Nylon 6,6 Copolyamides of Bis(2-Carboxyethyl)Methylphosphine Oxide

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Synopsis

Copolyamides of nylon 6,6 with *bis*(2-carboxyethyl)methylphosphine oxide (CEMPO) were prepared by melt polycondensation of nylon 6,6 salt with CEMPO and hexamethylene diamine. The effect of CEMPO upon melting point, moisture regain, boiling water shrinkage, water wicking, tensile properties, thermal stability, static dissipation, and flammability of nylon 6,6 fibers and fabrics was determined. The fiber properties were greatly affected by the high water absorption and solubility characteristics of the phosphine oxide linkage. However, crystallinity and orientation were not greatly disturbed by up to 30–40M% CEMPO substitution in nylon 6,6. The copolyamides were of improved flame resistance compared to nylon 6,6, and were also found to give improved flame resistance in blends of the copolymer with various commercial plastics. In addition, CEMPO and the corresponding diamine, *bis*(3-aminopropyl)methylphosphine oxide were used to prepare a series of cycloaliphatic and aromatic ring-containing polyamides, but problems were encountered with moisture sensitivity and low melting points with some of these polymers.

INTRODUCTION

In recent years considerable emphasis has been placed upon the development of improved flame-resistant polymers and textile fibers. Flammability is commonly reduced through the incorporation of additives which contain halogens or phosphorus. However, the amount of additive required often seriously harms the desirable properties of the original polymer or fiber. In addition, the additive may also be subject to extraction by water or cleaning solvents. Such problems can be avoided by the judicious selection of appropriate comonomers, which allow introduction of the desired halogen or phosphorus material directly into the polymer backbone.

Phosphorus has been successfully incorporated into polyamides from diamines or dicarboxylic acids with phenylene or phenoxy structures linked by the phosphine oxide linkage.[1-3] In general, the melting points were in the low range for textile fibers ($< 230°C$). Even lower melting points resulted with aliphatic phosphine oxides.[2,4] Accordingly, these phosphine oxides are often copolymerized[3] with higher melting polyamides in order to achieve useful textile fibers. As an example, copolyamides from caprolactam and methylphosphacaprolactam have been studied.[5] The structurally similar nylon 6,6 copolyamide based upon *bis*(2-carboxyethyl)methylphosphine oxide (CEMPO) has been reported in the patent literature.[6]

This paper describes the influence of CEMPO substitution upon the polymer and fiber properties of nylon 6,6, several CEMPO polyamides, as well as polymeric blends with other materials. In addition, polyamides based upon

the diamine analog of CEMPO, *bis*(3-aminopropyl)methylphosphine oxide, are also described.

EXPERIMENTAL

Materials

Bis(2-carboxyethyl)methylphosphine oxide (CEMPO) and *bis*(3-aminopropyl)methylphosphine oxide (APMPO) were prepared from *bis*(2-cyanoethyl) methylphosphine[7] by the methods of Pellon and Carpenter.[2] CEMPO melted at 175–177°C and gave a neutral equivalent of 208.05 (Theory of 208.15), while APMPO (b.p. = 211°C/0.35 mm) had a N.E. = 89.65 (theory = 89.08).

The polymer resins from polypropylene, MB-80 polyurethane, polybutylene terephthalate, polystyrene, SAN, and ABS were obtained from commercial sources.

Methods

Polymerization. Polymers were prepared from mixtures of nylon 6,6 salt, CEMPO, hexamethylene diamine (HMD), and enough water to make a total charge to the polymerizer of 75% reactants. (Stoichiometric amounts of CEMPO and hexamethylene diamine were employed—the salt of HMD and CEMPO was not isolated because of its hygroscopic nature.) The polymerizer was charged with reactants in the following manner: to the dry nylon 6,6 salt in the autoclave was added a solution of HMD, CEMPO, and water. The reactants were then melt polymerized[8] and the finished polymer extruded through a 13-hole spinneret. The fiber was then taken up on a bobbin with a Leesona winder. This fiber bundle was then drawn to approximately 4.5 times its original length over a hot pin at 60–90°C. The resultant fiber denier was 50–100.

The random copolymer of 6,6–90M% 6,CEMPO, 6,CEMPO, and the APMPO homopolymers were prepared by polymerizing approximately 2 g of reactants in a tube polymerizer.[9] These compositions melted too low for the spinning of fibers with reasonable properties.

The polymers are designated by the following code: the first number shows the number of carbon atoms in the aliphatic diamine; the second shows the number of carbon atoms in the aliphatic dicarboxylic acid. Letter designations are used for other diacids or diamines. For example, 6,6-6,CEMPO is the random copolyamide of nylon 6,6 (hexamethylene diamine and adipic acid) with the polyamide of hexamethylene diamine and *bis*(2-carboxyethyl)methylphosphine oxide (CEMPO).

