

# New Industrial Polymers

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# New Industrial Polymers

**Rudolph D. Deanin**, *Editor*


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# ACS Symposium Series

**Robert F. Gould**, *Series Editor*

## FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the SERIES parallels that of its predecessor, ADVANCES IN CHEMISTRY SERIES, except that in order to save time the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. As a further means of saving time, the papers are not edited or reviewed except by the symposium chairman, who becomes editor of the book. Papers published in the ACS SYMPOSIUM SERIES are original contributions not published elsewhere in whole or major part and include reports of research as well as reviews since symposia may embrace both types of presentation.

## PREFACE

Plastics production in the United States is currently growing at an average rate of about 12% per year and may well reach 60 billion pounds by 1980. While the major growth is in the commodity thermoplastics, the number of families of commercial plastics is also increasing at a rapid rate.

The rapid growth of plastics production is attributed to the advantages they offer over older conventional structural materials in terms of processability, flexibility, strength/weight ratio, impact strength, range from lubricity to adhesion, abrasion resistance, energy absorption, thermal and electrical insulation, range of color and clarity, resistance to inorganic chemical corrosion, novelty, and economics. At the same time, there is a continual desire to increase their scope still further by additional improvement in their processability, rigidity, strength, toughness, scratch and mar resistance, thermal expansion, low and high temperature capabilities, weathering, chemical resistance, permeability, and economics. This accounts for the continual development of new plastics materials.

After commercial introduction, a new plastic often takes 10–20 years to find optimum major applications and markets. This time can be shortened greatly by improving communication between the developers of new plastics and their potential users in a great variety of industries. The purpose of this symposium was primarily to improve this communication.

For this purpose, 11 authors from eight companies have contributed 12 papers on 10 new industrial polymer families, and these are collected here. They present considerable detail on the chemistry, processing, properties, and suggested applications of these new materials and should contribute greatly to their more rapid utilization by industry.

While the symposium was being organized, a new major challenge suddenly developed in the plastics industry—the growing scarcity, cost, and political uncertainty of petroleum and natural gas as raw materials. To meet this challenge, the scope of the symposium was broadened by the addition of an impromptu round-table discussion on “Plastics without Petroleum.” The spontaneous audience participation in this discussion was a reaffirmation of the health, ingenuity, and aggressiveness that have always marked the polymer industries. The round-table discussion was collected and organized and is included as the final chapter of this volume.

Hopefully it will help the polymer industries to begin a major effort to broaden their raw material base and thus ensure their continued healthy growth and service to our modern civilization.

RUDOLPH D. DEANIN

Lowell, Mass.  
October 4, 1974



# Radial Block Thermoplastic Rubbers

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## Introduction

Butadiene and styrene have been combined in rubbery polymers in numerous ways to produce a wide variety of properties. Random copolymers made in emulsion systems have accounted for a large portion of total synthetic rubber; however, modifications in these are mainly due to changes in butadiene-styrene ratio and molecular weight with other variations also contributed by changes in initiator systems, polymerization temperature, modifiers, and finishing methods. In recent years, polymers have been produced in solution polymerization systems which allow much more latitude in control of microstructure, molecular configuration, and molecular weight distribution.

One result of solution polymerization technology is the preparation of block polymers - both those that are essentially "pure" block and those that contain some mixtures of block and random structures (1, 2, 3). It was found that copolymers with styrene blocks on the ends of the polymer molecule provide strong, elastomeric materials without vulcanization. This behavior has been broadly documented (2, 4, 5, 6) and polymers of this type are still under intensive study.

## Preparation and Structure

Block polymers of dienes and styrene are usually prepared in solution polymerization systems using alkylmetal initiators although exact methods of producing commercial polymers are not often disclosed. Block structures can be formed by sequential addition of different monomers combined with coupling of polymer chains if desired. Possible synthesis methods have been described in a number of publications (6, 7).

Several structural arrangements of butadiene-styrene copolymers are listed in Figure 1. As indicated, polymers with multiple blocks can be structured in several ways. One important distinction that can be made is between linear polymers and radial, branched polymers. Structures of these are further illustrated in Figure 2; Figure 3 demonstrates aggregations of several molecules of simple, linear and radial block polymers. At first glance, the latter may not appear too dissimilar, but some unique properties arise in the relationships between flow characteristics, structure and molecular weight of these polymers.

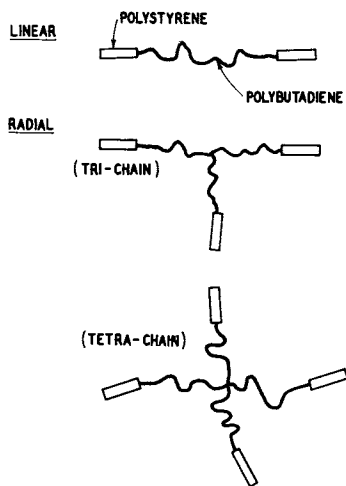
### Properties

Consider first the effects of linear, trichain and tetra-chain polymers of various molecular weight on solution viscosity as shown in Figure 4. This property is of special interest in adhesives. At equal molecular weight, viscosity is lower for tetrachain (or trichain), radial polymers than for linear polymers; or, at equal solution viscosity, one can use a radial tetrachain polymer of higher molecular weight. The same type of behavior persists with melt viscosity which is important to processors of solid compounds. Figure 5 depicts the effect of structure on melt flow (8) and the same trends have been shown in steady flow viscosity (9) and Mooney viscosity (10). Clearly, the rheological behavior is affected by the degree of branching. From the viewpoint of the adhesives, rubber, or elastics fabricator, a branched product with higher molecular weight can be used with the same level of processability given by a lower molecular weight, linear product. This may not always prove advantageous but, in many cases, higher molecular weight will yield some improvement.

Properties of some commercially available radial block polymers based on butadiene and styrene are shown in Table I.

*Figure 1. Examples of butadiene-styrene copolymer structures*

S/B (RANDOM)  
 S - B (BLOCK)  
 S - S/B  
 S - B - S  
 B - S - B  
 (S - B)<sub>3</sub>X  
 (S - B)<sub>4</sub>X  
 S - S/B - S  
 S - B - S - B - S



*Figure 2. Linear and radial branched polymers*

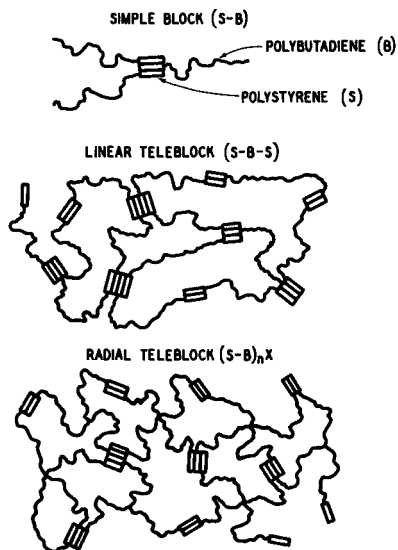
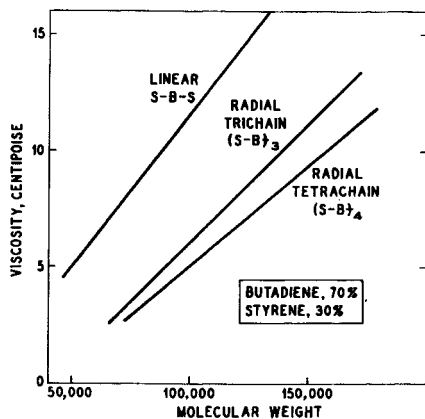


Figure 3. Structures of block polymers



Kautschuk und Gummi Kunststoffe

Figure 4. Effect of structure on viscosity of 5% solutions in toluene (10)

TABLE I  
RADIAL BLOCK THERMOPLASTIC RUBBERS

Solprene® Polymer	<u>411</u>	<u>414</u>	<u>406</u>	<u>475</u>
Butadiene/Styrene Ratio	70/30	60/40	60/40	60/40
Polystyrene, % of RHC	29	39	39	39
Oil Content, phr <sup>a</sup>	0	0	0	50
Specific Gravity	0.94	0.95	0.95	0.94
Melt Flow (180 C, 5 Kg), g/10 min	nil	2-4	nil	1-2
Shore A Hardness	80	90	90	65
300% Modulus, psi	300	600	600	300
Tensile Strength, psi	2800	4000	3800	2800
Elongation, %	700	750	700	1000
Glass Transition, <sup>b</sup>				
T <sub>g</sub> (lower), C	-87	-92	-92	-85
T <sub>g</sub> (upper), C	110	102	102	82

a - Naphthenic oil type.

b - Temperature of maximum in loss modulus at 35 Hertz.

