and the belt of the tire. In addition, tire design plays a very important role. Results of a mileage test on a medium-wear test track are given in Table V.

In actual end use tires are often misused because of neglect or lack of information. Driving on overloaded, underinflated tires is quite common. To evaluate our material for durability under conditions of misuse, steel-belted radial tires were tested to failure under overloaded, underinflated conditions on an indoor test wheel. PPT was used as a control. Results obtained are given in Table VI. The performance of the oxadiazole copolymeric fiber is particularly remarkable in light of its lower specific breaking strength.

## CONCLUSIONS

In our studies it has been demonstrated that high molecular weight *p*-phenylene oxadiazole/*N*-methyl hydrazide copolymers can be prepared by polycondensation of terephthalic acid, dimethyl terephthalate, and hydrazine sulfate in fuming sulfuric acid (oleum) and subsequent coagulation in aqueous sulfuric acid. Polymer solutions obtained in the polymerization step are directly spinable into aqueous acid to yield fiber of excellent properties. Yarn obtained is shown to be usable as cord material for the reinforcement of the carcass as well as the belt of automobile tires. While data indicate that fibers of aromatic oxadiazole/*N*-methyl hydrazide copolymers have potential as a high-performance organic (HPO) material, considerable further evaluations are required to fully qualify these fibers for the contemplated end uses.

An extensive research effort such as the one presented requires an extensive team of dedicated collaborators to be successful. Team members will appear as coauthors on subsequent publications concerning this fiber system. Special gratitude is due to W. J. Boles, Jr., and W. E. Waters for their dedicated assistance.

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