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## ABSTRACT

Title of Thesis: High Temperature Resistant Crosslinked  
Phenol, O-Chlorophenol and Formaldehyde  
Copolymer Fiber

Suh Joon Han, Master of Science in Engineering Science  
(Chemistry), 1989

Thesis directed by: Associate Professor, George Lei

Phenolic copolymer fibers which possess clearly distinguishable physical and chemical properties from other synthetic and natural fibers were prepared. Acid catalyzed condensation polymerization of phenol, formaldehyde and o-chlorophenol was carried out by a two-stage polymerization. Initially, phenol-formaldehyde and o-chlorophenol-formaldehyde oligomers were separately prepared by refluxing the corresponding monomers at 100 °C under strong agitation. At the second stage, these two oligomers were combined and vacuum-distilled to form a block copolymer which was then melt spun into fibers and subsequently cured by succinyl chloride in a mineral spirit. Using a flame test and thermogravimetric analysis, it was found that these cured fibers are hard to ignite and self-extinguish. They become charred when exposed to a flame for an extended period of time. Based on the oxygen index, this copolymer fiber has a better flame retardancy than that of Du pont's commercial Nomex fiber.

**HIGH TEMPERATURE RESISTANT CROSSLINKED PHENOL, O-CHLOROPHENOL  
AND FORMALDEHYDE COPOLYMER FIBER**

BY

SUH JOON , HAN

Thesis submitted to the Faculty of the Graduate School of  
the New Jersey Institute of Technology in partial  
fulfillment of the requirements for the  
degree of  
Master of Science in Engineering Science (Chemistry)  
1989

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**APPROVAL SHEET**

Title of Thesis: High Temperature Resistant Crosslinked  
Phenol, O-Chlorophenol and Formaldehyde  
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## DEDICATION

This thesis is dedicated to my wife, Kate Han and my parents, Yongphil Han and Soonkyung Kim. Without their sacrifices and endless support, this project would not have been completed.



## ACKNOWLEDGEMENT

I would like to express my appreciation and gratitude to Dr. George Lei for his patience, encouragement and guidance for my research. I am deeply indebted to him for the knowledge and experience that I have acquired as a result of his expertise in the field of polymer chemistry.

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## GLOSSARY

PF	: phenol formaldehyde
CF	: o-chlorophenol formaldehyde
PCF	: phenol, o-chlorophenol, formaldehyde copolymer
PTSA	: para-toluene sulfonic acid
OA	: oxalic acid
IR	: infra Red
VPO	: vapor pressure osmometry
OI	: oxygen index
TGA	: thermogravimetric analysis
[ $\eta$ ]	: intrinsic viscosity
$\bar{M}_n$	: number average molecular weight
m.p.	: melting point
$T_g$	: glass transition temperature
$T_m$	: melting transition temperature
psi	: pound per square inch
um	: micro meter
$^{\circ}\text{C}$	: celcius degree

## INTRODUCTION

In recent years considerable emphasis has been put on the development of fibers with improved flame resistance. For example, there are great demands for improved protective clothing for industrial workers and firemen who are regularly in contact with flammable material or work in an area where a fire hazard exists.

Ideally, a fire resistant fiber is a fiber which must not only be resistant to burning or melting in a flame, but must also yield low smoke and toxic by-products and should still possess characteristics commonly associated with a fabric after exposure to a flame. Up to now, there is no textile fiber which possesses such required properties.

Table 1. Flame resistance of commercially available fibers

Behavior in a flame	Fiber
melts and burns	Nylon, Polyester, Acrylic
chars and burns	Cotton, Rayon
chars and self-extinguishes	Wool, Nomex
melts without burning	Teflon, glass fiber
non-melting and non-burning	Carbon

Generally, there are two basic approaches to produce a fire resistant fiber. First of all, the fiber can be produced by adding flame retardants such as phosphorous compounds, boron compounds and halogen compounds in the processing of the fiber (table 2). These additives should be compatible with the polymer and must not deteriorate the properties of the end product. Secondly, the fiber can be produced which has its intrinsic flame resistant properties from the molecular structure, such as highly crosslinked and aromatic structures.

In this project, a new generic flame resistant phenolic copolymer fiber, which is a part of series of phenolic fibers developed by Dr. Lei, was derived from phenol, o-chlorophenol, formaldehyde copolymer. This polymer contains the flame retardant element, chlorine, in its repeating unit and is cured with succinyl chloride to get an aromatic, crosslinked structure.

The potential applications of this fiber are fire insulation in such areas as aircraft and buildings, and protective clothing for firemen, astronauts, auto racers and mill workers.



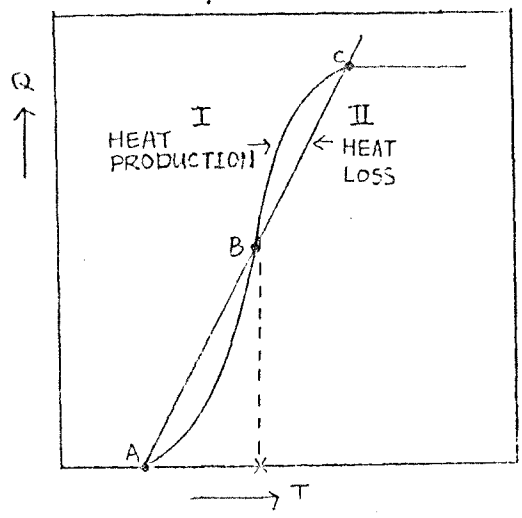
Table 2. Flame retardants

general formula	reactive functionality	manufacturer
$\text{PCl}_3$	P-Cl	Aldrich
$\text{PCl}_5$	P-Cl	FMC
$\text{NH}_4\text{H}_2\text{PO}_4$	P-OH	Riedel Dehaen
$(\text{NH}_4)_2\text{HPO}_4$	P-OH	Riedel Dehaen
$\text{NH}_4\text{BF}_4$		Allied
$\text{Zn}(\text{BF}_4)_2$		Allied
$\text{CH}_2=\text{CH}-\text{CH}_2\text{Br}$	$\text{CH}_2=\text{CH}-$	Dow
$\text{Cl}-\text{CH}_2-\text{C}=\text{C}-\text{CH}_2\text{Cl}$	$-\text{C}=\text{C}-$	GAF
$\text{BrCH}=\text{CBr}-\text{CH}_2\text{OH}$	$-\text{OH}$	GAF

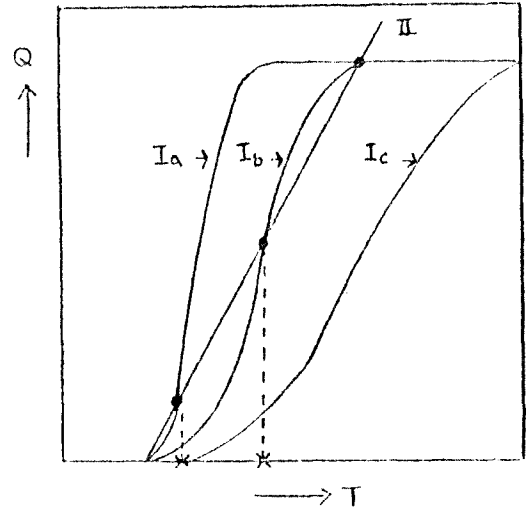
#### Flamability, ignition, combustion and extinguishment

Flamability is a property of a system comprising the basic elements: combustible material and heat. A fire does not originate without heat. After ignition, the flame itself produces the heat required for the constant production of combustible gases (figure 1).

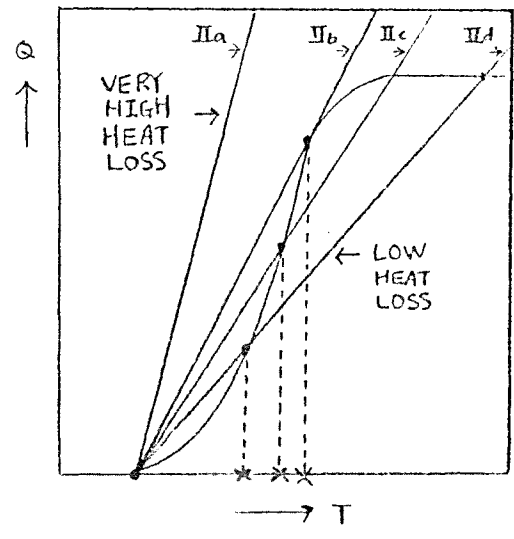
According to the diagram by Frank-Kamenetzky, the generation of heat depends on the rate of combustion and increases exponentially with temperature until a maximum is reached which corresponds to complete conversion. The loss of heat is roughly proportional to the difference in temperature between the combustion zone and the environment so that it can be represented by an approximately straight line.



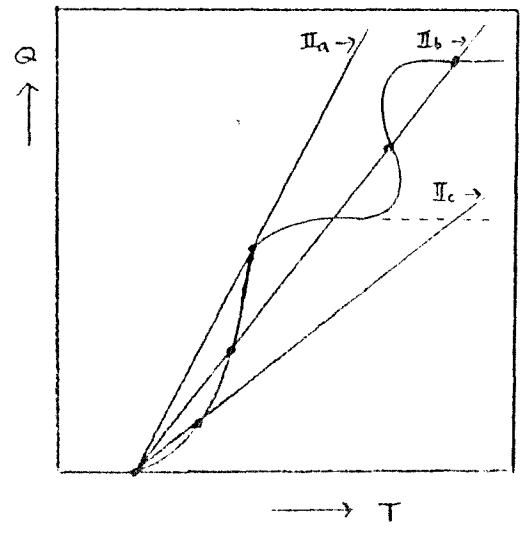
(1)  
Flame stability diagram



(2)  
Three degrees of flamability:  
Ia, Ib, Ic



(3)  
Four different surroundings:  
IIa, IIb, IIc, IId



(4)  
Two stage combustion

Fig. 1. Stability diagram of combustion

Equilibrium between heat generation and heat loss is realized at the points of intersection of I and II, so in points A, B and C; A (ambient temperature) and C (stationary temperature) are stable and B is unstable (diagram 1). To the left of B, the heat loss exceeds the heat generation; to the right of the B, the reverse occurs. Therefore, the temperature corresponding to B is the ignition temperature. During a fire, the material must be heated to such an extent by heat feed back from the flame that at least this ignition temperature is reached. The temperature at B is also the temperature of self-extinguishment; at lower temperature, heat loss exceeds heat generation. Diagram 2 shows three materials with different degrees of flammability in the same environment. The first curve represents high flammability, the second curve represents moderate flammability, while the third curve indicates flame resistant under these conditions.

Diagram 3 represents a material in different environments. An increased heat loss may be caused by environmental conditions such as a higher flow of air, less insulation, etc. It is evident that a flammable material may be barely flammable or even nonflammable under different conditions. It depends only on whether there is a point B or not. Sometimes the combustion (or decomposition) takes place in two steps. This situation is shown in diagram 4, again with new possibilities.

The combustion reaction during burning

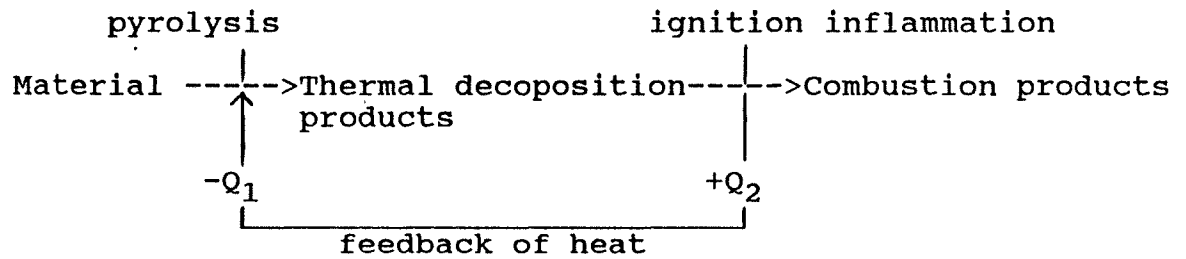


Fig. 2. Consecutive reactions during burning

For burning , there are two successive chemical processes; decomposition and combustion, which are linked together via themal feedback. An ignition mechanism is essential.

First, the material decomposes (pyrolysis), which requires heat. The decomposition products are combusted (after ignition), which generates heat. This heat is again (partially) utilized for pyrolysis. The process is heterogeneous, so that the contact area plays an important role.

From this basic mechanism, it can be seen that the themal effects  $-Q_1$  and  $+Q_2$  and the contact area ( $A$ ) are specially important. A high  $Q_1$  value (hard to ignite), a low  $Q_2$  value (less heat generation) and a low  $A$  value (less combustable surface) favor flame resistance.