Polymers of this type dissolve readily in a number of solvents and this plus high tensile without need for vulcanization provides an excellent product for use in adhesives where a strong and flexible bond is required. For other applications these products can be easily shaped using procedures common for thermoplastics yet provide elastic properties typical of rubbers at temperatures below the softening point of polystyrene. Set is low at room temperature but will of course be high if deformation occurs at elevated temperatures followed by cooling. Recycling of scrap is feasible since vulcanization is not used.

Stress-Strain Properties. Tensile strength improves with an increase in styrene content (at least up to 50% styrene) as shown in Figure 6 or an increase in molecular weight (11). The latter effect may not be evident at room temperature but is more significant at elevated temperature or in compounded stocks as illustrated in Tables II and III. Data in Table II as well as reference (11) also indicate that the high tensile observed at room temperature decreases as temperature is raised thus limiting the maximum service temperature of these polymers.

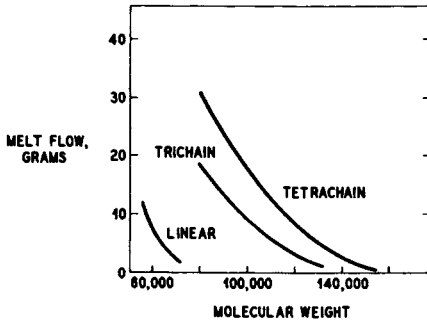


Figure 5. Melt flow of teleblock polymers 70/30 butadiene/styrene (8)

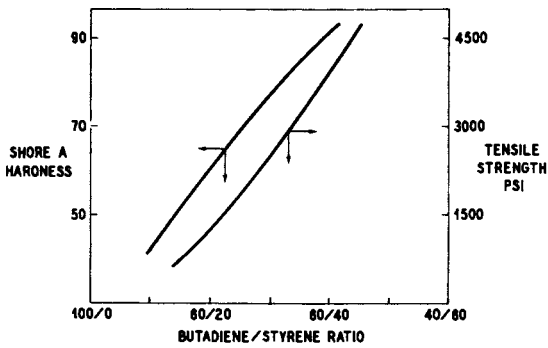


Figure 6. Effect of styrene content on hardness and tensile strength

TABLE IIMOLECULAR WEIGHT EFFECTS - 60/40 BUTADIENE/STYRENE

<u>Molecular Wt., Mw</u>	<u>Tensile, psi</u>		
	<u>80 F</u>	<u>120 F</u>	<u>140 F</u>
130,000	4000	1800	650
250,000	3800	2400	1800

TABLE IIIEFFECT OF MOLECULAR WEIGHT IN A COMPOUND<sup>a</sup>

<u>Molecular Wt., Mw</u>	<u>Melt Flow, g</u>	<u>Tensile, psi</u>	<u>NBS Abrasion Index</u>	<u>Flexures to Break (Ross)</u>
125,000	183	560	52	2,000
160,000	43	630	72	12,000
250,000	0.2	1330	89	> 100,000
a - Polymer (60/40 Bd/S)		100		
Hard Clay		80		
Naphthenic Oil		50		
Stearic Acid		3		

All properties except molecular weight are for the compounds.

Hardness. A wide range in hardness can be achieved by (1) variation of butadiene-styrene ratio in the copolymer (Figure 6) and (2) manipulation of compounding ingredients such as fillers, oils and resins. Oil is an inexpensive ingredient to reduce hardness if its use can be tolerated. Hard clays, silicas or carbon blacks and polystyrenes are useful to increase hardness while materials such as whiting and polyindene resins have minimal effects on hardness. Hardness can also be influenced by molding conditions, especially if appreciable amounts of polystyrene are added to a compound. Data in Figure 7 illustrate this point but it must be emphasized that the effects can vary depending on the formulation, polymer type, rates of heating and cooling, etc. The formulation for results in Figure 7 was as follows:

Radial Block Polymer-Oil Masterbatch	150
Whiting	80
Oil	50
Polystyrene	variable
Polyindene Resin	20
Titanium Dioxide	10
Stearic Acid	3

Shear Resistance (Adhesives). The resistance of adhesives based on butadiene-styrene polymers to failure under shear is influenced by monomer ratio, molecular weight and branching (12, 8). As indicated in these references, higher molecular weight, higher styrene and increased branching all lead to better shear resistance. Increases in molecular weight and styrene also raise viscosity but increases in branching reduce viscosity. At equal formulation viscosity, a tetrachain polymer gives excellent performance as shown in Table IV taken from reference (8).

TABLE IV

TELEBLOCK POLYMERS AT EQUAL FORMULATION VISCOSITY

<u>70/30 Butadiene/ Styrene Polymer</u>	<u>Molecular Weight</u>	<u>Formulation Viscosity, cps</u>	<u>Shear Resistance, Hours to Fail at 90 C</u>
Linear	84,000	1520	1.0
Trichain	136,000	1580	2.4
Tetrachain	182,000	1820	2.8

Peel Strength (Adhesives). This property follows a trend similar to that for shear resistance and best peel strengths are obtained with fairly high styrene (near 40%) and with high molecular weight polymers. Other considerations such as tack and viscosity may, however, dictate a limit on increases in molecular weight or styrene content.

Abrasion. Resistance to abrasion is adequate for many applications including footwear and can be improved by addition of reinforcing pigments (hard clay, silicas, carbon blacks) and through use of added plastic materials such as polystyrene or polyolefins. Abrasion resistance is reduced by oils, some resins and large-particle fillers. It is also improved with increased molecular weight of the polymer (Table III).

Crack Growth. Resistance to crack growth is usually quite good, especially in compounded stocks. Oils, resins, fillers and polystyrene all have shown some beneficial effects on resistance to crack growth although there are optimum levels for some ingredients.



Low Temperature Properties. Brittle points or freeze points are quite low, due to the very low T<sub>g</sub> of the rubbery polybutadiene portion, and even polymers with 40 or 50% styrene may have low brittle temperatures. Soling compounds, for example, have displayed satisfactory resistance to cracking at -20 F.

Coefficient of Friction. This property depends on styrene level and on materials which may be added in compounding but falls in the same range as other rubbers (natural rubber, SBR, etc.) rather than in a lower range displayed by even the more flexible plastics.

### Melt Processing

Radial block polymers are relatively easy to process. The temperature range for satisfactory mixing or fabrication of products is fairly broad - temperatures must be high enough to soften the polymer and within certain limits on the high side to avoid excessive stickiness or degradation. A preferred range is generally between 250 and 350 F although higher temperatures may be desirable for some molding operations.

Mixing. Internal Mixer Preferred  
Cycles Similar to Other Rubbery Polymers  
Heat Generated During Mixing  
Dump at Temperatures of 280-350 F

Molding. Compression or Injection Methods  
Injection Preferred  
Cylinder Temperature - 350 F Range  
Mold Temperature - 120 to 150 F

Extrusion. Low Compression Screw Preferred  
L:D Ratios - 10:1 to 25:1  
Barrel Temperature - 240 to 340 F  
Die Temperature - 280 to 340 F  
Preferred Melt Temperature - 275 to 375 F

The response of melt viscosity to changes in shear rate over the range normally encountered in mixing, extrusion and injection molding is generally similar to that of thermoplastics such as polyethylene or polystyrene. Melt viscosities for a radial block polymer based on butadiene and styrene, an oil masterbatch and a compound based on the masterbatch are shown in Figure 8. The compound shown contains oil and fillers<sup>a</sup> and would be suitable for injection molded soling. Its viscosity is in the range of a molding grade polyethylene. The clear polymer shown

a - The compound based on radial block polymer-oil masterbatch contains 110 phr total oil, 90 phr filler and 80 phr polystyrene.

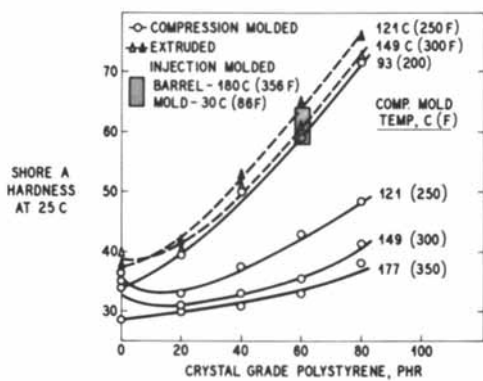


Figure 7. Effect of molding conditions

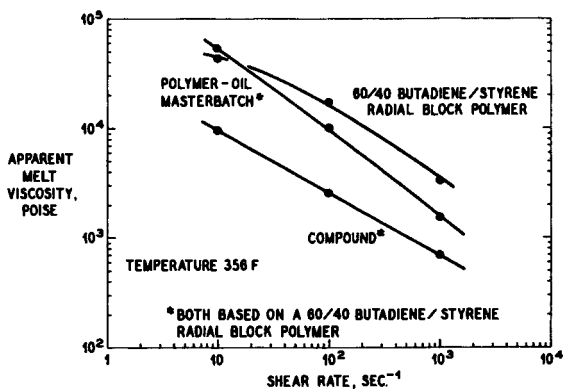


Figure 8. Melt viscosity vs. shear rate

is more comparable in viscosity to polystyrene or an extrusion grade polyethylene.