The techniques for measurement of polymer melting point, intrinsic viscosity, moisture regain, boiling water shrinkage, fiber denier, tenacity, elongation, and modulus have been described previously.[8] The fiber properties of denier, tenacity, elongation, and modulus were measured at 72% relative humidity (RH), and 74°F.

Yarn Resistivity. The specific resistance of finish-free yarn was calculated from the measurement of the yarn resistance using the Keithley Model 610C electrometer.[10] Measurements were made on samples preconditioned 24 h at 68% RH, and 72°F.

Static Measurements. Static properties were determined on finish-free circular knit fabrics (knit from 70/13 yarn) using the Static Honestometer[11] (Shishido and Company, Ltd, Tokyo). Measurements were made on fabrics preconditioned in the environment for 24 h at 40% RH, and 75°F.

Moisture Wicking. Measurements were made by carefully placing a drop of water on a preconditioned (24 or 96 h at 68% RH, and 76°F) piece of finish-free circular knit fabric which was stretched across the mouth of a small beaker. Only enough tension to produce a taut surface was applied to the fabric, which was secured to the beaker with a rubber band. The time duration required for disappearance of the drop was then measured.

Reignition number. Finish-free drawn yarn (70/13 den/fil) was plied to a total of 15,000 denier and a 22-inch length of this yarn was suspended from a clamp. The yarn was ignited with a paper match at the bottom of the filament bundle. The flame remained in contact with the yarn until ignition was observed, then the match was removed. When the yarn had ceased burning, the bundle was reignited. The number of relights required to burn the sample to within approximately 1 inch of the clamp is the reignition number.[12]

Oxygen Index. Oxygen index was measured using AATCC test method D2863-74. Samples were generally circular knit fabrics prepared from plying one ply of the 70 denier drawn yarn bundle with one ply 50 denier Owens-Corning fiberglass (ECD-900 1–/0 lz 630).[13] Polymer blends were measured as films of 0.01 inch thickness, which were prepared by pressing between heated plates a mixture of finely ground polymer onto a fiberglass scrim.

RESULTS AND DISCUSSION

Basic Polymer and Fiber Properties

The properties of the homopolyamides of CEMPO proved unacceptable for textile fibers. The 6,CEMPO polymer ($[\eta]_{\text{m-cresol}} = 0.99$)* was so hydroscopic that a thin shaving of the polymer dissolved in its own absorbed water after several days exposure to the atmosphere. Considerable difficulty was encountered in the melting point determination of this sample, as the high moisture regain produced considerable broadening of the melting point. Similar problems were experienced in melting point measurements of the 6,6 copolymers with 75 and 90M% 6,CEMPO substitution. Accordingly, these copolymides and all the homopolyamides were dried at 100°C under a vacuum for 24 h prior to measurement.

A second polyamide of CEMPO was prepared with *trans*-1,4-cyclohexane-*bis*(methylamine) (t-CBMA). The polymer ($[\eta]_{\text{m-cresol}} = 1.23$) was successfully spun from the melt. The melting point could not be readily established via birefringence loss, as a melting range of 175–315°C was obtained. Furthermore, differential thermogravimetric analysis (DTA) did not display a melting peak. The yarn did not burn readily, as ignition could only be supported as long as a flame was in contact with the fiber. However, the fiber became quite tacky after 3 days of exposure to the laboratory atmosphere.
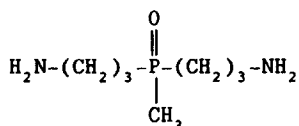
*$[\eta]$ = intrinsic viscosity

TABLE I
Polyamides of Phosphine Oxides

$$\underset{\underset{CH_3}{|}}{HO_2C(CH_2)_2\overset{\overset{\displaystyle O}{\parallel}}{P}-(CH_2)_2CO_2H}$$
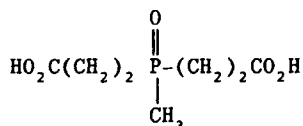
Bis(2-carboxyethyl)methylphosphine oxide

Diamine Component	Melting Point °C
$H_2N(CH_2)_6NH_2$	165-176 (lit. 100-140)[2]
$H_2N\ CH_2-\langle\ S\ \rangle-CH_2NH_2$ (trans)	175-315

$$\underset{\underset{CH_3}{|}}{H_2N-(CH_2)_3-\overset{\overset{\displaystyle O}{\parallel}}{P}-(CH_2)_3-NH_2}$$