Furthermore, it is well known that the hydrogen content of the material has a great influence on the resistance to decomposition and on flammability. The lower the hydrogen content, the more flame resistant the material. On the other hand, the larger the pyrolysis residue becomes, the smaller the amount of combustible gases and  $Q_2$ .

### Combustion process

The combustion of a solid can be explained by the diagram below. Three of these zones exist in the burning material, and three exist in the surroundings.

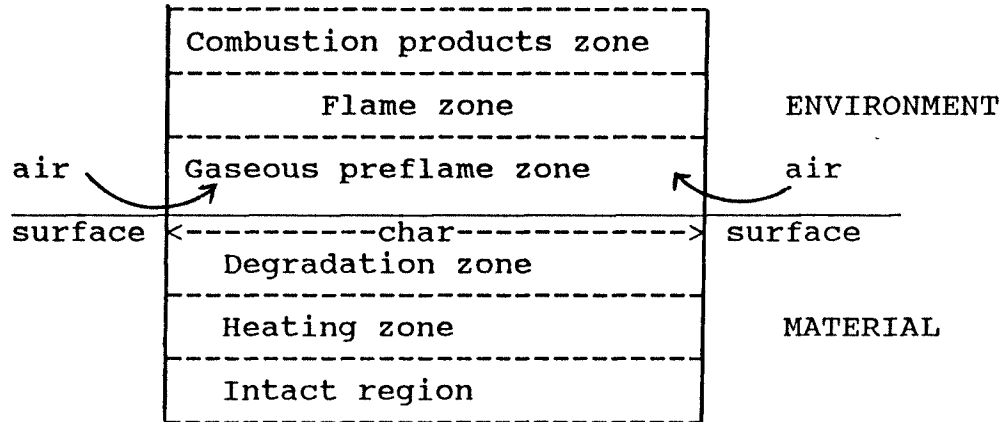


Fig. 3. Combustion zone model of a solid material

The three zones within the burning material are the intact region, the heating zone and the degradation zone. The intact region is that portion of the material which is not exposed to the effect of fire. The size and the location of the region depends on the thermal conductivity and the burning time. The heating zone exists above the intact zone and is where the molecules are beginning to react to the heat generated by combustion. The absorption of this thermal energy increases the temperature of the molecules (perhaps raising them above  $T_g$  or  $T_m$ ), and in the case of hygroscopic substances such as nylon, wool and cotton can cause substantial dehydration. When these molecules absorb sufficient energy, some of their primary bonds begin to break and the polymer is reduced to various compounds of low molecular weight. These compounds can be either

solid(char), liquid(tar) or gas. This breakdown occurs in the degradation (pyrolysis) zone, which exists at and below the surface of the polymer.

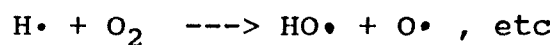
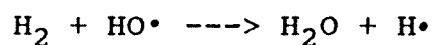
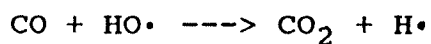
The three zones above the surface of the burning material are the gaseous preflame zone, the flame zone and the combustion product zone. The gaseous preflame zone is a region directly above the surface of the polymer. It is in this region that the gases and tars produced in the degradation zone mix with oxygen from the surroundings. Eventually, sufficient oxygen mixes with these gases and tars so that they ignite, producing large quantities of energy in the form of heat and light. This occurs in the flame zone. Much of the heat produced here travels away from the material, and the remainder goes back into the material to fuel the endothermic process in the degradation and heating zones. The combustion product zone exists directly above the flame zone, and in this region the compounds produced during the preceding processes begin to cool and become the smoke and toxic gases associated with combustion.

#### Flame retardancy by chlorine in the PCF copolymer

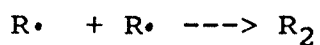
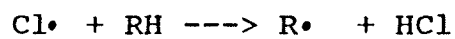
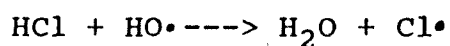
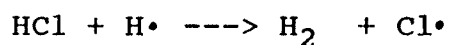
Starting with the hypothesis that all organic materials can be destroyed by burning, the role of a flame retardant is to influence the pyrolysis by diminishing the formation of fuel. Its action is mainly in the solid phase. Secondly, it can influence the free radical chain reaction in the gas phase by increasing the chain termination.

For the PCF copolymer fiber, the role of chlorine is suggested to be chain termination in the gas phase formed on decomposition, by capturing OH radicals which play an essential role in the combustion mechanism.

Combustion chain :



Radical capturing :



## I. EXPERIMENTAL

### 1. Synthesis of PCF copolymer

#### Chemicals

O-chlorophenol ( FW 128.56 ) purified, Fluka Chemical Co

Phenol ( FW 94.11 ) Aldrich Chemical Co

Formaldehyde, 37 % w/w ( FW 30.01 ) Fisher Scientific

P-toluenesulfonic acid ( FW 190.22 ) reagent grade, Aldrich  
Chemical Co

Oxalic acid ( FW 30.11 ) reagent grade, Aldrich Chemical Co

#### Apparatus

500 ml four-necked reaction kettle, condenser, thermometer, Thermowatch 161000P, LAUDA IC-6, mechanical stirrer and motor, Glas-col heating mantle, Variac, vacuum gauge, vacuum pump, nitrogen gas cylinder

#### Procedure

##### (1) Preparation of phenol-formaldehyde oligomer

The apparatus used for preparing the phenol-formaldehyde oligomer consisted of a 500 ml four-necked reaction kettle, a heating mantle, a mechanical stirrer as shown in the appendix, a thermometer, a condenser and an oil bubbler. The reaction kettle was purged with nitrogen gas for about 5 minutes before the reactants, 94.11 g phenol ( 1 mol ), 66.55 g formaldehyde ( 0.82 mol ), 1.0 g oxalic acid, and 10 ml distilled water were charged. The reaction mixture was then slowly heated up to its refluxing



temperature, 98 °C, under vigorous agitation. At refluxing, an additional 1 g oxalic acid was also added. The reaction was allowed to proceed for 90 minutes before 300 ml of distilled water was added to the reaction mixture and the motor was stopped. On standing, the reaction mixture separated into two immiscible layers, an aqueous layer (top), a viscous polymer layer (bottom).

## (2) Preparation of O-chlorophenol-formaldehyde oligomer

In a separate setup like (1), 128.56 g o-chlorophenol ( 1 mol ), 81.16 g formaldehyde ( 1 mol ), 6.08 g PTSA ( 2.29 % of monomers ) were charged into the kettle. With agitation, the reaction mixture was heated up to refluxing and kept at refluxing for 3 hrs before 300 ml of distilled water was added to stop the reaction. The reaction mixture separated into two immiscible layers, an aqueous layer (top) and a viscous polymer layer (bottom), when the stirring was stopped

## (3) Preparation of PCF copolymer

The two oligomers obtained from the above two reactions were separately washed with distilled water and later combined for vacuum distillation. The vacuum distillation was conducted in a reaction kettle at 2 cm Hg. The copolymerization occurred during vacuum distillation (for 1 hour) between 190 - 195 °C. The resulted copolymer was cooled (in nitrogen) and weighed 300 g, representing a yield of 77 %.

#### (4) Preparation of PF and CF polymers

Similar to the preparation of the copolymer, a two-stage procedure was applied to prepare PF or CF polymer for the second stage vacuum distillation after the first stage refluxing reaction.

#### 2. Fiber spinning

20 g of pulverized PCF copolymer resin was charged into a home made spinning apparatus consisting of a stainless steel column for sample, a spinneret with two orifices (0.39 mm in diameter), a Lindberg compact tube furnace (model 55035), a nitrogen cylinder, a Variac and a plastic bobbin mounted on a rotating motor. The polymer in the stainless steel column was slowly heated up to the melt point (180 °C) under 5 psi nitrogen pressure. The molten polymer first appearing at the orifice of the spinneret was initially drawn on to the rotating bobbin by a tweezer. Once the filament was wound on the bobbin, it would automatically wind up on the rotating bobbin. The diameter of the fiber could be controlled by the nitrogen pressure, the winding speed and the temperature of the furnace.

The blended polymer samples were made by 1:1 and 2:1 mol ratio of CF to PF polymer (based on the polymer's formula weight of repeating unit). The condition for fiberization of the blended polymer was the same as that of PCF copolymer.

### 3. Curing of the fiber

#### Chemicals

Mineral spirit, Kirker

Succinyl chloride ( FW 154.98 ) Fluka Chemical Co

Sodium bicarbonate ( FW 84.01 ) Aldrich Chemical Co

Aluminum chloride ( FW 133.34 ) Aldrich Chemical Co

Sodium hydroxide ( FW 40.00 ) Aldrich Chemical Co

#### Apparatus

A 500 ml four-necked reaction kettle, a thermometer, a thermowatch L61000P, a magnetic stirrer, a condenser with oil bubbler, fiber glasses, a variac, Corning hot plate stirrer PC-350 were used.

#### Procedure

##### (1) Purification of mineral spirit ( curing lacquer )

275 ml of mineral spirit and 5 ml of succinyl chloride ( 3 % solution ) were refluxed between 110 °C - 140 °C for 1 hour with 2.5 g sodium bicarbonate as catalyst for the purpose of removing impurities from the curing lacquer. When the solution was cooled down to room temperature, the impurities were crystallized out and filtered from the curing lacquer.

##### (2) curing.

The PCF copolymer fibers were wrapped in a bundle with a thread of glass fiber. The bundle was placed in a flame dried reaction kettle containing the purified curing lacquer. The curing lacquer was slowly heated up to 60 °C

and left at 60°C for 24 hours with moderate stirring. At the end of 24 hours, an additional 3 % succinyl chloride was added to the curing lacquer and raised the temperature to 70°C. It was kept at 70°C for 3 hours before a further 3 % succinyl chloride was added to the curing lacquer and raised the temperature to 80°C. The procedure was repeated for 3 hours, at even 10 degree intervals until reaching the refluxing temperature 110°C. The fiber was removed from the kettle, rinsed with mineral sprit, acetone and warm distilled water, and dried in a oven at 70°C overnight.

The blended fibers were cured in 200 ml of curing solution containing 12 % HCl (wt) and 12 % formaldehyde (wt). The heating program for these fibers was from room temperature to 40°C for 12 hours, 40 to 60°C for 3 hours, 60 to 80°C for 3 hours, and 80°C to refluxing temperature for 3 hours and refluxed for 1 hour before the sample was removed from the curing solution for acetone and water washing and oven drying.

#### 4. Characterization of the polymer

##### A. Intrinsic viscosity

The solution viscosity of the sample was measured with a Ubbelohde viscometer, K333, in a constant temperature bath kept at  $25 \pm 0.05$  °C. The polymer concentration in butyl acetate (Fisher Scientific co.) was 0.7982 - 3.3526 g/dl. For this measurement, the viscometer was cleaned with cleaning solution before use.

##### B. Infrared spectroscopy

The IR absorption spectrum of the sample was examined on a Perkin-Elmer model M-457 spectrometer. The pellet was made from 5 mg of polymer sample and 0.1 g of dried KBr. The scan speed was set at 3 minutes. The samples were PCF copolymer, 1:1 and 2:1 CF-PF blended polymers and cured phenolic fibers.

##### C. Number average molecular weight, $\overline{M}_n$

The number average molecular weight of the polymer sample was determined from the vapor pressure osmometer, Wescan instruments model 233, using tetrahydrofuran (THF; Aldrich. purity 99.9 % HPLC grade) as solvent. The calibration curve was first established with standard biphenyl (FW 154.21).

To operate the osmometer, the following procedure was observed: The solvent, THF, was placed onto the two thermistors separately by the front and rear micro syringes. After successive additions of the solvent, the reading was

stabilized and recorded. The rear solvent syringe was then replaced by a solution syringe containing biphenyl standard solution. The measurements were performed at five different concentrations of the standard. The K value was then determined from the interception of a plot,  $\Delta V/C$  vs concentration. The procedure was repeated for each polymer sample and number average molecular weight,  $\overline{M}_n$  of the polymer was determined from the interception of the plot,  $\Delta V/C$  vs concentration using the value of K obtained from the standarization of the instrument.

#### D. Melting point

The melting point of the polymer was determined by the Uni Melt Capillary Melting Point apparatus, Thomas Hoover Company. The sample was made of different parts of the resin so that it could represent the whole batch of the polymer.