Effects of injection pressure and temperature on flow of another compound<sup>a</sup> based on a radial teleblock oil masterbatch are illustrated with spiral flow data in Figure 9. Apparent viscosities at variable shear rates for this compound are much like those shown earlier:

Shear Rate, <u>sec<sup>-1</sup></u>	Apparent Viscosity, <u>poise</u>
10	$8.0 \times 10^3$
100	$2.1 \times 10^3$
1000	$6.5 \times 10^2$

### Compounding Ingredients

Fillers of various types may be used to advantage. Carbon blacks, silicas and clays may increase tensile at low levels but reduce tensile if added in large amounts. However, their use is quite important for the beneficial effects that occur in abrasion resistance and flex life (crack growth). Whiting is less beneficial but does improve flex life.

Polystyrene is a useful additive. Its use results in improvements in tear, abrasion and flex properties and in higher hardness. Low density polyethylene has a similar effect and can be used in moderate amounts. Other resins which impart useful properties include polyindenes, coumaroneindene, esters of hydrogenated rosin, mixed olefin resins, and a number of others. These various resins are especially interesting as modifiers in both adhesives and thermoformed compounds - different resins will affect the ratio of properties in different ways - some increase melt flow with small effect on hardness while others have the reverse effect.

Preferred oils are naphthenic or paraffinic in nature, compatible with the polybutadiene portion of the polymer. Plasticizers compatible with the polystyrene blocks tend to reduce strength.

Blends of radial block rubbers with other polymers provide useful variations in properties. Thermoplastics such as polyethylene and polystyrene have already been mentioned. There are several polymers which can be added to butadiene-styrene block

a - Radial Block Polymer-Oil Masterbatch	150
Whiting	80
Oil	50
Polystyrene	60
Polyindene Resin	20
Titanium Dioxide	10

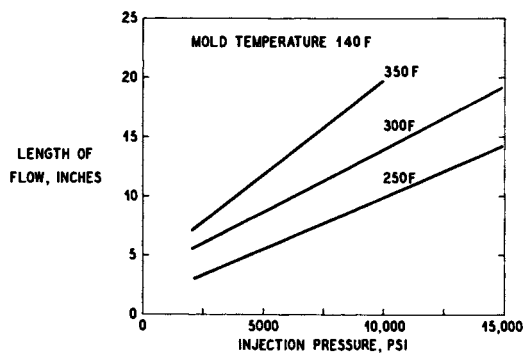


Figure 9. Spiral flow data

polymers to provide ozone resistant products which are still strong and elastomeric without vulcanization. These include ethylene-propylene copolymers, polyurethanes, neoprenes or ethylene-vinyl acetate polymers.

Protection against changes in color or properties caused by ultraviolet radiation can be imparted by use of finely-divided grades of zinc oxide or titanium dioxide. Carbon black is effective where it can be used. A number of commercially available UV absorbers, including benzotriazoles and benzophenones, are also useful in this connection.

### Applications

Consideration of properties discussed helps define areas of application. These areas are those which require elastomeric materials and/or high coefficient of friction which will not be subjected to excessively high temperatures. Uses for radial teleblock polymers generally fall into three categories: (1) adhesives, (2) articles which are thermally formed by sheeting, extruding, molding, etc. and (3) modification of other elastomeric or plastic polymers by blending.

Adhesive applications can be widespread including contact cements, pressure-sensitive adhesives and hot melts. In solid compounded articles footwear is a large volume application such as molded-in-place soling or unit soles to be cemented to uppers. Additional uses are in toys, milk tubing, cove base, mats and miscellaneous coatings or molded parts. Potential uses include blends with ethylene-propylene rubber and ethylene-vinyl acetate copolymers to provide ozone-resistant formulations or blends to improve crack- or impact-resistance of plastics.

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# A New Thermoplastic Syndiotactic 1,2-Polybutadiene.

## I. Production, Fundamental Properties, and Processing

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### INTRODUCTION

A new thermoplastic syndiotactic 1, 2-polybutadiene (1, 2-PBD) has been developed by Japan Synthetic Rubber Co., Ltd. (JSR).

The polymer is of more than 90% 1, 2-unit content, with crystallinity controlled between 15 and 25%, and the weight-average molecular weight of the polymer is more than 100,000. Many papers on syndiotactic 1, 2-PBD have been reported for a long time. As the polymers reported there had a high crystallinity (>40%) and high melting point, they were rather difficult to process with ordinary plastics machines without deterioration of the polymer because of their high molding temperatures. On the other hand, since the crystallinity of the new 1, 2-PBD is controlled between 15-25%, the melting point is kept below 90°C. Consequently, the 1, 2-PBD does not deteriorate during processing in the molding machine. JSR is the first in the world to succeed in developing a unique 1, 2-PBD, which can be processed with conventional plastics molding machines.

Meanwhile, since the structure of 1, 2-PBD has two chemical reactive sites, which are (1) hydrogen bonded to the tertiary carbon atom and to the allyl position and (2) the vinyl group, this polymer may be regarded as a novel functional polymer, namely, as a reactive thermoplastic. Having found the new catalyst system in 1966, JSR has engaged for the past seven years in fundamental research, application research and development, process development, and marketing research. As a result, JSR has decided on the commercialization of 1, 2-PBD and constructed a plant of 5,000MT/Y at the end of 1973. The plant is under expansion to 10,000MT/Y and will be completed at next spring. JSR has filed more than 107 patents concerning production and applications of 1, 2-PBD throughout the world.

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### PRODUCTION OF A NEW SYNDIOTACTIC 1, 2-POLYBUTADIENE

JSR 1, 2-PBD is produced by solution polymerization technique using Ziegler type catalyst system containing Co Compound as one component. The representative catalyst system consists of Co halide-Ligand-trialkyl aluminum-H<sub>2</sub>O. All ingredients in this catalyst system are indispensable component for 1, 2-polymerization of butadiene, because the polymerization of butadiene can not be obtained from the Co halide-AlR<sub>3</sub> and Co halide-Ligand-AlR<sub>3</sub> systems, alone. The Co halide-AlR<sub>3</sub>-H<sub>2</sub>O system is the catalyst for cis 1, 4-polymerization of butadiene. Adding the ligand to the cis 1, 4-polymerization catalyst system, we can obtain 1, 2-polybutadiene. Therefore, as far as the production of our 1, 2-PBD is concerned, the most important ingredients are ligand and H<sub>2</sub>O. The above mentioned relations are summarized as follows:

CoX <sub>2</sub> - AlR <sub>3</sub>	No polymerization
CoX <sub>2</sub> - Ligand - AlR <sub>3</sub>	No polymerization
CoX <sub>2</sub> - AlR <sub>3</sub> - H <sub>2</sub> O	Cis-1, 4 polymerization
CoX <sub>2</sub> - Ligand - AlR <sub>3</sub> - H <sub>2</sub> O	1, 2 polymerization

The roles of H<sub>2</sub>O in 1, 2-polymerization of butadiene are shown in Fig. 1. When H<sub>2</sub>O/Al = 1.0, Yield, 1, 2-unit contents and molecular weight show maximum value. Considering the general Ziegler type catalyst aspects, it is surprising that such a lot of H<sub>2</sub>O to AlR<sub>3</sub> is necessary for polymerization.

### SOME FUNDAMENTAL PROPERTIES

#### Structure of 1, 2-polybutadiene

1, 2-unit content was more than 90% by IR analysis<sup>(1, 2)</sup>. As shown in Fig. 2, the polymer does not contain any trans 1, 4-units. The absorbance at 745cm<sup>-1</sup> indicates the existence of small amounts of cis 1, 4-unit. By X-ray diffraction studies, 2θ of 1, 2-PBD was the same as that of the syndiotactic 1, 2-PBD reported by G. Natta<sup>(3)</sup>, as shown in Fig. 3. The tacticity of 1, 2-PBD was analyzed by V.D. Mochel's <sup>13</sup>C NMR spectra method<sup>(4)</sup> using a JEOL JNM-PS/PFT-100 spectrometer at 25.15 MHz. As shown in Table 1, there is no isotactic 1, 2-PBD. The syndiotactic content increases with its crystallinity and is much greater than heterotactic content.