Bis(3-aminopropyl)methylphosphine oxide

Diacid Component	Melting Point °C
$HO_2C-\bigcirc-CO_2H$	181-195
$HO_2C-\langle\ S\ \rangle-CO_2H$ (trans)	266-291
$HO_2C-\bigcirc-\bigcirc-CO_2H$	199-211
$HO_2C-\bigcirc-\overset{\overset{\displaystyle O}{\parallel}}{\underset{\underset{\displaystyle O}{\parallel}}{S}}-\bigcirc-CO_2H$	192-209
$HO_2C-\bigcirc-O-(CH_2)_4-O-\bigcirc-CO_2H$	169
$HO_2C-\bigcirc-O-(CH_2)_2-O-\bigcirc-CO_2H$	125
$HO_2C\ CH_2O-\bigcirc-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\bigcirc-O\ CH_2CO_2H$	130

As the choice of ring-containing diamines was limited for melt polymerization, a series of polyamides of *bis*(3-aminopropyl)methylphosphine oxide (APMPO) was prepared (Table I) in an effort to obtain higher melting, less hygroscopic polymers. Of these, only the polyamide with 1,4-cyclohexane dicarboxylic acid proved conveniently high melting for more extensive analy-
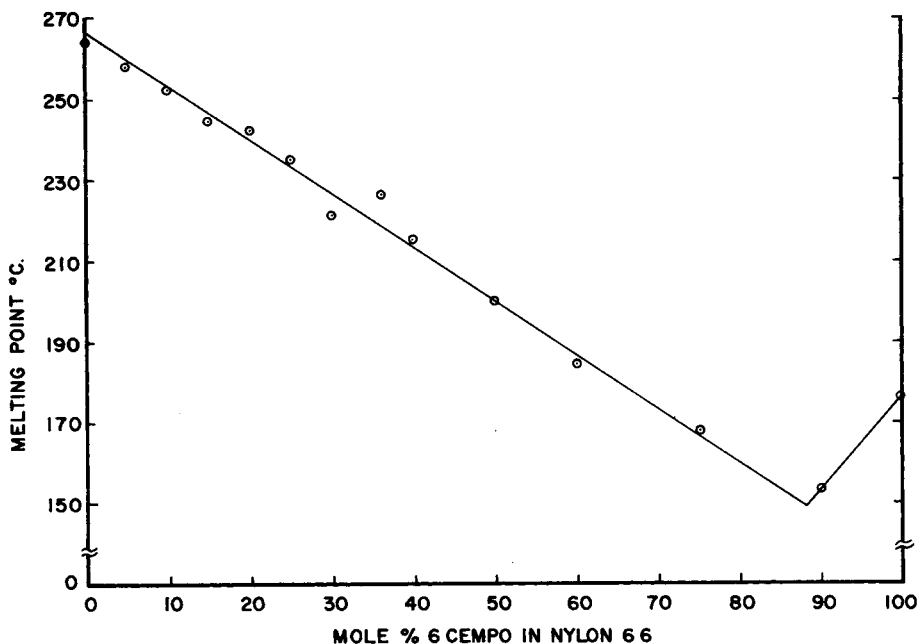
Fig. 1. Melting point vs. composition curves of nylon 6,6-6,CEMPO copolyamides.

sis. The polymer ($[\eta]_{\text{m-cresol}} = 0.82$) was melt spun, and like the t-CBMA-CEMPO polymer proved quite resistant to burning. This polyamide was also quite hygroscopic—indeed, an intrinsic viscosity of 0.24 was obtained in water.

Surprisingly, relatively low melting polymers were obtained with terephthalic and 4,4′-dibenzoic acid. No increase in melting point resulted upon the introduction of the sulfoxide link, while the expected melting point reduction occurred with ether-link substitution. However, copolyamides of 6,6-6,CEMPO were readily prepared; intrinsic viscosities generally ranged from 1.1 to 1.4. Substitution of 6,CEMPO into nylon 6,6 produces a gradual reduction in melting point as 6,CEMPO levels are increased (Fig. 1). A melting eutectic occurs near 90M% 6,CEMPO substitution.

The moisture regain (Fig. 2) exhibits a relatively linear increase with increased 6,CEMPO content up to 50M%. (Fiber data for the random copolyamides of > 50M% 6,CEMPO was not obtained because of fiber tackiness from the high fiber moisture absorption.)