## 5. Characterization of cured fiber

### A. Oxygen index

The oxygen index of the cured fiber was measured in a oxygen indexer. The sample was initially ignited by a hydrogen lighter. The flow of  $O_2$  and  $N_2$  were adjusted to have a minimum percentage of  $O_2$  to sustain the burning of the sample. The percentage of  $O_2$  was recorded as oxygen index of the sample.

### B. Tensile strength

To prepare the sample for the Instron (model 4201) test, a strand of fibers was first combed to separate them as individual fibers with little gap between them. Those individual fibers were then taped at both ends so that it could be tested on the Instron (single fiber is too weak to be tested) and the number of fibers in the bundle could be counted. Each bundle contained about 10 to 20 single fibers. After the Instron test, the number of fibers was counted and the diameter of each fiber was measured by a micrometer (with the aid of a magnifier).

### C. Electron microscopy

The outer surface and the cross-sectional area of the fiber (cured and uncured) were examined on an electron microscope at a magnification of 780 X to 2200 X by Mr. Naugie Abraham, FMC (see Figures 20 and 21 ).

#### D. Thermogravimetric analysis

The thermal stability of the fiber was measured under the following conditions:

Sample : PCF copolymer fiber, CF fiber, Kynol, Nomex,

1:1 CF-PF blended fiber

Size : 0.868 - 4.5364 mg

Heating range : 25 C to 700°C

Heating rate : 25 C / min.



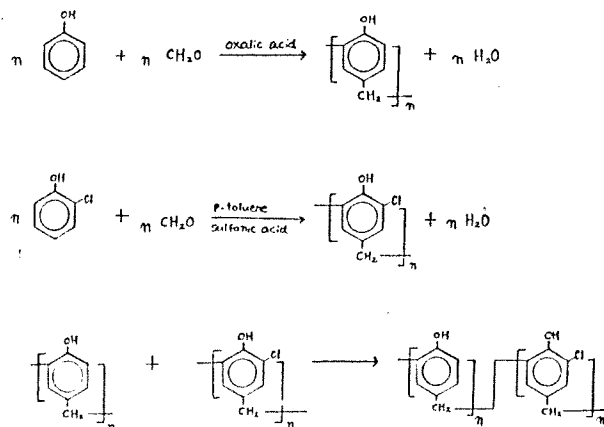
## II. RESULTS AND DISCUSSIONS

### 1. Polymerization of PCF

Table 3. Preparation of the PCF copolymer

run #		1	2	3	4	5
First	phenol: formaldehyde (mol)	1: 0.85	1: 0.835	1: 0.82	1: 0.82	1: 0.82
	oxalic acid (g)	1,1	1,1	1,1	1	1
	refluxing (min.)	90	50	50	50	60
Stage  (reflu- xing)	o-chlorophenol :formaldehyde (mol) PTSA (g)	1:1 6.0818	1:1 6.0818	1:1 6.0818	1:1 6.0818	1:1 6.0818
	refluxing (hr)	3	3	3	3	3
Second  Stage (vac. distill.)	Vacuum temp. (°C)	180 - 190	180 - 190	180 - 190	180 - 190	180 - 190
	Vacuum time (hr)	1	1	1	1	1
	m.p. (°C)	gelled	gelled	75-80	80-85	90

Fig. 4. Mechanism of PCF copolymerization



Copolymerization of phenol, o-chlorophenol, formaldehyde ( 1:1:1.6, mol ratio) has been attempted for a single batch process. However, the reactivity of phenol and formaldehyde was much higher than that of o-chlorophenol and formaldehyde so that the reaction mixture became gelled during polymerization due to the excess mol ratio effect of formaldehyde to phenol. As a result, two separate batch process were applied to avoid gellation during copolymerization.

For making the PF resin, the critical mol ratio of formaldehyde to phenol has been found to be 0.82. Any ratio larger than this has resulted in a gelled copolymer. However, a 1:1 mol ratio of o-chlorophenol to formaldehyde was found to be adequate for CF polymer.

## 2. Curing of fiber

### (1) curing of PCF copolymer fiber

The chemical reaction of curing is perceived as shown in Figure 5.

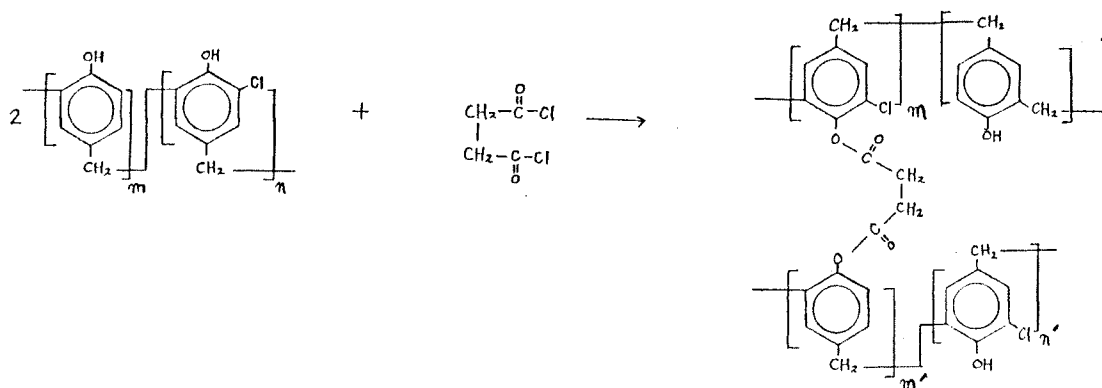


Fig.5. Chemical reaction of curing PCF fibers

Since the fiber dissolves in the curing agent (succinyl chloride), direct curing of the fiber in the pure curing agent is impossible. By trial and error, it has been found that the fiber will not dissolve in a 3 % curing lacquer with purified mineral spirit as the solvent. The curing proceeds in two stages. The first stage is shell curing (curing below 60 °C to form a cured shell on the fiber surface). Once the shell of the fiber is cured, the fiber will not stick together. In the second stage of curing (60 °C to boiling), the heating rate and the concentration of the lacquer can be increased step-wise until the concentration of curing lacquer reaches 15 % and the system has been boiled for an hour. The curing proceeds inwards as the curing agents diffuse into the fiber. This process transforms the PCF fiber into a three-dimensional network

through the formation of the succinic ester cross-linkages. The electron microscope picture of the cured fiber is shown in Figures 20 and 21.

(2) Curing of 1:1 CF-PF blended fiber

The curing of the blended fiber may be represented by the chemical reaction in Figure 6.

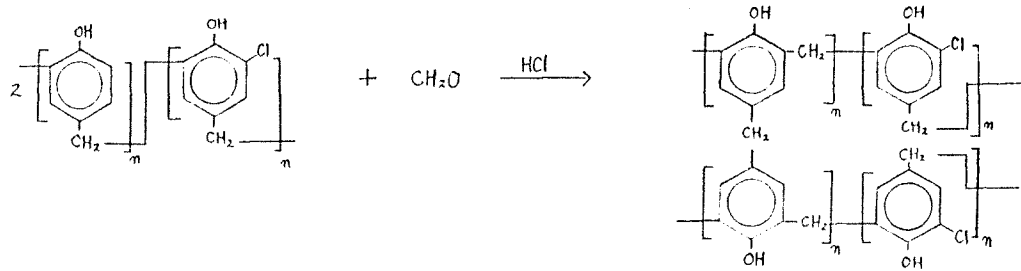


Fig. 6. Chemical reaction of curing 1:1 CF-PF blended fiber

The blended fiber was also cured by a two stage process like (1) with acidic aqueous curing lacquer containing formaldehyde through the formation of a methylene linkage in the ortho or para position in the phenol ring.

### 3. Characterization

#### A. Intrinsic viscosity

Using butyl acetate as a solvent, the flow times of dilute solutions of the polymer sample are given in table 4 - 8. Based on the Huggin's equation,  $n_{sp}/C = [\eta] + k'[\eta]^2C$ , a plot of  $n_{sp}/C$  vs  $C$  (see fig. 7 - 10) yielded the intrinsic viscosity of the sample.

##### 1) PCF copolymer

Table 4. Flow times of dilute solutions of the PCF polymer

Concentration , (g/dl)	Average flow time at $25 \pm 0.05^\circ\text{C}$ , (sec)	$n_{sp}/C = (t - t_0)/ct_0$ , (dl/g)
3.3526	36.27	0.1619
2.3947	32.18	0.1540
1.8626	29.85	0.1448
1.5239	28.63	0.1429
1.0477	26.92	0.1384
0.7982	25.96	0.1306

(the flow time of solvent,  $t_0 = 23.51$  sec)

$[\eta] = 0.1241$  dl/g (see Fig. 7)

##### 2) CF polymer

Table 5. Flow times of dilute solutions of the CF polymer

Concentration , (g/dl)	Average flow time at $25 \pm 0.05^\circ\text{C}$ (sec)	$n_{sp}/C = (t - t_0)/ct_0$ , (dl/g)
3.3526	28.49	6.316
2.3947	26.93	6.075
1.8626	26.10	5.915
0.7982	24.50	5.276

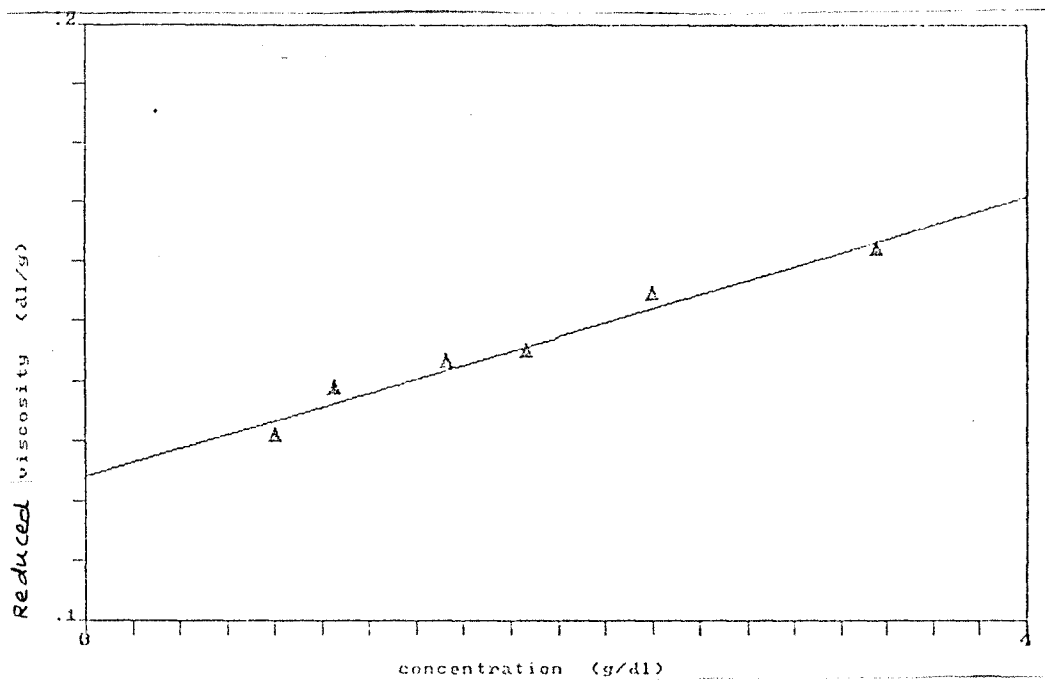


Fig. 7. Plot of reduced viscosity vs concentration for PCF copolymer

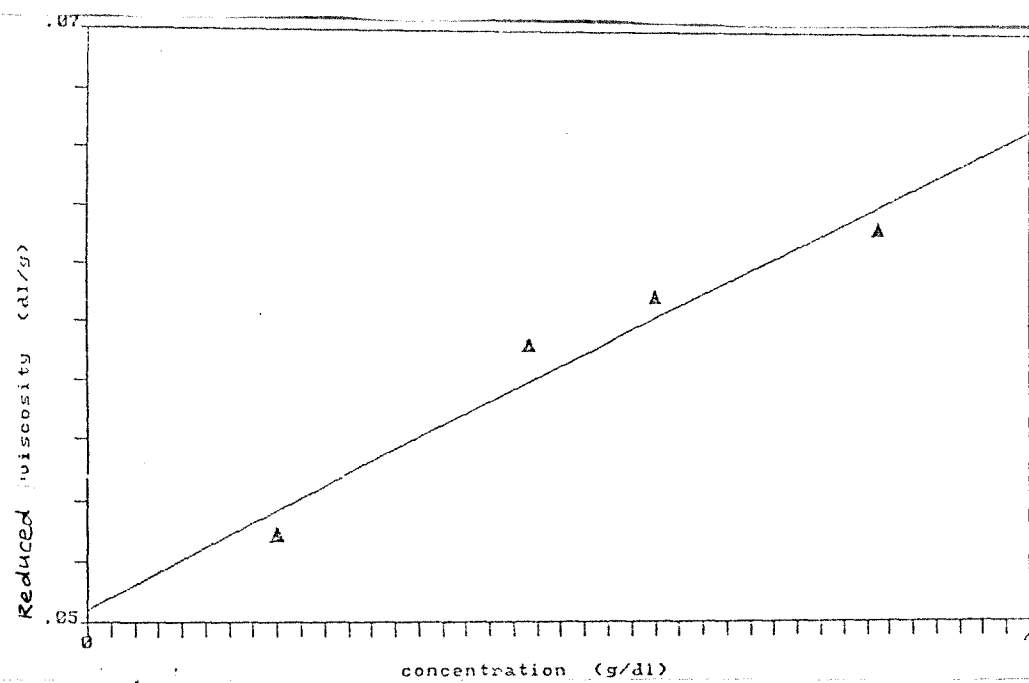


Fig. 8. Plot of reduced viscosity vs concentration for CF polymer

(the flow time of solvent,  $t_o=23.51$  sec.)