Table 1. Tacticity of JSR 1, 2-polybutadiene

Crystallinity (%)	Microstructure			Tacticity		
	cis (%)	trans (%)	1, 2 (%)	iso. (%)	hetero. (%)	syndio. (%)
18	10	0	90	0	49	51
25	8	0	92	0	34	66



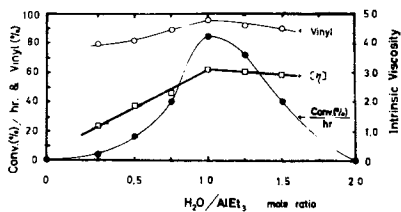


Figure 1. Effects of H<sub>2</sub>O/Al mole ratio on the intrinsic viscosity, vinyl content, and conversion (%)/hr.

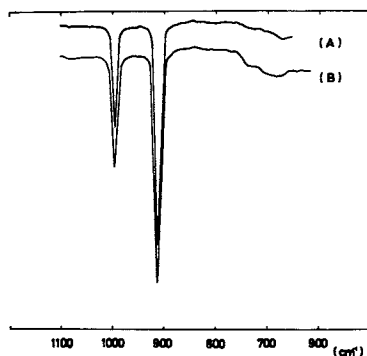


Figure 2. Infrared spectrum of CS<sub>2</sub> solution of 1,2-polybutadiene at room temperature

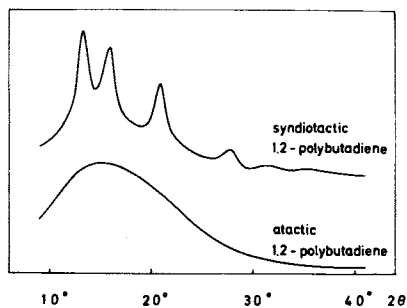


Figure 3. X-ray diffraction diagram of 1,2-polybutadiene

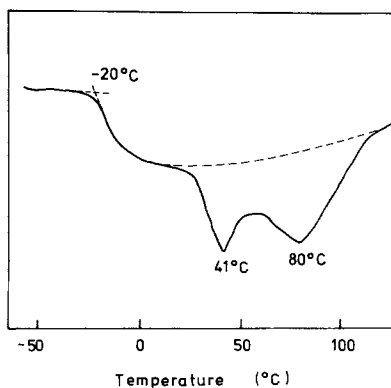


Figure 4. DSC thermogram of 1,2-polybutadiene having 25% crystallinity at 16°C/min.

As the results of X-ray and NMR analysis, it is confirmed that the polymer is syndiotactic 1, 2-polybutadiene.

The crystallinity was determined by the density gradient tube method. We assumed that the density of 100% crystallinity is 0.963<sup>(5)</sup> and the density of 0% crystallinity is 0.892. 1, 2-PBD of 0% crystallinity was synthesized by a JSR catalyst system and it was confirmed that it was amorphous by X-ray analysis.

The DSC curve of 1, 2-PBD as having 25% crystallinity is shown in Fig. 4. It is assumed that the distribution of crystalline size is broad. We have not discovered yet why the endothermic peak of the DSC is broad.

Even low crystalline 1, 2-PBD at 25% crystallinity has fine crystallines, as shown in photograph I. On the other hand, amorphous 1, 2-PBD prepared by our catalyst does not show any crystallines (photograph II).

#### Molecular Characterization of 1, 2-polybutadiene

GPC data were measured with a Model 200 of the Waters Co. the result is shown in Fig. 5. Although the polymerization is carried out by Ziegler type catalyst, the molecular distribution of the 1, 2-PBD is rather sharp.

The results of the molecular characterization of the 1, 2-PBD are tabulated in Table 2.

Table 2. Molecular characterization of JSR 1, 2-polybutadiene

Crystallinity (%)	18		25	
	Intrinsic viscosity (30°C, toluene)	1.44	1.82	1.43
$M_n \times 10^{-4}$	11.1	12.2	10.7	12.1
$M_w \times 10^{-4}$	20.6	31.4	17.7	23.4
$M_w/M_n$	1.9	2.6	1.7	1.9
$\lambda \times 10^5$	0.3	0.4	0	0.03
$\lambda M_w$	0.6	1.4	0	0.1

Since  $\lambda$  and  $\lambda M_w$  are almost zero, it is assumed that the long branch of 1, 2-PBD having 25% crystallinity is almost zero, but the branches tend to increase with the reduction of the crystallinity. The viscosity molecular weight equation<sup>(6)</sup> used was  $[\eta] = 9.1 \times 10^{-5} \times M_n^{0.80}$  and the measurement of the viscosity was carried out in toluene, at 30°C.

#### Physical Properties

Some physical properties of 1, 2-PBD of 25% crystallinity

(Butadiene Resin, JSR RB820) were evaluated in accordance with various testing methods and are shown in Table 3. Roughly speaking, it seems to be quite all right to consider that the properties of 1, 2-PBD are similar to LDPE with greater elongation, except its thermal properties.

T<sub>g</sub> and T<sub>m</sub> are determined by DSC. As shown in Fig. 4, the determination of T<sub>m</sub> is unclear because of two broad peaks. However, we decided that the temperature of the main peak can be regarded as T<sub>m</sub>. Because T<sub>g</sub> of the polymer is -23°C, this point must be considered in using 1, 2-PBD at extremely low temperatures.

A typical stress-strain curve of 1, 2-PBD compared with LDPE and rubber indicates that the 1, 2-PBD has intermediate properties between plastics and rubber (Fig. 6). The relationship between "dynamic elastic modulus"(E) and temperature of 1, 2-PBD having 25% crystallinity is shown Fig. 7. The E of 1, 2-PBD is similar to that of EVA and smaller than that of LDPE above 40°C. The E of 1, 2-PBD is the smallest than those of EVA and LDPE below 20°C.

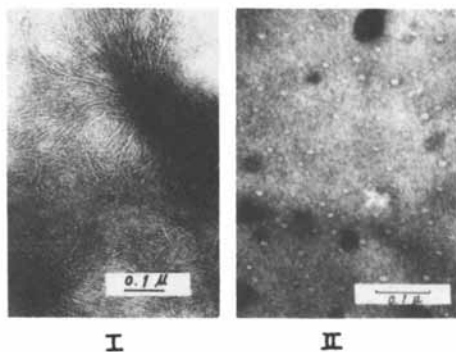
### Chemical Properties

Since each monomer unit of 1, 2-PBD has (1) the hydrogen bonded to tertiary carbon atom and to the allyl position, and (2) a vinyl group, the polymer is can be activated by heat, U.V. and other energy sources. Also, 1, 2-PBD can be easily made to react with other chemical reagent due to its chemical reactivity.

The stability, very important from the industrial point of view, can be controlled by choice of kinds and quantities of various stabilizers. If 1, 2-PBD contains only thermal stabilizers, the polymer is deteriorated within a few months under outdoor exposure. Especially, in summer, the thin film is deteriorated within a few weeks. Thus, 1, 2-PBD is considered to be a photodegradable plastics. Fig. 8 shows the possibilities of its life control through the use of various stabilizers.

The photodegradation of the 1, 2-PBD is caused by the cross-linking reaction, of which we explained at a conference in Nov. 1973<sup>(7)</sup>. The photodegradation does not occur in the presence of light of more than 350 mμ. in wave length, as shown in Table 4. 1, 2-PBD is stable under ordinary illumination lamps in its light-deterioration. Also, when covered with an opaque surface, the polymer is safe and stable for a long time.

The chemical reactivity of 1, 2-PBD is similar to the liquid 1, 2-polybutadiene. Industrially applicable reactions may be the ene addition reaction, cross-linking reaction and graft polymerization.



Electron micrographs of 1,2-polybutadiene. I: crystallinity 25%; II: amorphous.