The boiling water shrinkages of the copolymers (drawn yarns) also rises sharply with increased 6,CEMPO substitution (Fig. 3). Again, the relationship appears linear up to 50M% 6,CEMPO. (In contrast, dry heat shrinkage at 100°C only rose from 8 to 21% over the same 6,CEMPO concentration range.) Interestingly, the spun yarns with 40 and 50M% 6,CEMPO shrank in room temperature (23°C) water to give 4 and 38% shrinkage, respectively. These phenomena may be the result of increased water affinity in high 6,CEMPO-substituted polymers. As mentioned previously, the 6,CEMPO homopolymer was water soluble. About three-fourths of the 90M% 6,CEMPO copolymer
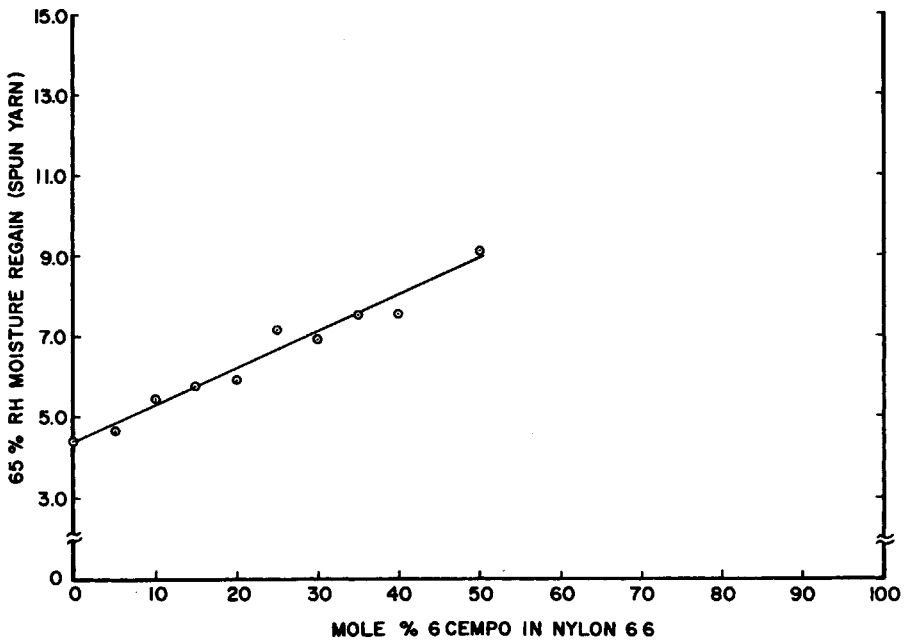
Fig. 2.   Effect of 6,CEMPO upon the percentage moisture regain at 65% RH of nylon 6,6 spun yarn.
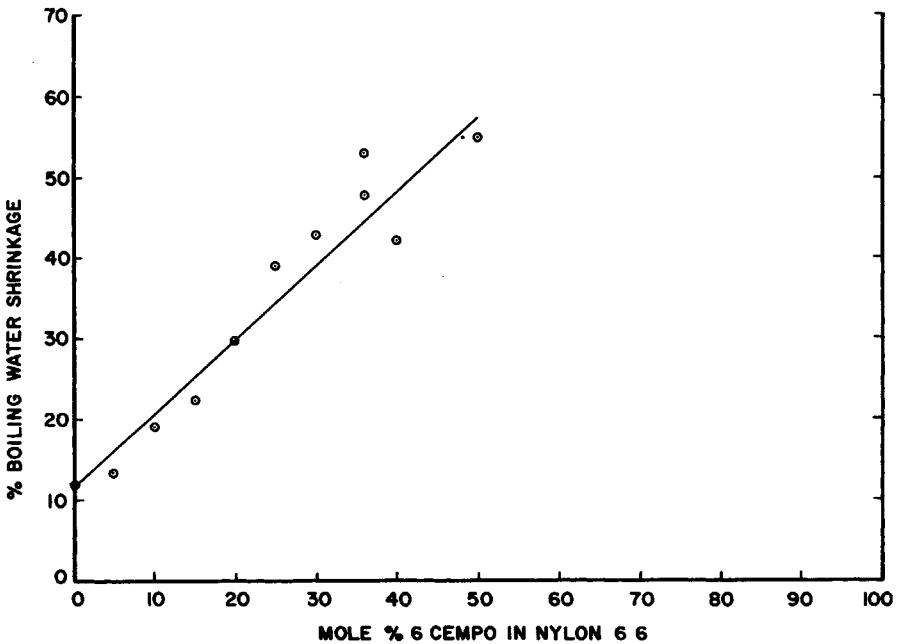

Fig. 3.   Effect of 6,CEMPO upon the boiling water shrinkage of nylon 6,6 fiber.

proved water soluble, while considerable swelling in water was observed in the 50, 60, and 75M% 6, CEMPO copolymers.

The 6,6-6,CEMPO fibers change from translucent to transparent at 40M% 6,CEMPO substitution, which normally indicates a loss of crystallinity in a nonisomorphous copolymer series.[14] This is the result of the crystal lattice of one polymer dissolving into that of the other component with accompanying lattice disruption. This region often corresponds to the melting point eutectic area. Generally, other physical properties, such as boiling water shrinkage, moisture regain, and density will also show abrupt changes in properties in the region of crystallinity disruption. However, such changes are not observed at the 40M% 6,CEMPO level. (Densities were not measured).