$[\eta]=0.05043$  dl/g ( see Fig. 8)

3) 1:1 PF - CF blended polymer

Table 6. Flow times of dilute solutions of the 1:1 CF-PF blended polymer

Concentration , (g/dl)	Average flow time at $25 \pm 0.05^\circ\text{C}$	$n_{sp}/C=(t-t_o)/ct_o \times 100$ , (dl/g)
3.3525	29.96	8.1832
2.3947	27.94	7.8686
1.8626	26.82	7.5589
1.5239	26.20	7.5083
1.0477	25.35	7.4701

(the flow time of solvent,  $t_o = 23.51$  sec.)

$[\eta] = 0.07037$  dl/g (see Fig. 9)

4) 2:1 CF - PF blended polymer

Table 7. Flow times of dilute solutions of the 2:1 CF-PF blended polymer

Concentration , (g/dl)	Average Flow time at $25 \pm 0.05^\circ\text{C}$ , (sec)	$n_{sp}=(t-t_o)/ct_o$ , (dl/g)
3.3526	29.27	7.3078
2.3947	27.49	7.0693
1.8626	26.59	7.0336
1.5239	25.97	6.8663

( the flow time of solvent,  $t_o = 23.51$  sec.)

$[\eta]=0.06561$  dl/g (see Fig. 10)

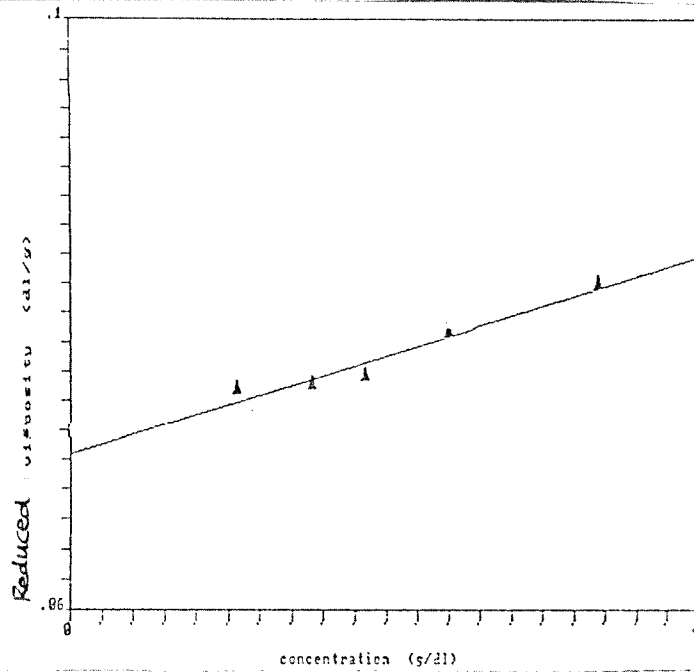


Fig. 9. Plot of reduced viscosity vs concentration for 1:1 CF-PF blended polymer

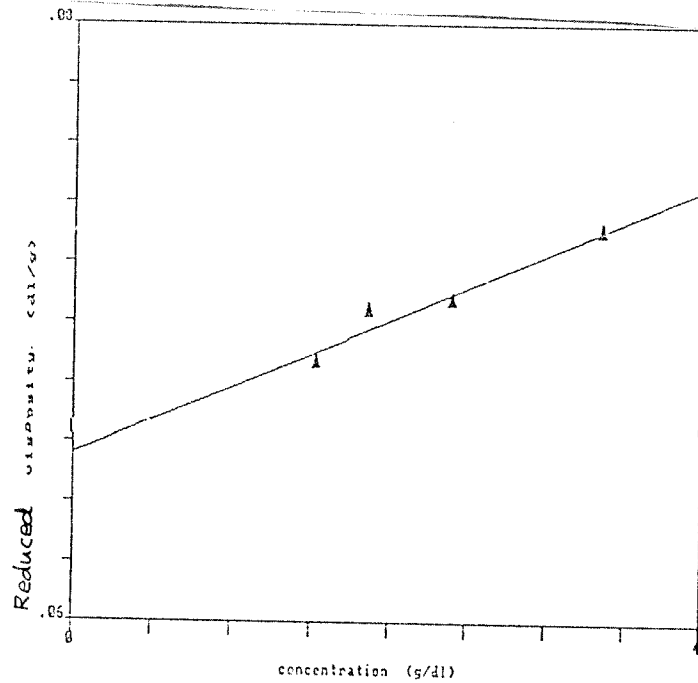


Fig. 10. Plot of reduced viscosity vs concentration for 2:1 CF-PF blended polymer



## 5) PF polymer

Table 8: Flow times of dilute solutions of PF polymer

Concentration , (g/dl)	Average flow time at $25 \pm 0.05$ °C, (sec)	$n_{sp}/C = (t - t_0) / ct_0$ , (dl/g)
3.3526	31.98	0.1075
2.3947	29.42	0.1050
1.8626	27.99	0.1023
1.5239	27.07	0.0994

( the flow time of solvent,  $t_0 = 23.51$  sec.)

$[n] = 0.09391$  dl/g (see Fig.11)

The intrinsic viscosities of the five polymers are summarized in table 9.

Table 9. Intrinsic Viscosity

Sample	$[n]$ , dl/g
PCF copolymer	0.1241
CF polymer	0.05043
1:1 CF-PF blended polymer	0.07037
2:1 CF-PF blended polymer	0.06561
PF polymer	0.09391

It is interesting to note that the intrinsic viscosity of the PCF copolymer is considerably higher than that of the blended and homo-polymers.

It is also interesting to note that the viscosities of blended polymers are inversely proportional to the mol ratio of CF polymer content. This implies that the interaction of the solvent, butyl acetate with CF polymer molecules is

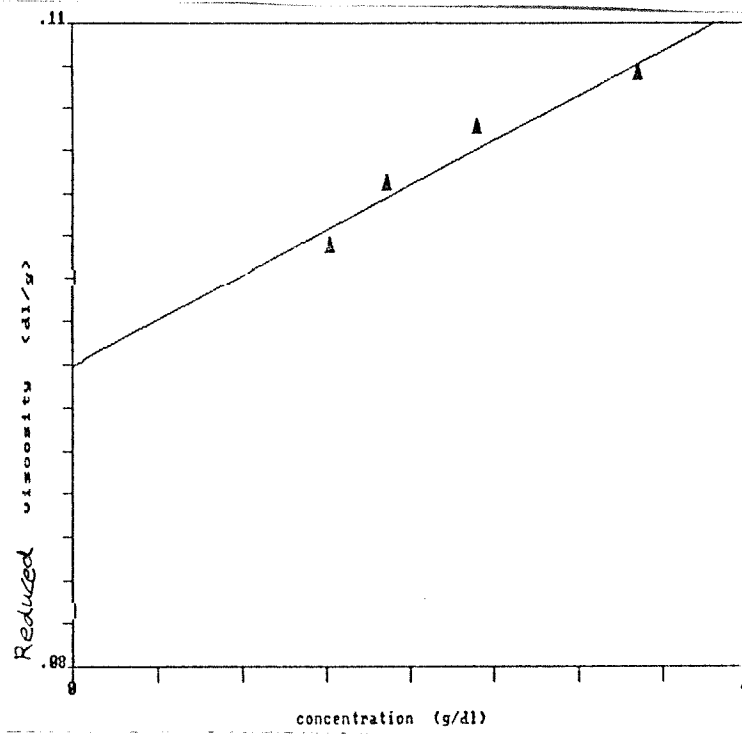


Fig. 11. Plot of reduced viscosity vs concentration for PF polymer

less than that of PF polymer molecules. This effect may be due to the repulsion of the chlorine atoms in the CF polymer to the solvent molecules. As a result, butyl acetate is a poorer solvent for the CF polymer as compared to that for the PF polymer.

#### B. Vapor pressure osmometer (VPO)

The number average molecular weight, ( $\overline{M}_n$ ) of the PCF copolymer was determined by VPO. The solvent calibration constant K in the following equation was determined with biphenyl as the standard.

$$\Delta V / C = K / M_n + A_2 C K$$

where,  $\Delta V$  : difference in signal response of voltage

between sample and solvent

C : concentration, g/dl

K : solvent constant

$A_2$ : second virial constant

Data obtained from the VPO measurements are listed in table 10.

Table 10. VPO data of the standard solution (biphenyl, FW : 154.21)

##### a) Sensitivity at 7.0

C (g/l)	0	0.2	0.4	0.6	0.7
V	1.5	-8.8	-8.3	-5.6	-4.7
$\Delta V/C$	0	-51.5	-24.5	-11.8	-8.8

From Fig. 12, the intercept,  $k/M = -64.55$  (V X l/g)

and  $K = 154.21 * (-64.55) = - 9954$

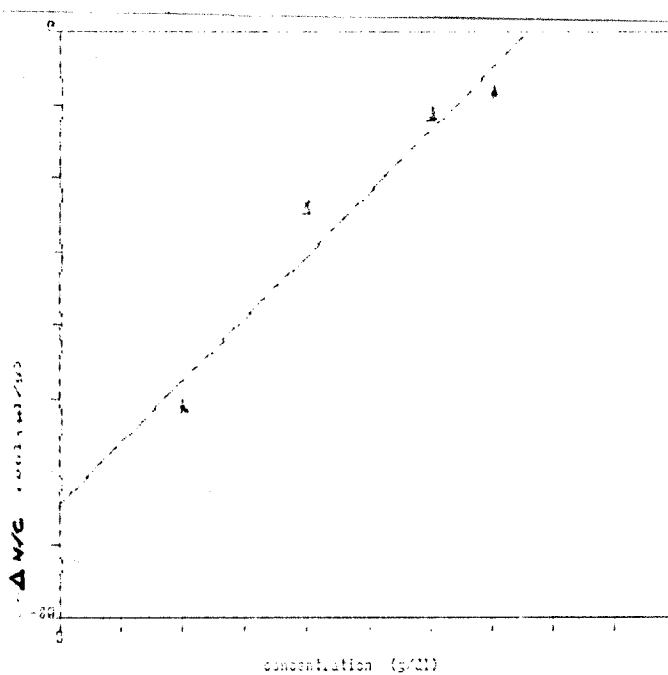


Fig. 12. Plot of  $\Delta V/C$  vs concentration for biphenyl standard (sensitivity : 7)

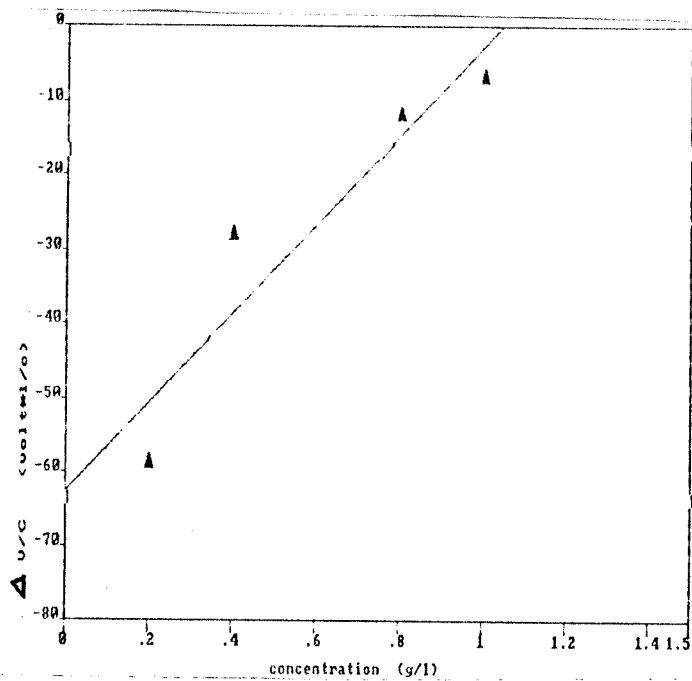


Fig. 13. Plot of  $\Delta V/C$  vs concentration for biphenyl standard (sensitivity : 10)

## b) Sensitivity at 10

C (g/l)	0	0.2	0.4	0.8	1.0
V	-5.1	-16.9	-16.4	-14.8	-12.1
$\Delta V/C$	0	-59	-28.25	-12.12	-7.0

From Fig. 13, the intercept,  $k/M = -62.63$  (V X l/g)

and  $K = 154.21 * (-62.63) = -9658$ . So the average value of  $K = (-9954 -9658)/2 = -9806$ .