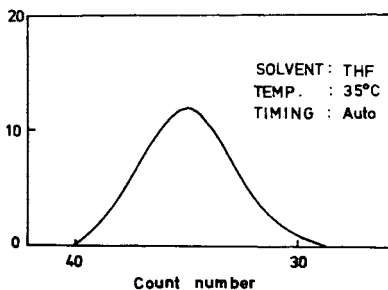


Figure 5. CPC chromatogram of syndiotactic 1,2-polybutadiene (crystallinity: 25%)

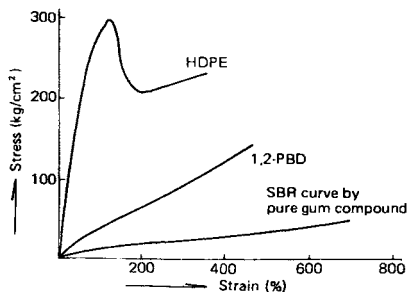


Figure 6. Stress-strain curve of 1,2-polybutadiene [(crystallinity: 25%  $[\eta]$  (30°C, toluene) = 1.3)]

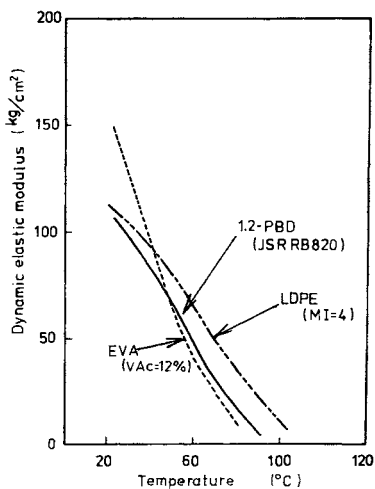
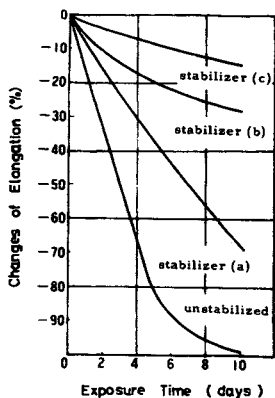


Figure 7. Relationship between dynamic elastic modulus and temperature of 1,2-PBD (crystallinity: 25%) compared with LDPE and EVA

Table 3. Typical properties of syndiotactic 1, 2-polybutadiene

Properties	Test methods	Units	Determined values
Crystallinity	Density-gradient tube method	%	25
Intrinsic viscosity, (toluene, 30°C.)			1.3
Microstructure 1, 2-bond content	Infrared absorption spectrum	%	90
Density	Density-gradient tube method		0.91
Melt index; 150°C., 2160 g	ASTM D1238	g./10 min.	2.3
<b>Thermal properties:</b>			
Softening point (Vicat's test)	ASTM D1525	°C.	60
Glass transition point	(DSC method)	C.	-23
Melting point	(DSC method)	C.	90
<b>Tensile properties:</b>			
300% tensile strength	ASTM D638	kg./cm <sup>2</sup> .	90
Tensile strength at fracture	ASTM D638	kg./cm <sup>2</sup> .	110
Tensile elongation at break	ASTM D638	%	410
Hardness (Shore hardness test)	ASTM D1706		31
Bending strength	ASTM D790	kg./cm <sup>2</sup> .	47
Bending modulus	ASTM D790	kg./cm <sup>2</sup> .	560
Isod impact strength (room temperature)	ASTM D256	kg·cm./cm <sup>2</sup> .	Does not break.



Exposure period: Nov. 1-Nov. 11, 1971  
Exposure location: Yokkaichi, Japan

Figure 8. Weathering test of syndiotactic 1,2-polybutadiene film by outdoor exposure

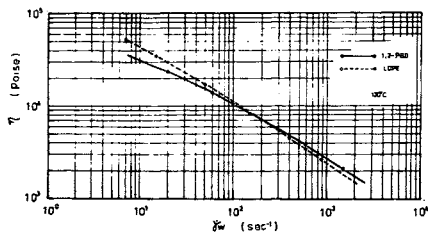


Figure 9. Relationship between  $\eta$  and  $\dot{\gamma}$  of syndiotactic 1,2-polybutadiene (crystallinity: 25%,  $[\eta] = 1.3$ )

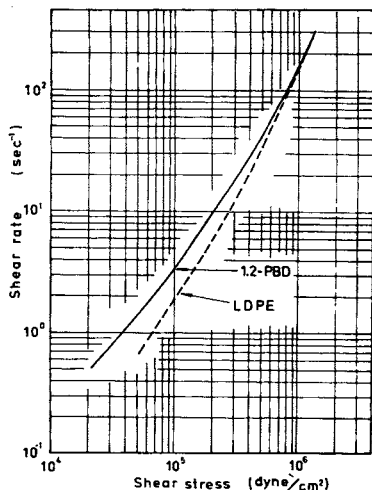


Figure 10. Relationship between  $\tau$  and  $\dot{\gamma}_w$  of syndiotactic 1,2-polybutadiene (crystallinity: 25%  $[\eta] = 1.3$ )

Table 5. Representative processing condition of syndiotactic 1, 2-polybutadiene (crystallinity: 25%,  $[\eta] = 1.3$ )

Extruder	: 40 <sup>m</sup> /m full-flight screw
	$L/D = 24$ , C.R. = 2.0
Die	: spiral die 75 <sup>m</sup> /m $\phi$ x 0.7 mm
Preset temp.	: C <sub>1</sub> (100°C) C <sub>2</sub> (120°C) C <sub>3</sub> (130°C)
	Die (140°C)
Screw rotation	: 40 r.p.m.

Table 4. Photodegradability of syndiotactic 1, 2-polybutadiene effect of wave length of light\*

Lamp-Model	Dominant Wave-Length Radiated ( $m\mu$ )	Light Intensity at Surface of Sample ( $mW/cm^2$ )	Energy Level of Dominant Wave-Length (Kcal/mol)	Radiation Level Required for Occurring Degradation ( $mW\cdot Hr/cm^2$ )
GL 15	254	12.0	112	Less than 120 ( 10 Hr )
FL 20 SE	314	12.6	86	Less than 250 ( 20 Hr )
FL 20 SBLB	352	11.9	77	Less than 600 ( 50 Hr )
FL 20 SW/NL	582	11.8	50	Not degraded

\* Produced by Tokyo Shibaura Electric Co., Ltd.

Table 6. Testing items of some Japanese Regulations used to confirm the nontoxicity of syndiotactic 1, 2-polybutadiene

	Regulation No.	Test Item
Specification for plastics packaging for foods	No. 434	1. Phenol 2. Formaldehyde 3. Heavy metals 4. Residue on evaporation 5. Potassium permanganate-reducing substances
Specification for plastics used in medical practice	No. 301 Disposable blood donor set and solution administration set	1. Heavy metals 2. Extractive substances i. Transparency and appearance ii. pH (The difference to the blank solution) iii. Heavy metals iv. Potassium permanganate-reducing substances v. Residue on evaporation 3. Acute systemic toxicity
	No. 278 Disposable blood oxygenator set	1. Extractive substances i. Transparency and appearance ii. Foam test iii. pH (The difference to the blank solution) iv. Potassium permanganate-reducing substances v. Residue on evaporation vi. Zinc vii. Lead 2. Hemolysis test 3. Pyrogen test

### PROCESSING CONDITION

The relation between  $\eta$  and  $\dot{\gamma}$  (viscosity and shear rate), the rheological behavior of 1, 2-PBD, is shown in Fig. 9.  $\eta$  vs  $\dot{\gamma}$  curves of 1, 2-PBD and LDPE have a very similar appearance. Also, the relation between  $\tau$  and  $\dot{\gamma}$  (shear stress and shear rate) is similar to LDPE (Fig. 10). Since the Melt Flow Index of this LDPE is 4, the 1, 2-PBD is regarded as a high flow resin. Therefore, it is assumed that the processing condition of 1, 2-PBD is almost the same as that of LDPE. Actually, having examined many times the processing of the 1, 2-PBD, we have found that the polymer can be processed by ordinary molding machine, under due care to the thermal stability of the 1, 2-PBD.

For example, the thin films of 1, 2-PBD were made by ordinary T-die extrusion and blown film extrusion. The representative processing conditions of 1, 2-PBD are tabulated in Table 5. The preset temperature is an important processing condition. Of course, it depends on the mechanism of processing machine. And it is desirable to keep the temperature under 140°C. Another required condition is a special technique for cooling of the molding, because of its low melting point.

### NONTOXICITY OF JSR 1, 2-POLYBUTADIENE

The additives used in the production of 1, 2-PBD, such as thermal stabilizers, antioxidants, lubricants, anti-fogging agents, U.V. absorbers and others, should be only those which have been approved by the F.D.A. Therefore, it may be all right to consider that the 1, 2-PBD is safe for food. However, we attempted to obtain some test results about the nontoxicity of the polymer and examined the Regulations of the Ministry of Health and Welfare of Japan. The test items used to confirm the nontoxicity of the 1, 2-PBD tabulate in Table 6. No. 434 is the specification for plastic packaging for foods, except PVC. No. 273 and No. 301 are the specification for plastics used in medical practice, in Japan. These testing items consist of extraction test, heavy metal analysis, acute toxicity test, hemolysis test and pyrogen test. All the results of the examination passed the regulations and indicate that the 1, 2-PBD is safe enough to be used as a plastic packaging for foods. In the case of acute toxicity, the number of deaths of the mice was zero. Further, it is assumed that the 1, 2-PBD has the possibility to be applied to the medical plastics field.