Wide-angle x-ray diffraction analysis on drawn fibers of the 6,6-6,CEMPO series revealed that the crystallinity of the copolymers appeared unchanged up to 40–50M% 6,CEMPO substitution. However, some loss of orientation began at the 40M% composition. Such loss was expected because the draw ratios of the 40 and 50M% copolymers were only about half that of the lower series members. Narrow-angle x-ray analysis showed that less lateral ordering of the crystallites in the lamellar structure occurred at the higher 6,CEMPO levels. This became noticeable by 30M% 6,CEMPO substitution and marked at the 40 and 50M% levels. X-ray data are consistent with the lack of abrupt change observed in moisture regain and shrinkage, and would appear to indicate a high degree of isomorphous character in the adipic acid—CEMPO substitution of up to at least 30M%. Still unexplained is the fairly large increase in boiling water shrinkage which would appear to indicate crystal lattice disruption, and yet x-ray analysis has not indicated such. It is possible that the high shrinkages reflect an increasing water solubility in the copolymer, and not a crystallinity or orientation loss.

Aqueous extraction studies of the 6,CEMPO copolyamides and nylon 6,6 further confirm the high water solubility of 6,CEMPO. Drawn fiber samples (without finish and dried at 70°C, 25″ vacuum for 24 h) were boiled in water for up to 96 h, and the weight loss determined after redrying the extracted sample. Weight loss increased with increased 6,CEMPO substitution (Table II).

As would be expected from the higher moisture affinity of the 6,CEMPO copolymers, wicking time (absorption rate of a drop of water into a fabric) decreased with increased 6,CEMPO levels (Table III). The 6,CEMPO copolyamides of lower moisture regains proved most sensitive to conditioning time. Wicking rates were much slower in fabrics conditioned 4 days compared to

TABLE II
Water Extraction Studies on 6,6-6,CEMPO Yarns

Composition	% Weight loss after		
	1 h	24 h	96 h
6,6	0.33	—	—
6,6-15M% 6,CEMPO	1.25	—	—
6,6-30M% 6,CEMPO	1.93	—	—
6,6-40M% 6,CEMPO	—	3.1	5.9

TABLE III
Water Wicking Times of 6,6-6,CEMPO Fabrics[a]

	Wicking time (sec)	
M%6,CEMPO in 6,6	Cond. 1 day[b]	Cond. 4 days[b]
0	343	612
5	390	883
10	354	517
15	196	304
20	106	125
25	188	298
30	5	7
35	2	2
40	3	3

[a] Circular knit tubing.
[b] Conditioned at 68% RH, 76°F.

those conditioned 1 day. The higher regain (30 and 40% 6,CEMPO) samples showed no effect due to conditioning time, and rapidly absorbed the water droplet (< 10 sec for dissipation).

Tensile Properties

The spun fibers were drawn at draw ratios adjusted to give average elongations of 35%. Both tenacity and initial modulus decrease as 6,CEMPO levels rise in nylon 6,6 (Fig. 4). However, acceptable fiber properties are
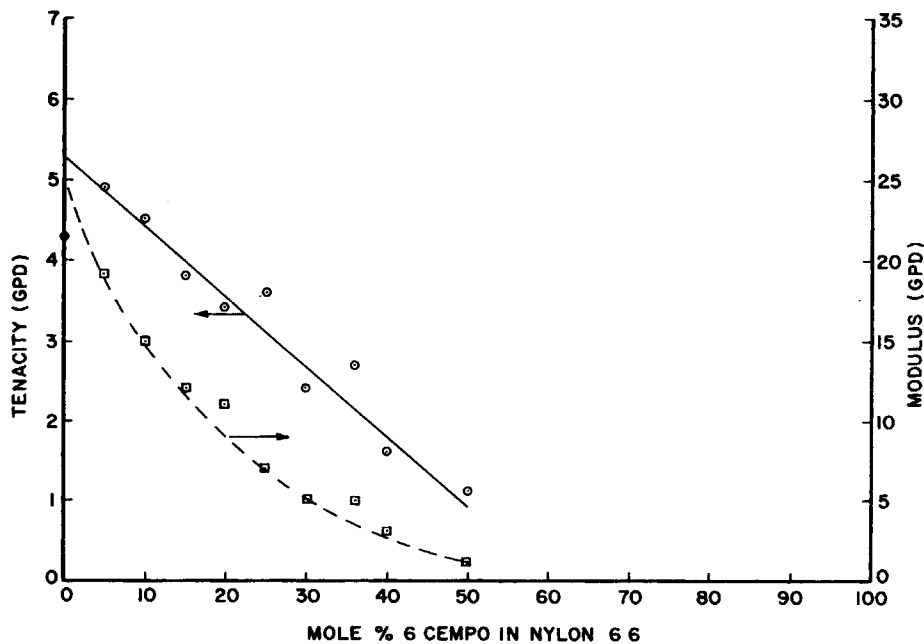