Table 11. VPO data of polymer samples

## a) For PCF copolymer

C (g/dl)	0	6.0	9.0	12.0	15.0
V	2.8	-64.2	-60.4	-51.8	-43.4
$\Delta V/C$		-11.17	-6.97	-4.55	-3.07

From Fig. 14, the intercept,  $K/\overline{M}_n = -15.81$  (V X l/g) and the molecular weight,  $\overline{M}_n = (-9806)/(-15.81) = 620$

## b) For CF polymer

C (g/dl)	0	2	4	6	8
V	-5.7	-18.7	-24.8	-29.8	-32.4
$\Delta V/C$		-6.5	-4.7	-4.0	-3.3

From Fig. 15, the intercept,  $K/\overline{M}_n = -7.2$  (V X l/g) and the molecular weight,  $\overline{M}_n = (-9806)/(-7.2) = 1362$

## c) For 1:1 CF-PF blended polymer

C (g/dl)	0	1.6	2	4	6
V	4.5	-10.1	-11.3	-14.4	-19.8
$\Delta V/C$		-9.1	-7.9	-4.7	-4.1

From Fig. 16, the intercept,  $K/\overline{M}_n = -10.3$  (V X l/g) and the

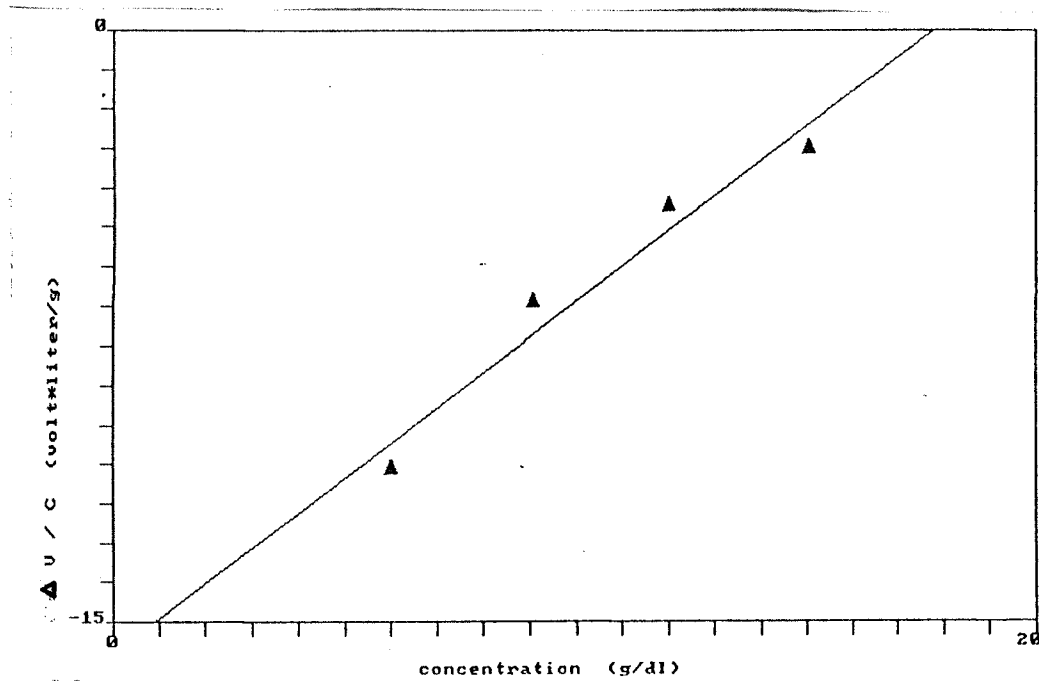


Fig. 14. Plot of  $\Delta V / C$  vs concentration for PCF copolymer

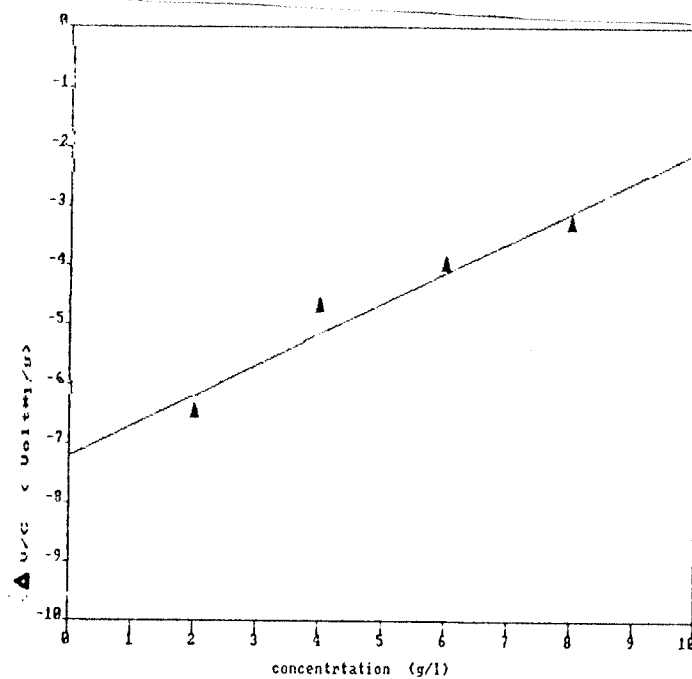


Fig. 15. Plot of  $\Delta V / C$  vs concentration for CF polymer

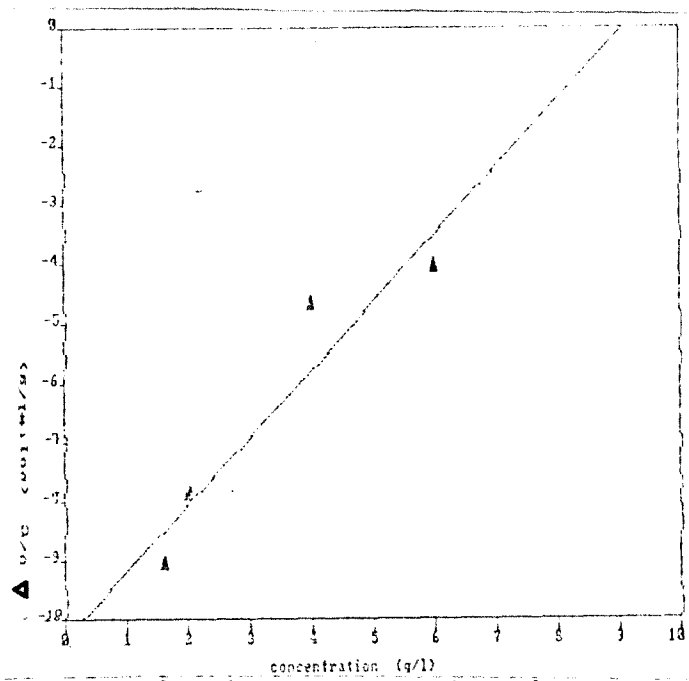


Fig. 16. Plot of  $\Delta V/C$  vs concentration for 1:1 CF-PF blended polymer

molecular weight,  $\overline{M}_n = (-9806)/(-10.3) = 952$

### C. Infra red spectroscopy

The IR spectra for the cured and uncured PCF copolymer are shown in fig. 17 - 19.

The peak at  $1580 \text{ cm}^{-1}$  of the uncured polymer represents the -OH group in the phenol ring and the new peak at  $1730 \text{ cm}^{-1}$  in the polymer cured by succinic chloride represents the succinic ester group. It is interesting to note that this peak is absent in the blended polymer cured by formaldehyde. An analysis of the absorbance is listed in table 12.

Table 12. IR absorption peak for phenolic polymers

Absorption, $\text{Cm}^{-1}$	functional group
1580	-OH
1730	$\text{CH}_2\text{-CO-O-R}$ , ester
1575	C-C stretching
1480	aromatic ring

### D. Melting point

Table 13 lists melting points of several selected polymers.

Table 13. Melting points of polymers

Polymer	m.p. , ( $^{\circ}\text{C}$ )
PCF	85 - 90
CF	105 - 110
PF	103 - 105
1:1 CF-PF	103 - 110