### ACKNOWLEDGEMENTS

The authors would like to thank Japan Synthetic Rubber Co., Ltd. for the permission to publish this in the symposium. We are



grateful for the help given by Mr. N. Nomura, Mr. O. Nomura and Mr. K. Kawamoto, Illumination Laboratory, Tokyo Shibaura Electric Co., Ltd.

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# 3

## A New Thermoplastic Syndiotactic 1,2-Polybutadiene.

### II. Applications

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#### INTRODUCTION

A new thermoplastic syndiotactic 1, 2-polybutadiene (1, 2-PBD) have been developed by Japan Synthetic Rubber Co., Ltd. (JSR). The 1, 2-PBD is a low crystalline polymer (15-25% crystallinity) and a unique thermoplastic having property between plastic and rubber. On the other hand, the 1, 2-PBD is regarded as a novel functional polymer, namely, as a reactive thermoplastic. The characteristic points of 1, 2-PBD are summarized as follows; ① Safety for food ② high reactivity ③ good transparent ④ pliability and flexibility ⑤ photodegradability. Its possible applications are very wide from above described characteristics. It may fairly be said that its applications cover all the polymer's field like Figure I which are shown schematically some of it's possible applications.

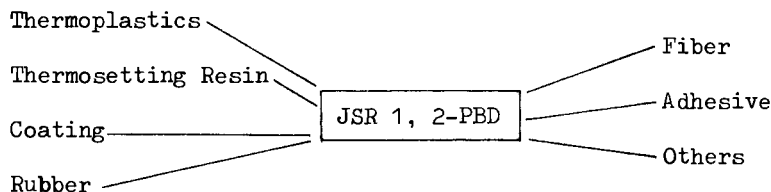


Figure 1. Application fields of JSR 1,2-polybutadiene

The 1, 2-PBD can be applied to films and tubes in thermoplastics field. In rubber field, cross-linking foam like EVA is a possibility. In coatings, photo-curing paint is a possibility.

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In the adhesion field, hot-melt type adhesive is a possibility. In the fiber field, graphite fiber is a possibility. In other fields, photo-sensitive polymer is a possibility.

We will describe the following some of possible applications of the 1, 2-PBD that are useful from an industrial view point.

#### APPLICATION EXAMPLES IN THERMOPLASTIC FIELD

We developed the stretch film of the 1, 2-PBD as a representative example in thermoplastics field (photograph I, II).

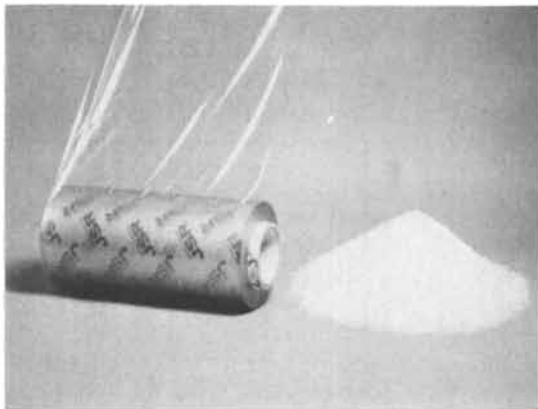
The general physical properties of 1, 2-PBD film are shown in Table 1 compared with film properties of other soft plastics commercially available. The datas show that 1, 2-PBD film is comparable to LDPE, EVA and plastisized PVC in some physical strength. The characteristic points of 1, 2-PBD film may be summarized as follows:

- 1) Good transparency
- 2) High gas permeability
- 3) Good elongation and stretch
- 4) High tear resistahce (Elemendorf)
- 5) High coefficient of friction
- 6) Pliability and flexibility
- 7) Lower heat-sealing temperature and high welding efficiency

The gas permeability of 1, 2-PBD depends on the film thickness, as shown in Fig. 2. When the film thickness is increased to several few millimeters, the gas permeability of 1, 2-PBD is reduced and approaches that of LDPE. In this film the gas permeability of 1, 2-PBD is high, which is assumed to be attributable to the good solubility of CO<sub>2</sub>, O<sub>2</sub> and ethylene oxide gas in the 1, 2-PBD film surface, in view of the small gas diffusion coefficient of 1, 2-PBD measured by J.D. Ferry et al.<sup>(2)</sup>. From these fundamental physical properties and nontoxic in respect to food hydiene described previous paper <sup>(1)</sup>, the 1, 2-PBD will be suitable for food packaging materials. Because of its good gas permeability in this film, 1, 2-PBD is used, as the most superior application example, for stretched film as a wrapping for fresh vegetables, fruits and others.

#### APPLICATION TO EVA SPONGE FIELD

We have developed many kinds of cellular sponge instead of EVA sponge utilizing its rubber-like properties and reactivity with chemical reagents. The 1, 2-PBD sponge is superior to EVA in the following points.



*Photo I. Stretch film and pellets of syndiotactic 1,2-polybutadiene*



*Photo II. Some packaged fresh foods with syndiotactic 1,2-polybutadiene stretch film*



*Photo III. Various kinds of cellular sponge shoe soles made of syndiotactic 1,2-polybutadiene*

Table 1. Comparison of general physical properties of syndiotactic 1, 2-Polybutadiene (crystallinity: 25%,  $[\eta] = 1.3$ ) films and films of soft plastics commercially available.

Test item	Unit	Testing methods	JSR 1, 2-PBD		LDPE <sup>*</sup>	EVA <sup>**</sup>	Soft PVC <sup>***</sup>
			T-die extrusion	% inflation			
Density	g/cc		0.91	0.91	0.92	0.93	1.26
Film thickness	$\mu$		50	50	53	47	47
Tensile strength							
Machine direction	kg/cm <sup>2</sup>	JIS	180	200	170	175	250
Transverse direction		Z 1702	170	200	140	180	250
Elongation	%						
Machine direction		JIS	500	500	290	400	240
Transverse direction		Z 1702	710	570	410	560	240
Tear resistance							
Machine direction	kg/cm	JIS	97	78	13	15	58
Transverse direction		Z 1702	150	76	33	19	67
Friction angle			>70	>70	10	45	>70
Light transmittance	%	ASTM	91	91	80	88	91
		D 1003					
Haze	%	ASTM	1	1	14	6	1
		D 1003					
Gas permeability							
CO <sub>2</sub>	CC·0.1mm/ m <sup>2</sup> ·24 hrs· atm	ASTM	31,000	28,000	7,900	11,400	3,000
O <sub>2</sub>		D 1434	7,100	6,000	1,500	1,800	9,300
Ethyene oxide			320,000		20,900		
Water vapor permeability	g·0.1mm/ m <sup>2</sup> ·24 hrs.	JIS	110	98	25	45	100
Optimum heat-sealing temperature (2 kg/cm <sup>2</sup> , 2 sec)	°C		75~80	75~80	100	80~85	85~90

<sup>\*</sup> blow ratio = 2.5

<sup>\*\*</sup> blow ratio = 2.5, VAc. cont. 12%

<sup>\*\*\*</sup> blow ratio = 2.5, plastitizer 50%

- 1) The process requires only one step cure
- 2) Wide range adjustment of the expansion ratio is possible
- 3) Cell size of the sponge is uniform
- 4) High filler loading is possible
- 5) Compression set is smaller than EVA
- 6) Adhesion is easy
- 7) Performance coating with paint is good

In sponge production, 1, 2-PBD can be loaded with fillers and cured with sulfur, while EVA cannot be cured with sulfur, only with peroxide. Figure 3 shows the cure curves obtained with a JSR Curelasterometer using sulfur curing system. The cure rate of 1, 2-PBD is similar to that of SBR.

Considering that the cure agent of EVA is restricted only to peroxide, the 1, 2-PBD is also superior to EVA, as far as cure agent is concerned. Table 2 shows the results of the weatherability test qualitatively obtained with specimens prepared in accordance with some formulation. The cross-linking products of the 1, 2-PBD show excellent weatherability and ozone resistance like that of EPDM. This is surprising, considering its poor weatherability on non cross-linking products.

Some Japanese companies have developed cellular sponge into many kinds of shoe soles, as shown photograph III. Results from practical use have confirmed that these sponges have the same durability as rubber sponges.

#### APPLICATIONS IN THERMOSETTING RESIN FIELD

Firestone<sup>(3)</sup> has already reported that liquid 1, 2-PBD can be used for insulating materials like the usual thermosetting resins. Insulating materials of cured syndiotactic 1, 2-PBD plus fillers show as good properties as those of liquid 1, 2-PBD.