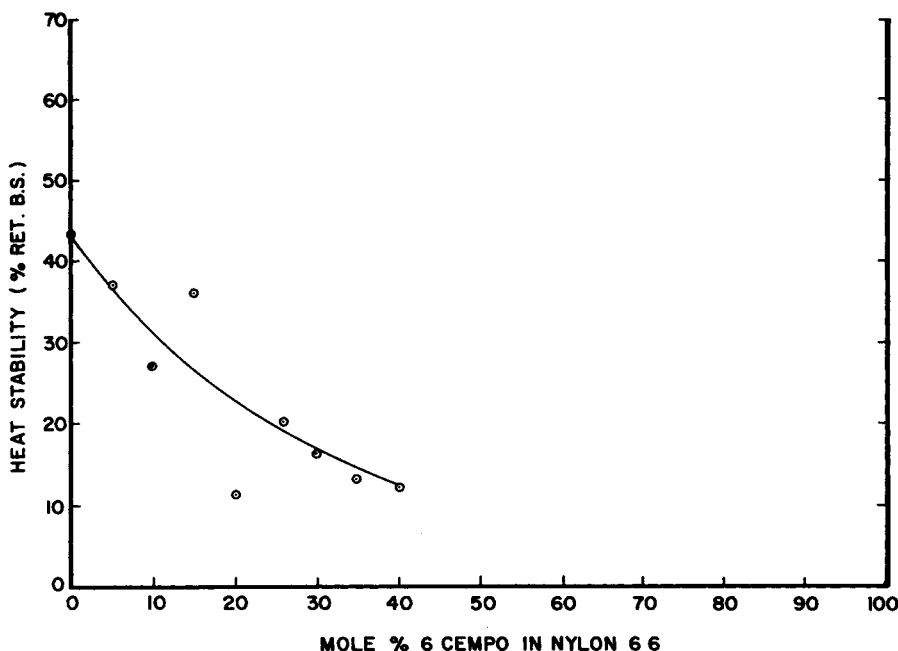Fig. 4.   Tenacity (⊙) and modulus (▣) values of 6,6-6,CEMPO fibers.

Fig. 5. Retention of breaking strength after 1 hour exposure at 188°C in air for 6,6-6,CEMPO fibers.

maintained up to about 35M% 6,CEMPO substitution. The loss of modulus and tenacity appear to reflect increased chain flexibility due to the phosphorus atoms in the polymer backbone,[1] as well as the plasticizing effect from absorbed water.

Exposure of the fibers to 188°C in air for 1 h indicate that thermal-oxidative stability has decreased with increased 6,CEMPO content (Fig. 5). Thermal stability as measured by thermal gravmetric analysis (TGA) also falls with increased CEMPO levels (Table IV).

The onset of initial weight loss tends to occur at somewhat lower temperatures in the 6,6-6,CEMPO yarns compared to nylon 6,6. The percent weight loss at 400°C is also greater in the copolymers than in nylon 6,6. However, differences between 40 and 75M% 6,CEMPO are slight.

TABLE IV
Thermal Stabilities (TGA) of 6,6-6,CEMPO Fibers

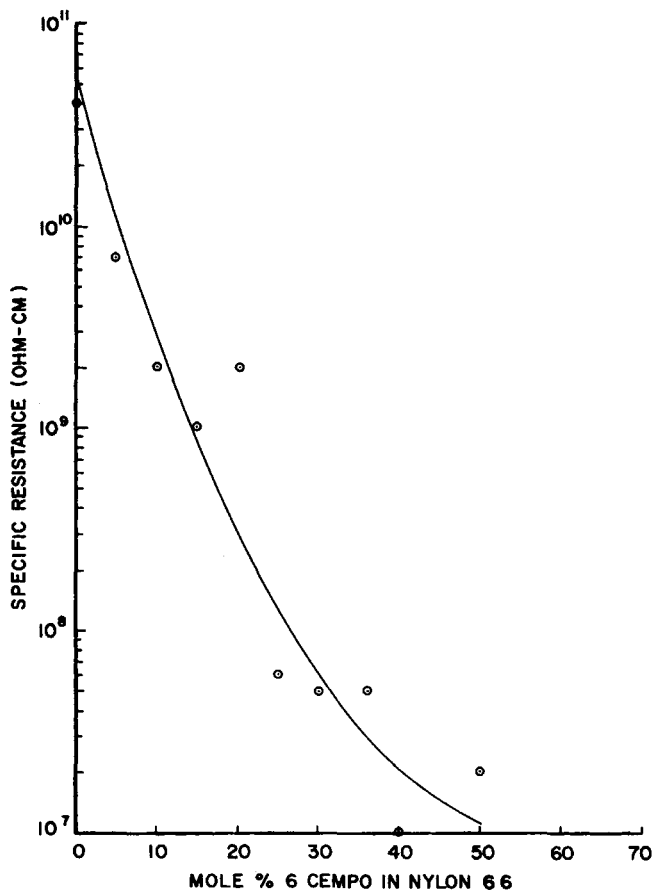|	N₂		Air	
Composition	Onset of wt. loss°C	% Retention 400°C	Onset of wt. loss°C	% Retention 400°C
6,6	390	94	375	92
6,6-15M% 6,CEMPO	365	83	343	79
6,6-40m% 6,CEMPO	348	45	358	67
6,6-50M% 6,CEMPO	350	—	350	45
6,6-75M% 6,CEMPO	350	50	350	51