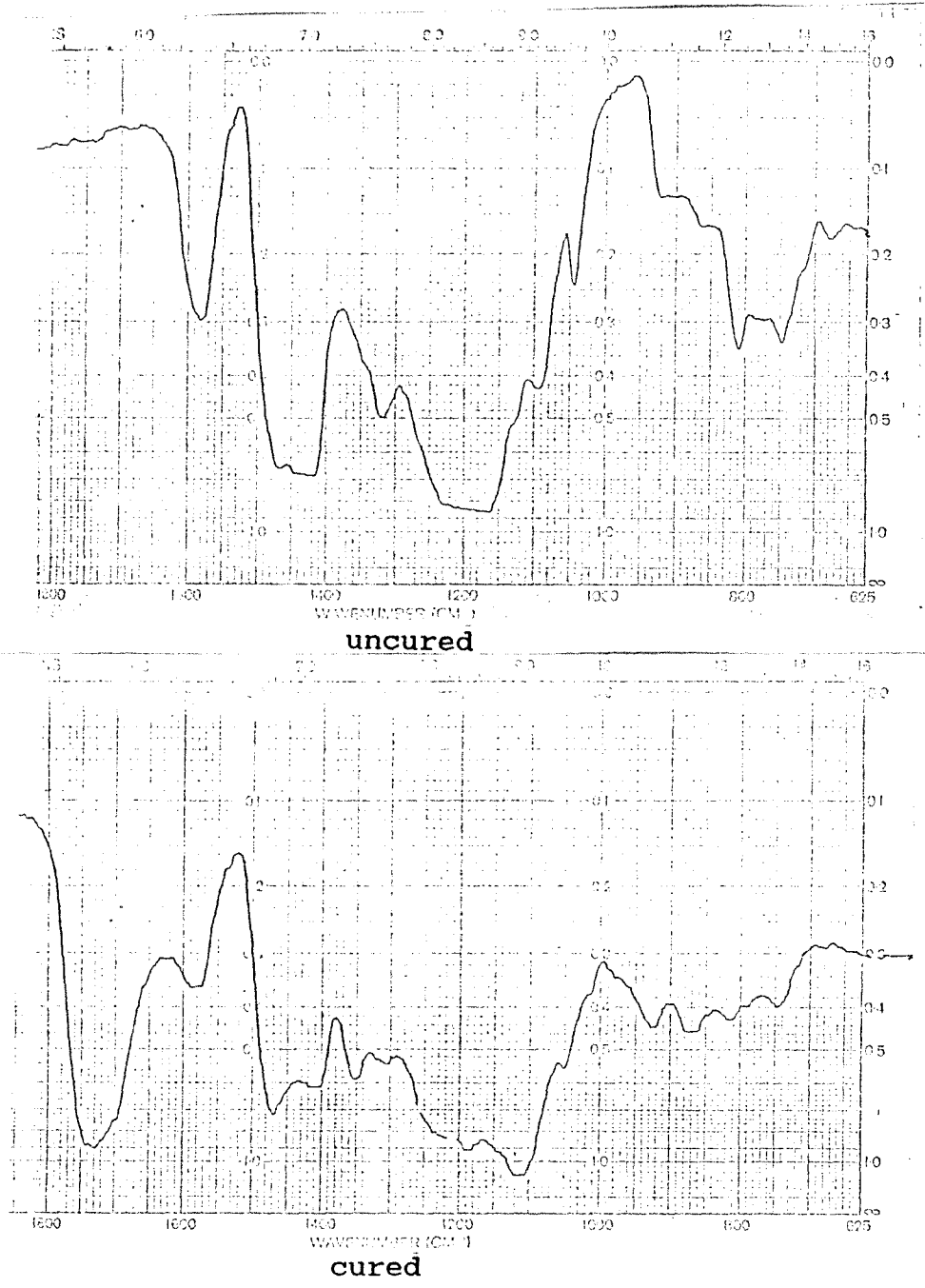


Fig. 17. IR spectrum of cured and uncured PCF fibers

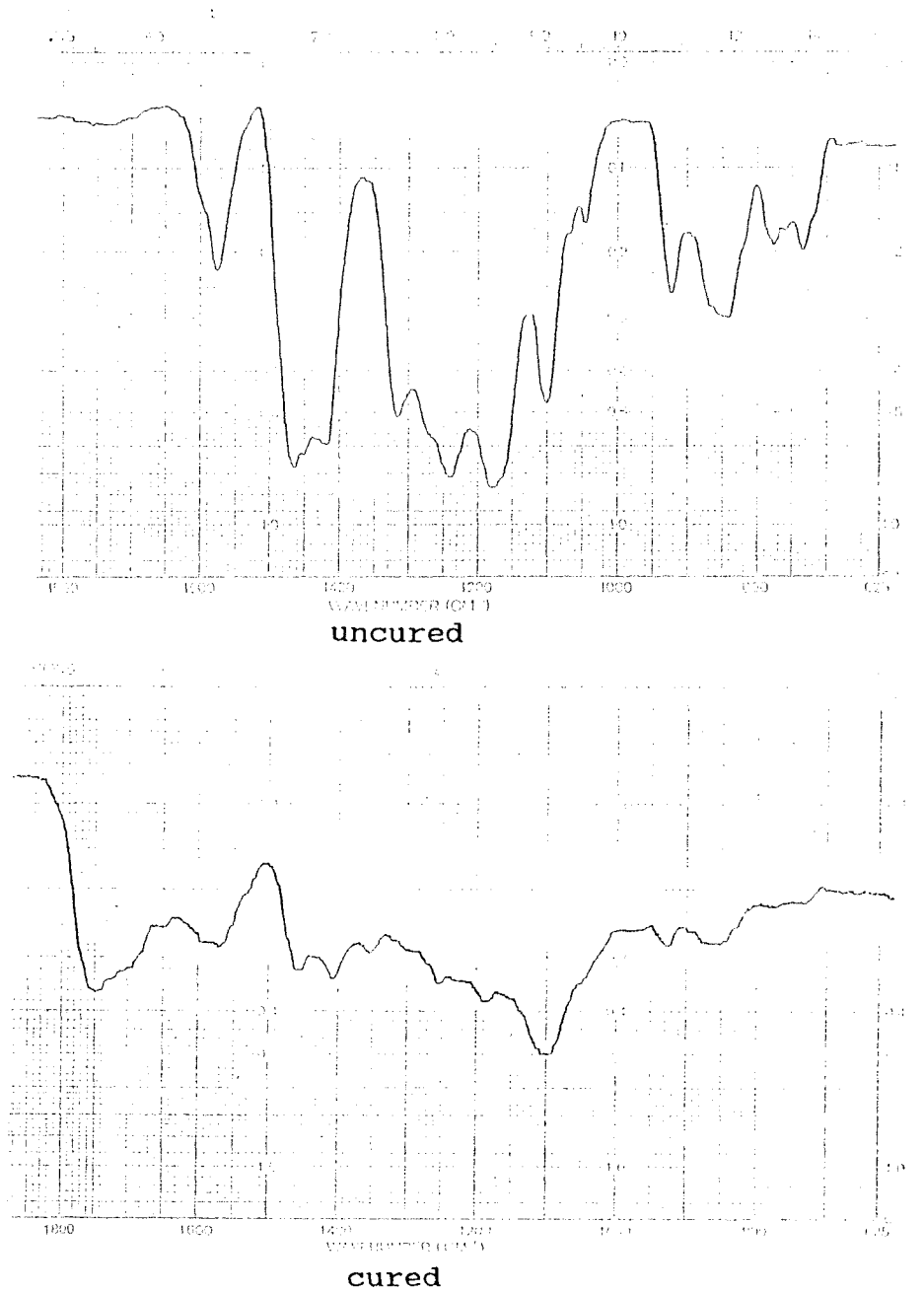
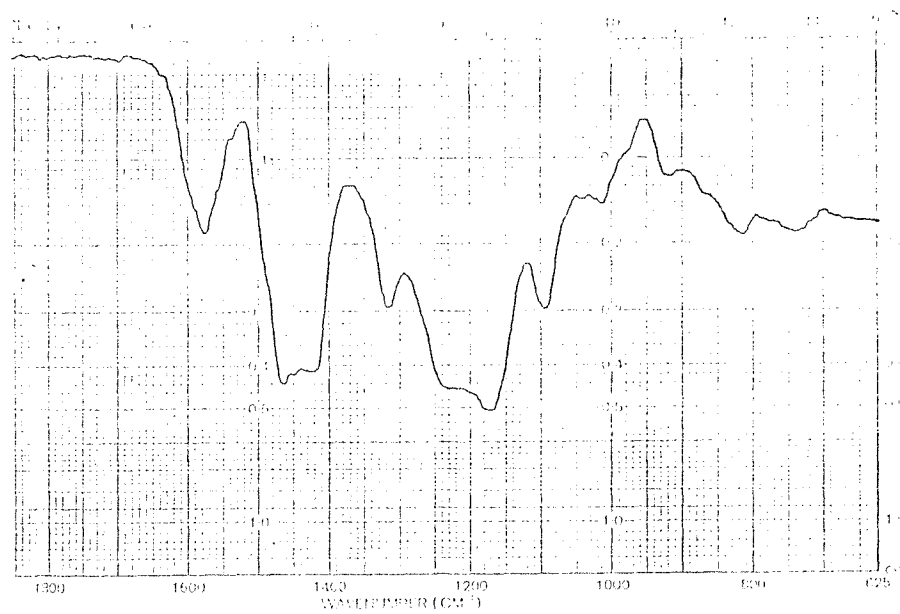
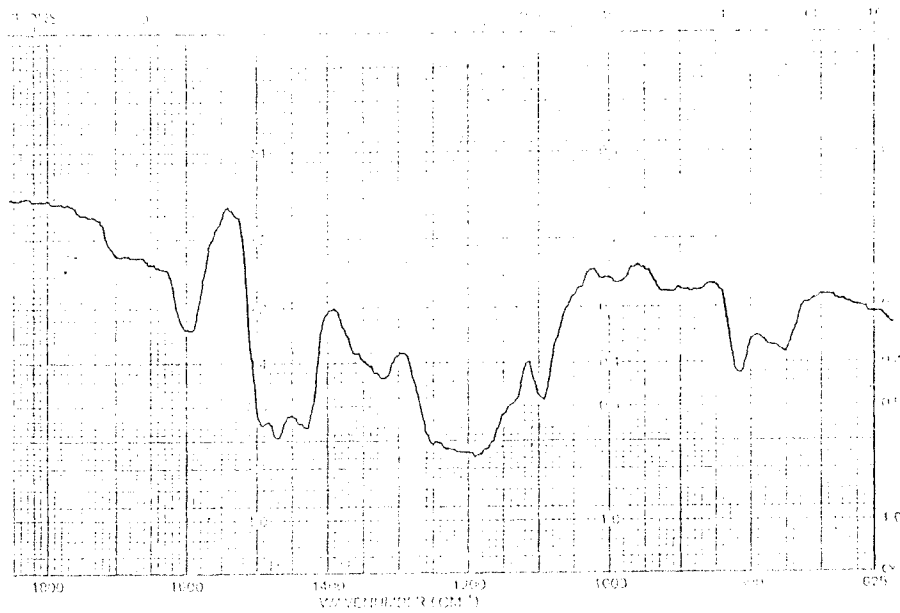


Fig. 18. IR spectrum of cured and uncured CF fibers



uncured



cured

Fig. 19. IR spectrum of cured and uncured 1:1 CF-PF blended fibers

### E. Oxygen index test of the PCF fiber

The oxygen index measured for the cured fibers are tabulated in table 14. The OI of Dupont's nomex fiber was measured for the purpose of comparison.

Table 14. OI of the phenolic fibers

Fiber	PCF copolymer	Nomex	1:1 CF-PF blended	2:1 CF-PF blended	CF polymer
OI	33	27	34	35	40

Oxygen index is a measure of the flame resistance of the specimen which is determined by the percentage of oxygen required in the  $N_2 - O_2$  mixture that sustains a minimum burning of the specimen. It is interesting to note that the oxygen indexes of phenolic samples are in the range of 33 to 40, which is considerably higher than the OI for the Dupont's commercial flame resistant fiber, Nomex. When the phenolic fibers are exposed to a flame, they do not melt but gradually char until completely carbonized without losing their initial fiber form and configuration. This behavior is attributable to the cross-linked, infusible structure of the fiber, retardant effect of the halogen atom and the high carbon content in the molecular structure (75 - 80 %). The greater the amount of the halogen atom in the molecular structure, the higher is the OI of the polymer.

## F. Tensile strength

The average diameter and the tensile strength of the fiber are listed in table 15 - 16.

Table 15. Tensile strength of the CF fibers

diameter	25 25 45	35 20	25 35 30
X $10^6$ m	40 40 25	40 40	50 30 30
	25 30 25	30 25	25 45 40
	30 30 30	30 30	30 30 45
	25 20 20	40 45	40 40
	45 20 35	60 35	
	30	35	
Avg. diameter X $10^6$ m	29.7	35.8	33
Area X $10^{12}$ m <sup>2</sup>	692.79	1006.6	855.3
Area X $10^6$ in <sup>2</sup>	1.0738	1.5602	1.3257
Force, lb	0.0238	0.0342	0.0317
Tensile strength X $10^{-4}$ psi	2.216	2.192	2.391

Avg. tensile strength =  $2.266 * 10^4$  psi

Table 16. Tensile strength of the 1:1 CF-PF fibers

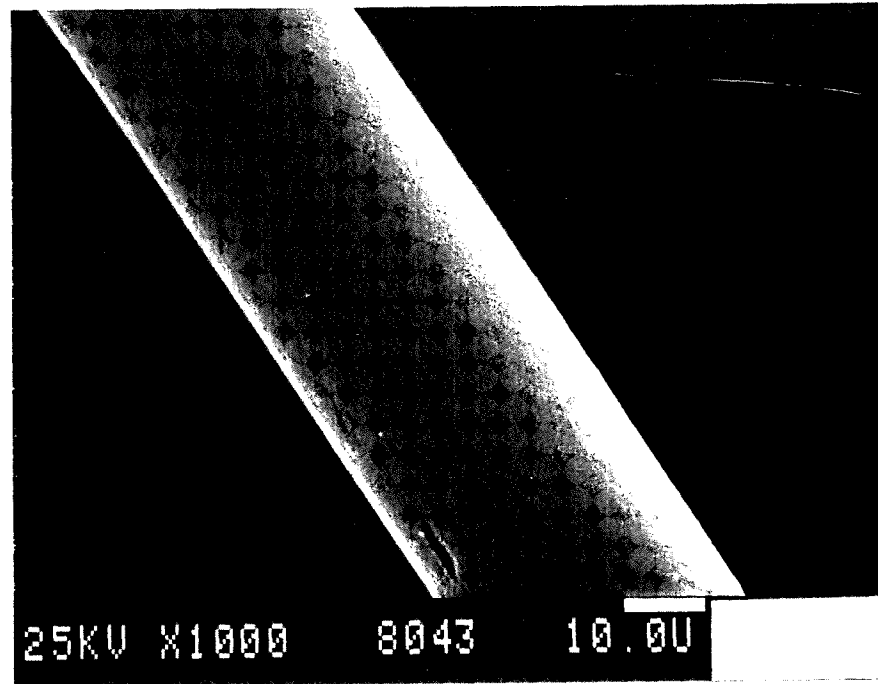
diameter	85 60 70	45 70 70	60 65 60
X $10^6$ m	95 80 75	65 70 80	75 60 80
	75 95 90	80 80 80	95 80 80
	85 90 90	90 90 95	75 80 95
	65	80 80 70	80 90 85
		70 70	80 50 75
			90 80 80
Avg diameter X $10^6$ m	81.2	71.4	76.9
Area X $10^{12}$ m <sup>2</sup>	5178.5	4003.9	4644.5
Area X $10^6$ in <sup>2</sup>	8.027	6.206	7.199
Force, lb	0.955	0.788	0.802
Tensile strength X $10^{-5}$ psi	1.189	1.269	1.114