#### APPLICATION TO PHOTO-SENSITIVE POLYMER FIELD

Since 1, 2-PBD is easily cured by U.V. irradiation, it can be regarded as a photo-sensitive polymer. If a photo-sensitizer is added to 1, 2-PBD, the sensitivity of the compounds is similar to that of other commercial photo-polymers. Moreover, adding a cross-linking agent like diazid compound, the compound containing these three components indicates its superior sensitivity compared with other photo-sensitive polymers.

For example, adding 4% of photo-sensitizer (p, p'-tetramethyl-diamino-benzophenone) to the polymer, the 1, 2-PBD was cross-linked by U.V. irradiation (low pressure mercury lamp,

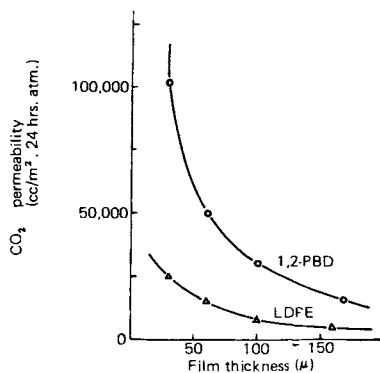


Figure 2. Relationship between film thickness and CO<sub>2</sub> gas permeability

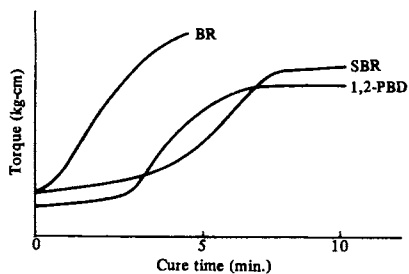


Figure 3. Cure curves obtained with JSR curelometer

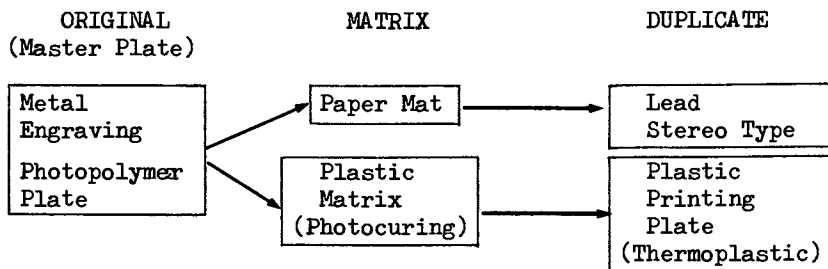
Table 2. Comparison between 1, 2-PBD and various rubbers in outdoor exposure weatherability test

Time of Exposure: one month in summer  
Location: Kobe City, Japan

	Outdoor Exposure Test Results	
	White stock formulation	Black stock formulation
Change in hardness	SBR > BR ≥ EPDM > 1,2-PBD	BR ≅ EPDM ≥ SBR > 1,2-PBD
Change in Tensile strength	SBR > EPDM ≫ BR ≅ 1,2-PBD	EPDM = SBR ≥ BR ≫ 1,2-PBD
Change in Elongation	BR ≥ SBR > 1,2-PBD ≅ EPDM	BR > 1,2-PBD ≅ EPDM ≥ SBR
Crack appearance (after 30 days' exposure)	BR > SBR > 1,2-PBD > EPDM (much) (little) (slight) (none)	SBR ≅ BR ≫ 1,2-PBD = EPDM (much) (little) (none) (none)
Change in color	BR ≥ SBR > EPDM > 1,2-PBD	

distance 5cm) and the exposed step numbers of the step tablet (21 steps) made by Kodak Co. for the purpose of measuring the photo-sensitivity put the 19th step at 30 sec. It is suggested that high photo-sensitivity of 1, 2-PBD makes useful it a photo-sensitive polymer.

A unique Plastic Matrix has been developed by Nippon Paint Co., utilizing the photo-sensitivity, the low softening temperature and the good flow property of 1, 2-PBD having 25% crystallinity. An ordinary letterpress plate system is shown in this schematic arrangement.



They wanted to improve the system for reasons of labor health conditions and environment, and considered that the lead printing plate should be changed to an other printing plate (for example, polypropylene). Therefore, it is necessary for the improvement that the paper mache matrix is changed to an other matrix by which any printing system could be produced. Some necessary conditions of the matrix are the reappearancivity of the relief images on the master plate, and the thermalstability when the relief images on the matrix are transcribed to the printing plate by press-molding. 1, 2-PBD having 25% crystallinity is a good reappearancivity of the relief images on the master plate, because of its high flow properties, but the thermal stability of 1, 2-PBD is no good at softening temperature of polypropylene. Considering that the thermal deformation temperature of cross-linking material is generally increased higher than that of non cross-linking material, they studied the improvement of the thermal deformation temperature to cross-link only surface of 1, 2-PBD. Their desired plastic matrix was completed by photo-curing the surface of 1, 2-PBD plate with U.V. irradiation.

Photograph IV shows that the plastic matrix before U.V. irradiation is lifted from the master plate. The matrix is impressed by a roller or hydraulic press onto these plates after the preheated 1, 2-PBD plate is placed on the master plate. Photograph V shows that the surface of 1, 2-PBD matrix is photo-cured by U.V. irradiation. Photograph VI shows that the relief





*Photo IV. The plastic matrix (1,2-PBD) before UV irradiation is lifted from the master plate*



*Photo V. The surface of the plastic matrix is photo-cured by UV irradiation*



*Photo VI. The relief images on the photo-cured matrix are transcribed to the printing plate (PP plate)*

Table 3. Effects of degraded 1, 2-polybutadiene fragments in soil on the growth of tomatoes

	No 1,2-PBD content	Containing 1,2-PBD			
		Soil A	Soil B	Soil C	Soil D
Loading level of degraded film fragments to the soil in a pot of 30cm diameter (about 7.51) (g)	0	1.14	5.70	11.40	17.10*
Equivalent quantity of degraded film fragments loaded per 10 ares of ground (depth of soil: 20cm volume of soil: 200m <sup>3</sup> ) (kg)	0	30	150	300	450
Height of Plants (cm)	12.5	10.4	12.8	14.2	13.8
Number of Leaves	4.9	4.6	5.0	5.8	6.0
Diameter of Stem (mm)	2.8	2.7	3.2	3.5	3.0
Weight of green plant (g)	8.0	7.8	8.7	9.0	8.5
upper part	2.2	2.0	2.8	2.8	3.0
lower part					
Weight of dried plant (g)	0.75	0.78	0.84	0.88	0.83
upper part	0.20	0.20	0.25	0.28	0.28
lower part					

Date of sowing: 5 October, 1971

Date of investigation: 15 November, 1971

Note (\*) When the film is used as a mulch once a year, the above loading level is equivalent to that of 20 years.

(by courtesy of Horticulture Department, Chiba University)

images on the photo-cured 1, 2-PBD matrix are transcribed to the printing plate by press-molding at the softening temperature of polypropylene. Many plastic printing plates can be molded, using this photo-curing matrix.

#### APPLICATION EXAMPLES AS A PHOTO-DEGRADABLE PLASTIC

When exposed to the sun, the molded products of 1, 2-PBD are changed to easily crushable form, because of the occurrence of hardening deterioration<sup>(4)</sup>. Consequently, the hard deteriorated 1, 2-PBD films are easily fragmented with but little force due to photodegradation. When the film is used as a mulching film, characteristics of the photodegradable 1, 2-PBD compare to other photodegradable plastics<sup>(5)</sup> which have lately been announced as follows:

- 1) Since 1, 2-PBD is not pulverized into powder after photodegradation, there is no possibility of secondary pollution by powdered dust.
- 2) When mixed into soil, the photodegraded 1, 2-PBD fragments give no adverse effect on vegetation and rather accelerate the growth of plants by improving drainage and aeration of the soil (Table 3).
- 3) Since the photodegraded 1, 2-PBD is not decomposed by numerous bacteria in soils of Chiba, Japan, it is suggested that there is no risk of high dimension pollutions.

However, the test results propose many problems concerning its utilization. The practical utility as a photodegradable plastic should be carefully studied to see what would be expected from it.

#### CONCLUSION

The New Thermoplastic Syndiotactic 1, 2-PBD developed by JSR, has been discussed in some applications, but the foregoing are several parts of our developed results. More detailed description will be given on another occasion.

JSR announced that the New Thermoplastic Syndiotactic 1, 2-PBD (JSR RB820 and JSR RB810) is put on sale, at the 18th of June. We expect cooperation from all industrial circles for further development of 1, 2-PBD utilization.