Fig. 6.   Specific resistance of 6,6-6,CEMPO fibers.

Static Properties

An indication of the static properties of a fabric can be obtained from measurement of the specific resistance[10] of the fiber itself. This technique determines the ability of the fiber to conduct an electrical charge away from the charge source. The 6,6-6,CEMPO fibers show a decreasing specific resistance as 6,CEMPO levels increase (Fig. 6). Antistatic behavior is confirmed by static dissipation (the half-life time required for dissipation of the initial charge applied to fabric) results on circular knit tubing samples. Static dissipation (40% RH) falls rapidly with increased 6,CEMPO substitution. Very rapid static decay occurs in copolymers at $> 30M\%$ 6,CEMPO (Fig. 7).

Flammability Properties of 6,6-6,CEMPO Copolymers

A preliminary estimate of fiber flammability was obtained from the reignition number. Care must be taken to control the denier/filament in the bundle or considerable variability may occur in the test results. Even so, high thermal shrinkages will interfere with the results, as this will reduce the number of lights required to burn the sample. In general, the reignition number rises as
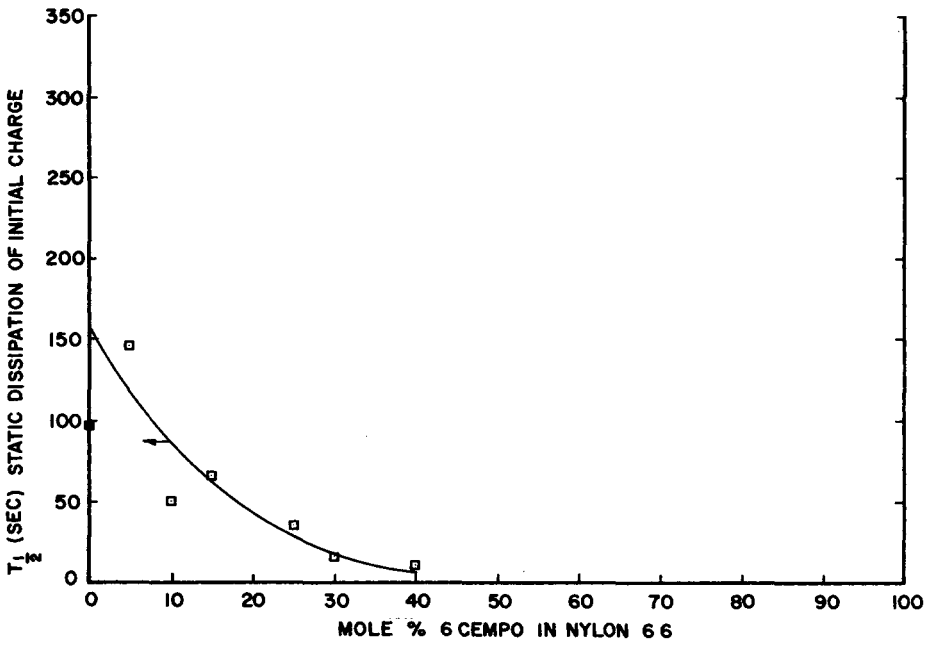
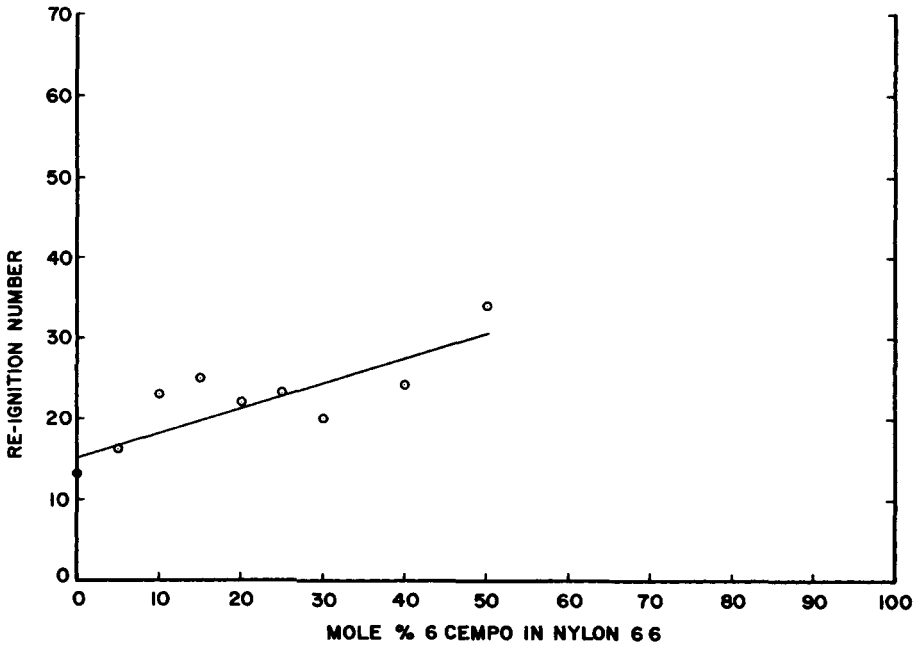Fig. 7. Static half-life times of 6,6-6,CEMPO fabrics.