Avg. tensile strength =  $1.19 * 10^5$  psi

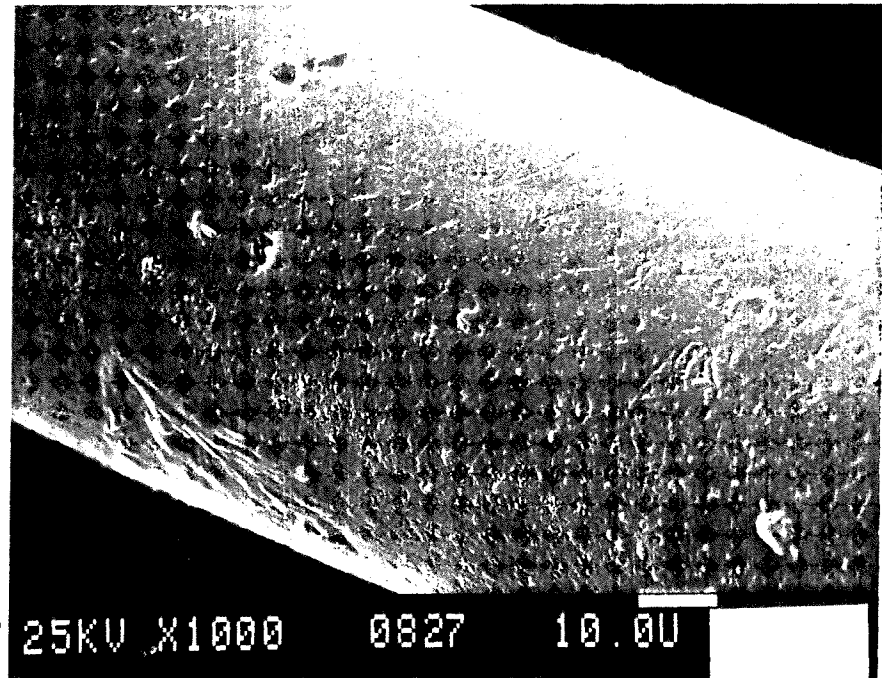
It was not possible to obtain the tensile strength of PCF fiber by the Instron because the fiber was too brittle to be tested as a result of insufficient curing.

#### G. Electron microscopy of the PCF fiber

The electron microscope pictures for the uncured and cured fibers are shown in fig. 20 - 21. It can be seen that the cured fiber has a rough surface which contrasts sharply with the smooth surfaces of the uncured fiber. However, the smooth core of the cured fiber is a sign of incomplete curing.

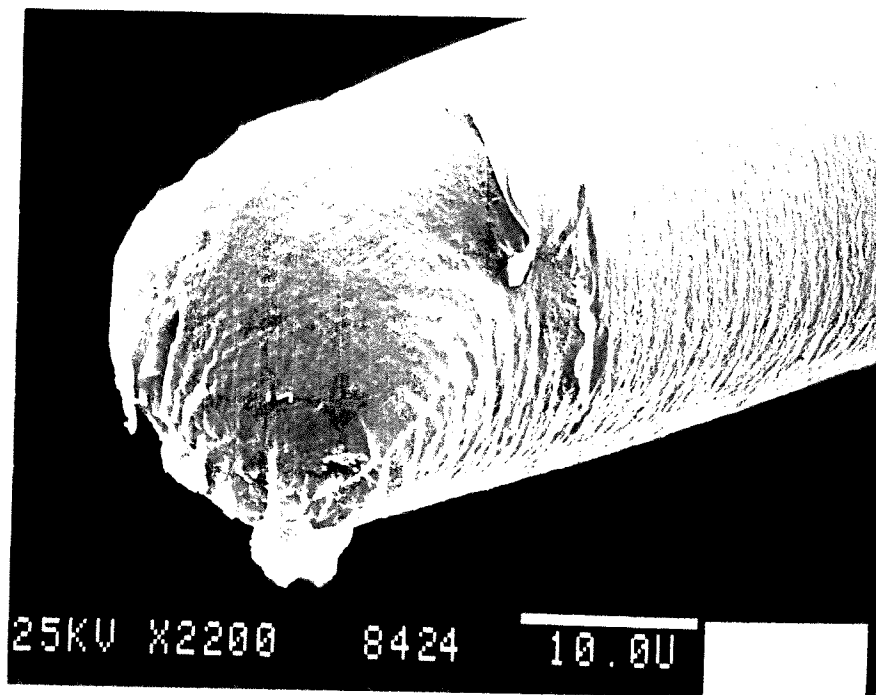


uncured

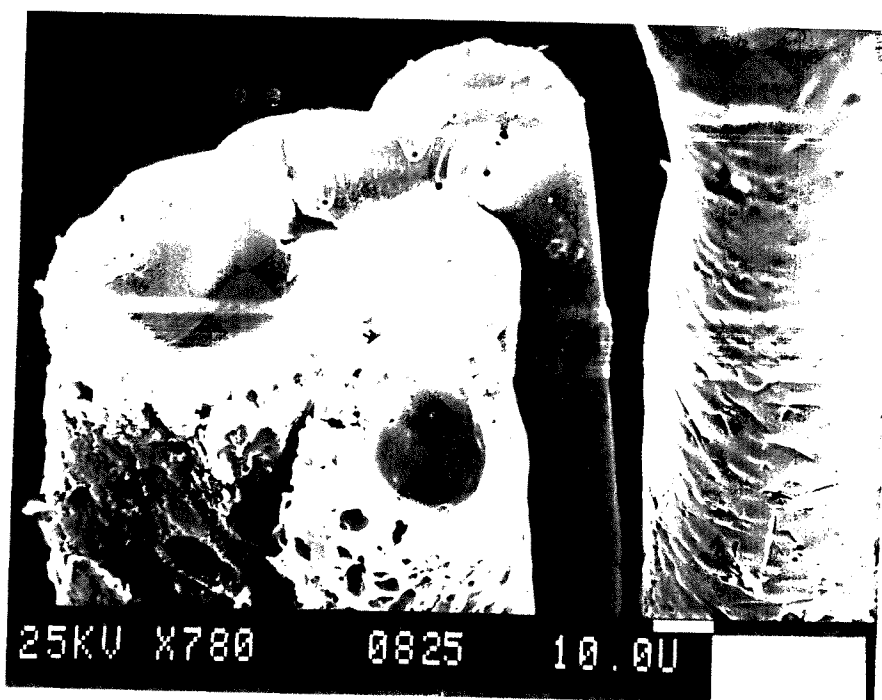


cured

Fig. 20. Surface pictures of cured and uncured PCF fiber



uncured



cured

Fig. 21. Cross-section pictures of cured and uncured PCF fiber



#### H. Thermogravimetric analysis

The weight percentage remaining at different temperature intervals are shown in Figures 22-25 and tabulated in table 17. Temperatures at 50 % weight loss for different fibers are compiled in table 18.

Table 17. TGA analysis on weight remaining at different temperature

fiber	Temp. at which loss commences	Total wt% remaining at temperature					
		200	300	400	500	600	700 (°C)
PCF	168	95	88	78	42	9	9
CF	200	100	93	87	67	30	24
1:1 CF-PF	145	97	95	84	43	6	6
Kynol	260	100	97	93	60	10	10
Nomex	390	100	100	98	76	13	13

Table 18. Temperature for 50 % weight loss

Fiber	Temperature for 50 % wt. loss, (°C)
Nomex	550
CF polymer	540
Kynol	520
1:1 CF-PF blended	497
PCF copolymer	495

The thermogravimetric data on the PCF copolymer fiber indicates that above 200°C in the presence of air, the fiber undergoes gradual weight loss until, close to 530°C, the fiber is fully carbonized, with a carbon yield of 9 - 10 %. Melting does not occur, and shrinkage is small, suggesting that the cross-linked structure of the material promotes

gradual transformation of the aromatic repeating unit into a char.

All of the phenolic fibers above maintain 90 % of their weight up to 300 °C. Such a high temperature, most ordinary organic compounds would decompose.

Below 400 °C, the Nomex fiber shows slightly better thermal stability than phenolic fibers. However, the Nomex fiber has a lower char yield than that of CF fiber, ie, 13 % vs 23 %.

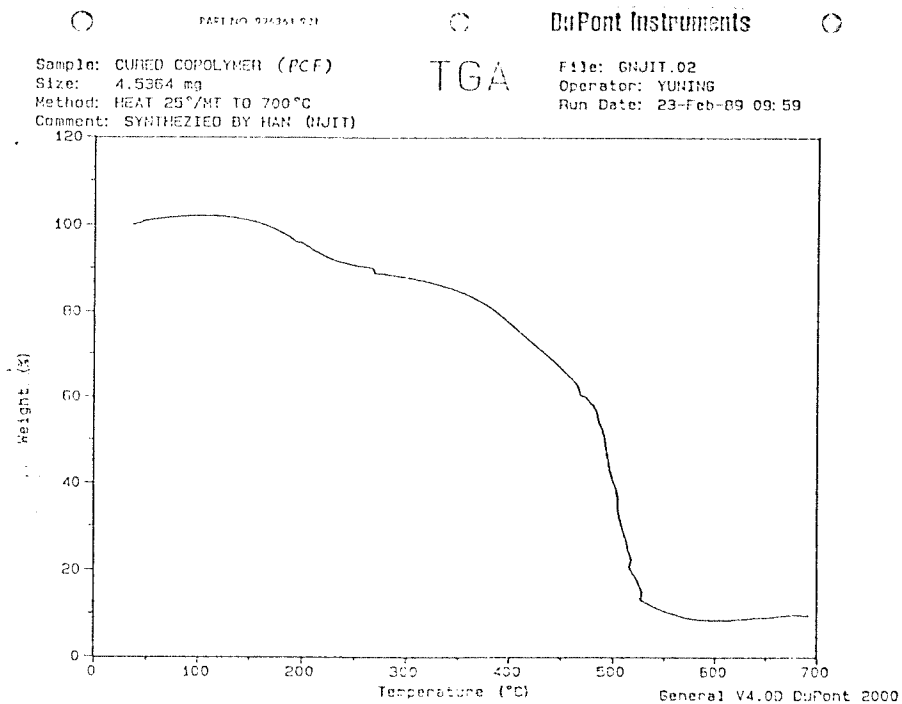


Fig. 22. TGA of PCF copolymer fiber

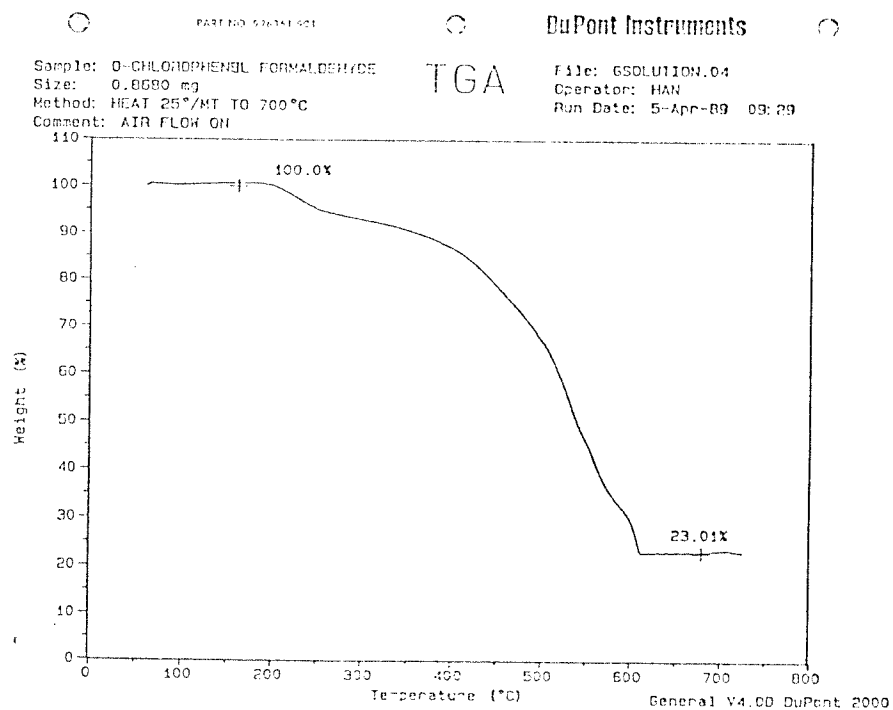


Fig. 23. TGA of CF polymer fiber

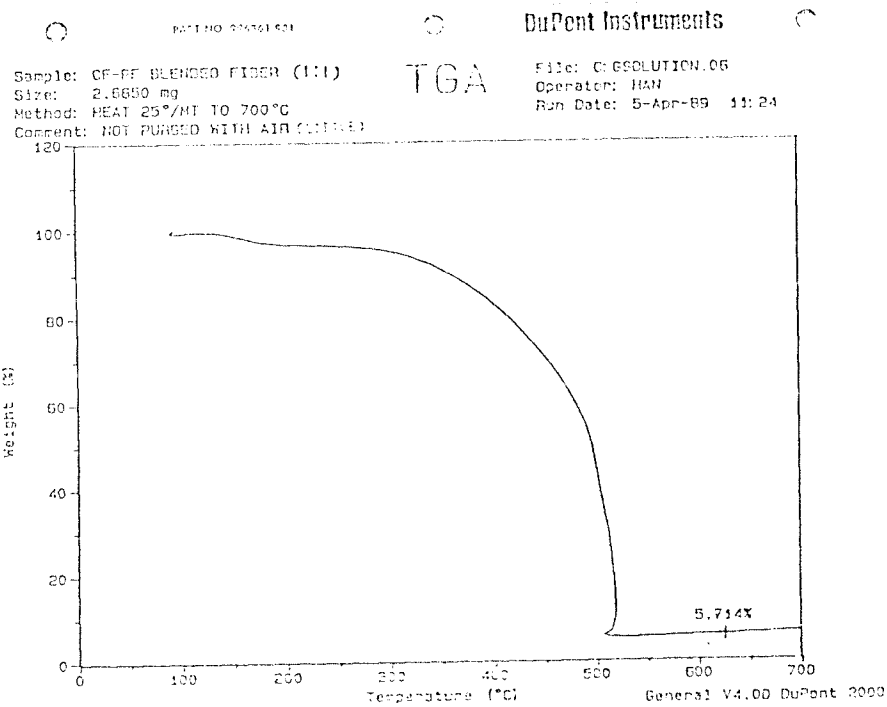


Fig. 24. TGA of 1:1 CF-PF blended fiber

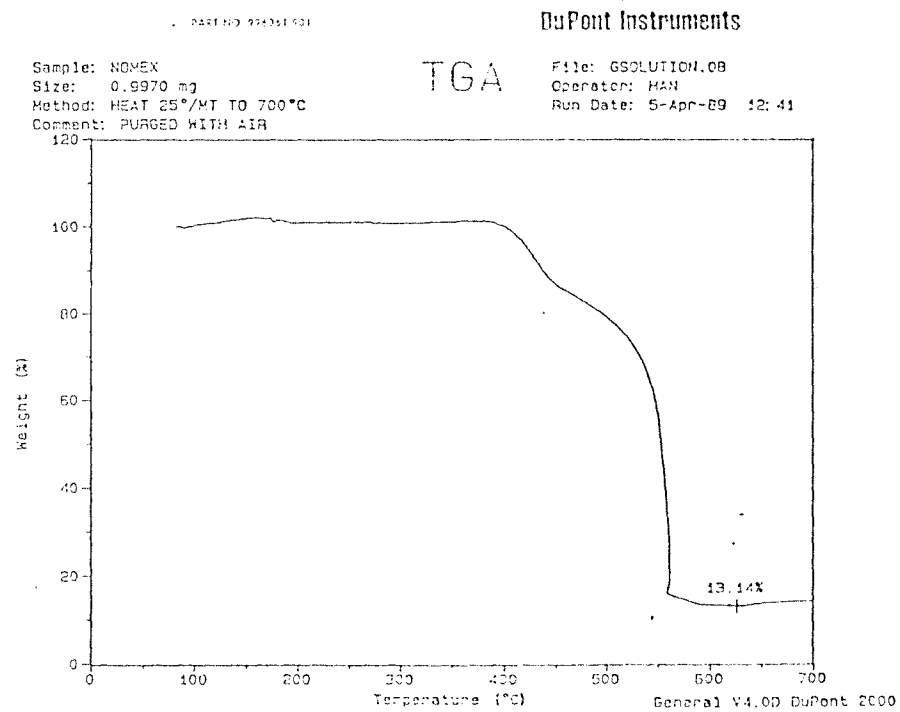


Fig. 25. TGA of Nomex fiber

PART NO. 926361.991

DuPont Instruments

Sample: KYNOL  
Size: 2.4040 mg  
Method: HEAT 25°/MT TO 700°C  
Comment: FIBER FROM HAN

TGA

File: C:GFIBER.01  
Operator: TV  
Run Date: 11-Apr-89 09:06

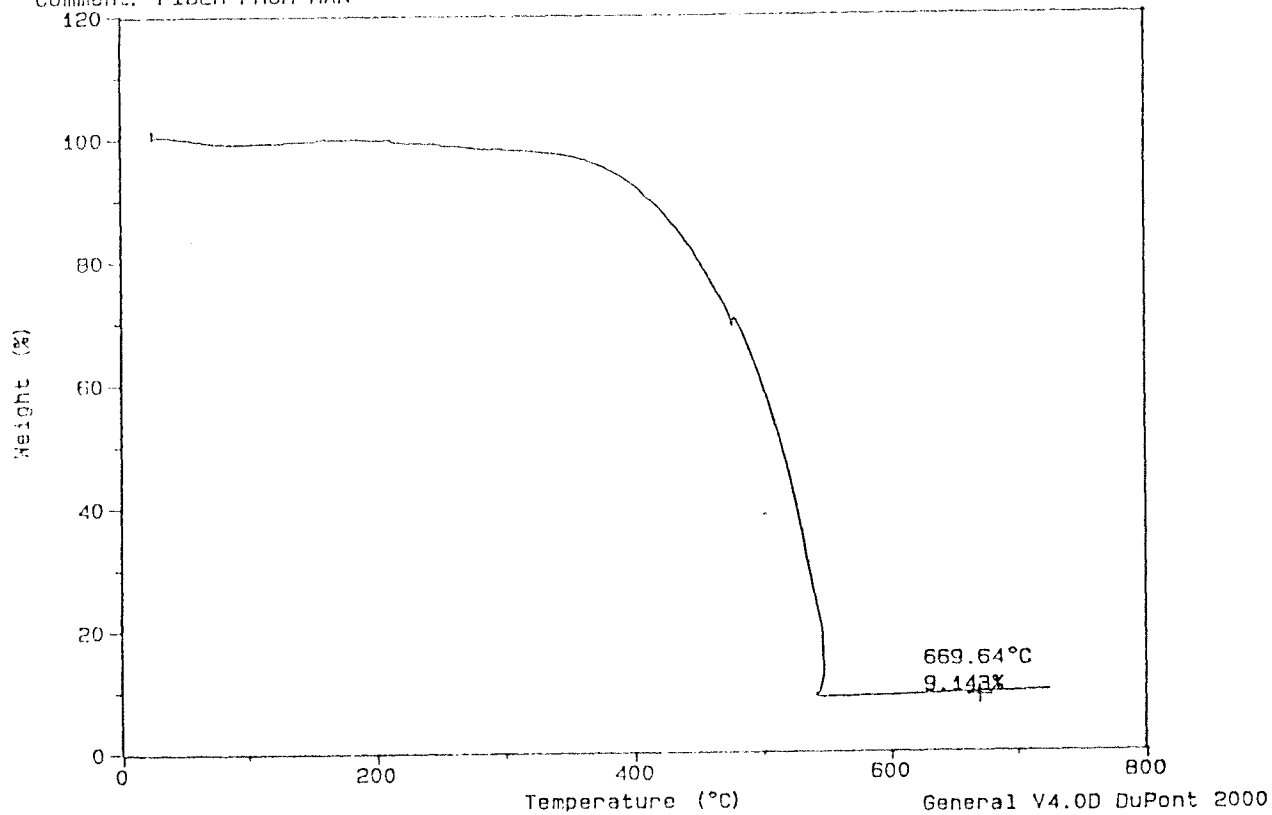


Fig. 26. TGA of Kynol fiber

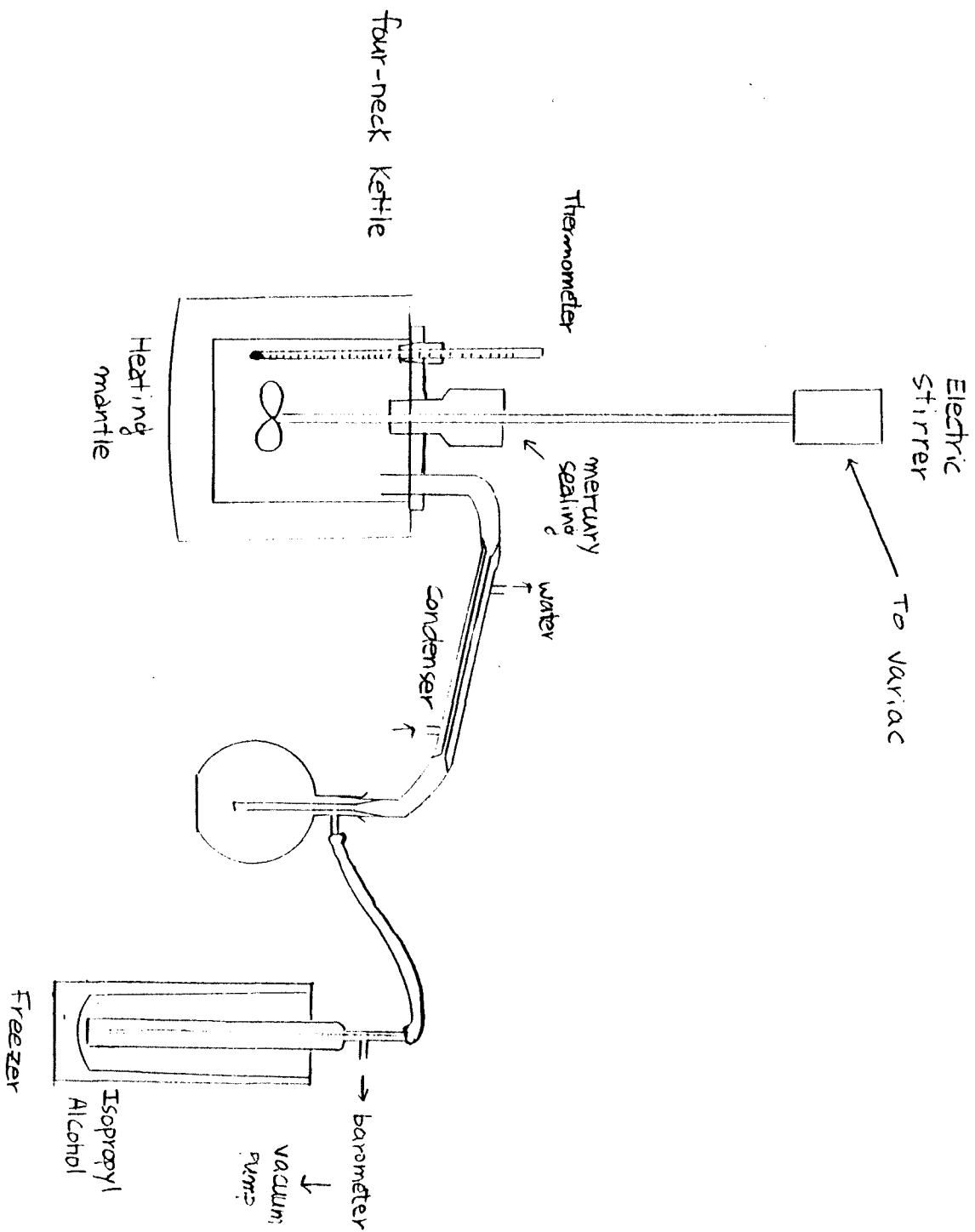
### III. CONCLUSIONS AND RECOMMENDATIONS

The intrinsically flame resistant PCF fibers were prepared, characterized and showed good flame retardancy. This fiber is hard to ignite and self-extinguishing. It becomes charred when exposed to a flame. Its oxygen index, (33) is higher than that of the Nomex fiber(27). However, these fibers show unexpected poor tensile strength and brittleness as a result of insufficient curing. In order to improve this deficiency, several recommendations are suggested as follows:

- \* The polymer should have a higher average molecular weight and melting point.
- \* We should use a swelling agent to help the diffusion of the curing agent into the core of the fiber.
- \* We should make a diameter of the fiber as small as possible so that the fiber can be easily cured because of minimum diffusion space.

Although the PCF fiber is brittle and has a low tensile strength, it can be used in non-woven fabrics such as felt for insulation.

APPENDIX  
EXPERIMENTAL SET UP



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