Fig. 8. Reignition number vs. composition of 6,6-6,CEMPO fibers

TABLE V
Oxygen Index (OI) Values of 6,6-6,CEMPO Fibers

Composition	OI
6,6	19.4
6,6-5M% 6,CEMPO	21.3
6,6-12M% 6,CEMPO	23.3
6,6-20M% 6,CEMPO	25.6
6,6-30M% 6,CEMPO	25.3

6,CEMPO levels in 6,6 increase (Fig. 8). The effects of thermal shrinkage are apparent over the 20-40M% 6,CEMPO range. However, the increased thermal shrinkages, while a nuisance in test measurement, can be considered beneficial to flame resistance. Such yarns would quickly shrink away from an ignition source, and hence burn less readily than fibers of lesser shrinkage—thus reinforcing the effect of the phosphorus in the fiber.

Further proof of the increased flame resistance of 6,6-6,CEMPO was obtained from the oxygen index (OI) test. This test gives the minimum concentration of oxygen (expressed as a percentage) in a mixture of oxygen and nitrogen which will maintain equilibrium burning conditions in an ignited sample. An increase in OI means that flammability resistance has increased. Care must be taken to use fibers of the same yarn count. The oxygen index results (Table V) show that OI increases with increasing 6,CEMPO substitution in nylon 6,6.

Blends of 6,6-6,CEMPO with Other Polymers

Flammability characteristics were also determined on films prepared with blends of 75% polymer resin with 25% of 6,6-50M% 6,CEMPO copolymer. Controls from the resins were also prepared. Compositions were selected on the basis of melting characteristics. With the exception of polybutylene terephthlate, the resins of SAN, ABS, polystyrene, polypropylene, and polyurethane generally require molding temperatures below 250°C because of

TABLE VI
Oxygen Index Values of Polymer Blends with 6,6-50M% 6,CEMPO

Polymer	OI		
	0% CEMPO blend	25% CEMPO copolymer blend	
		Measured	Calculated[a]
ABS	19.2	21.6	21.0
SAN	19.6	22.4	21.3
Polystyrene	18.3	21.7	20.3
Polypropylene	18.6	22.5	20.6
Polybutylene terephthalate	18.9	23.0	20.8
Polyurethane (MB-80)	19.1	22.8	20.9
6,6-50M% 6,CEMPO		26.4	

[a] Theoretical on weight basis.

polymer degradation. The polyurethane (MB-80) selected for study cannot be melted at temperatures above 230°C for similar reasons. Therefore, temperature considerations required the use of a CEMPO copolymer of fairly low melting point, high phosphorus content, but not greatly water soluble. The 6,6-50M% 6,CEMPO composition was therefore selected. A 3 : 1 weight blend of resin: CEMPO copolymer gave 1.5% phosphorus in the composite. This is sufficient to determine FR response, allow the use of suitable blending temperatures, and yet retain most of the original resin characteristics.

Somewhat greater than calculated OI increases were observed in the blends (Table VI).

CONCLUSIONS

The fiber properties of nylon 6,6 copolyamides with 6,CEMPO are greatly affected by the high moisture absorptions and water solubility characteristics induced by the phosphine oxide linkage. These effects are reflected in boiling water shrinkages, moisture absorption rates, fiber tenacity and modulus, and static properties. The fibers were found to give excellent flame-resistant properties either used alone, or in polymer blends.

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