ACKNOWLEDGEMENTS

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## K-Resin BDS Polymer: A New Clear Impact-Resistant Polystyrene

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### Introduction

In the third quarter of 1972 Phillips Petroleum Company started up a new plant to produce a new family of styrene plastics known as K-Resin BDS polymer. The initial plant capacity was 10 MM pounds per year but this is presently being expanded. The resins are clear and tough and their moderate pricing places them between the low cost resins such as polystyrene, polyethylene and polypropylene which are either clear or tough (but not both) and high priced resins such as cellulosics, clear ABS and polycarbonate, which are both clear and tough. The exceptional clarity and impact resistance make them desirable replacements for conventional polystyrenes and other clear resins in many applications(1). Applications thus far realized are in toys, housewares storage units, lids, and a wide variety of packaging uses including blister packs, injection molded tubs, bottles, and boxes having integral hinges.

These resins are copolymers of styrene and butadiene prepared by a solution polymerization process. Presently two resins, which are designated KR01 and KR03, are produced. The primary difference between the two is in the molecular weight distribution, with the KR03 resin being the broader of the two.

### General Properties

The general physical properties of these resins are shown in Table I. It is apparent that the two resins are quite similar in properties except for hardness, impact strength and elongation. The KR03 resin is clearly the tougher resin, having a dart drop impact strength of 163 in-lbs compared to 20 for the KR01 resin. Its elongation of 100% is approximately 10 times the value for the KR01 resin. However, the KR03 resin is softer, having a Shore D hardness of 70 compared to 74 for the KR01 resin. These resins differ also in molecular weight distribution

with the KRO3 resin having a heterogeneity index of 2.1 compared to 1.3 for the KRO1 resin. Typical gel permeation chromatograms are shown in Figure 1. As would be expected, this difference is reflected in the flow properties of the resins relative to each other. This will be discussed later with processability.

TABLE I  
THE PROPERTIES OF K-RESIN POLYMERS

<u>Properties</u>	<u>ASTM Test</u>	<u>Resin Values</u>	
		<u>KRO1</u>	<u>KRO3</u>
Density, gm/cc	D792-66	1.01	1.04
Flow Rate, Cond. G, gm/10 min.	D1238-65T	8	6
Tensile Strength, .2"/min, psi	D638-68	4,000	4,000
Elongation, .2"/min, %	D638-68	10	100
Modulus of Elasticity, psi	D638-68	180,000	200,000
Flexural Modulus, psi	D790-66	240,000	225,000
Flexural Yield Strength, psi	D790-66	6800	6800
Heat Distortion Temp., 264 psi Fiber Stress, °F	D648-64T	168	160
Izod Impact, ft-lbs/in notch (0.125" specimen thickness)	D256-56	0.4	0.4
Falling Dart Impact, in/lbs	-	20	163
Hardness, Rockwell	D785	D75	D72
Hardness, Shore D	D2240	74	70
Vicat Softening Point, °F	D1525-65T	200	200
Light Transmission, 100 mil, %	D1746-62T	90-95	90-95
Haze, 100 mil, %	D1746-62T	1-5	1-5
Refractive Index, $d_{25}^{25}$	-	1.5743	1.5743
GPC Molecular Weight <sup>a</sup>			
$M_w$		179,000	217,000
$M_n$		132,000	106,000
H.I.		1.35	2.1

a - Measured on Waters Associates Model 100 with  $10^7$ ,  $10^5$ ,  $10^4$ ,  $10^3$  Å column array.

Appearance. Clarity and impact strength are the two properties which make these resins a valuable new development. The clarity, as measured by haze, is as good or better than any of the competitive commercial resins, and these resins are colorless. Some competitive materials such as cellulosic and SAN frequently have a bluish or yellowish cast. Impact polystyrenes, on the other hand, are opaque. The haze of the commercial production thus far realized has been consistently near one per cent, which puts it in a class with general purpose polystyrene. Table II summarizes data on appearance.

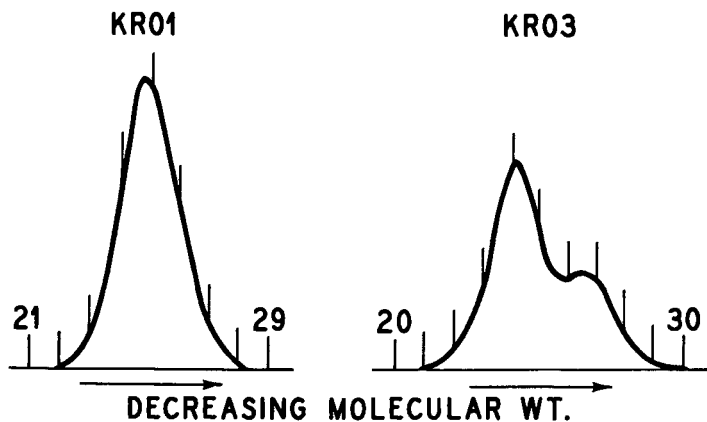


Figure 1. Gel permeation chromatograms of *k*-resin BDS polymers

TABLE II

A COMPARISON OF THE APPEARANCES OF VARIOUS RESINS

<u>Resin</u>	<u>Haze, % (ASTM D1746-62T)</u>	<u>Color</u>
K-Resin		
KR01	1-5	Water White
KR03	1-5	Water White
Polystyrene		
General Purpose	2-3	Water White
Medium Impact	Opaque	White
High Impact	Opaque	White
SAN	1.5	Yellowish
Cellulose Acetate	7.5	Bluish

Impact Strength. The polymers are notch sensitive and, therefore, the conventional notched Izod test cannot be used to determine their ultimate impact strength. In fact, by that test the impact strength is only comparable to general purpose polystyrene, but when measured by unnotched Izod or the falling dart test, the resins are substantially above general purpose polystyrene. Table III compares the impact strength of these resins with that of some competitive resins.

TABLE III  
A COMPARISON OF IMPACT STRENGTHS OF VARIOUS RESINS

<u>Resin</u>	<u>Izod Impact</u> <u>(ASTM D256-56)</u>		<u>Falling</u>	<u>Falling</u>
	<u>Notched,</u> <u>Ft-Lbs</u>	<u>Unnotched,</u> <u>Ft-Lbs</u>	<u>Dart</u> <u>Impact,</u> <u>In-Lbs</u>	<u>Ball</u> <u>Impact,</u> <u>Ft-Lbs</u>
K-Resin				
KRO1	0.4	5	20	0.2
KRO3	0.4	5	163	16.0
Polystyrene				
General Purpose	0.3	1.8	1	0.1
Medium Impact	0.9			0.7
High Impact	2.5			3.7
SAN	0.3	3.6	10	
Cellulose Acetate	2.8	37.5		

In order to obtain the ultimate impact strengths of these resins, they require orientation. A study of the impact strength of injection molded bowls illustrates this very well. Bowls were injection molded from twelve different polymers and then the impact strength was measured on various parts of the bowls. The mold gate was in the center of the bottom and was 0.213 inch in diameter. The polymer flowed through the gate into the bottom, which was 0.080 inch thick, and then out into the side (wall), which was 0.052 inch thick. The polymer in the walls was the most highly oriented, having flowed the farthest and having been sheared the most due to the ever decreasing thickness of the mold in the direction of flow. Table IV shows the impact strength of the various bowl sections. It is clear that on the sprue (lowest orientation), the impact strength was the lowest and on the sides (highest orientation), the impact strength was the greatest. In fact, even the resins which gave very low values (<10 in-lbs) on the bottoms gave high values (80 in-lbs) on the sides. It should be pointed out that the polymers used in this



study were developmental resins prepared with variations in the process which led to the non-uniformity in melt flows and impact strengths shown in the table. Resin from commercial production does not show such variation, but is consistently at the high impact end of the range.

TABLE IV  
THE IMPACT STRENGTH OF K-RESIN BOWLS

Melt Flow, @ 200 C g/10 Min	Falling Ball Impact on Bottom, Ft-Lbs	Falling Dart Impact, In-Lbs		
		Bottom on Sprue	Bottom on Edge	Sides
8.0	>16		>80	80
4.9	>16			80
5.4	>16	35	>80	>80
4.7	12.7	57		80
3.6	3.1	12		
5.2	1.8	<10		>80
5.0	1.3		57	80
6.1	1.2	<10		>80
4.7	1.2	<10		>80
6.4	0.74	<10	31	75
5.0	0.58	<10		71
5.2	-	<10		39

If an impact sample with low strength (the bottom of a bowl for instance) is impacted with a dart hard enough to deform but not break it, it can subsequently be impacted in the same spot at progressively higher forces without breaking. In fact, impact strengths of greater than 80 in-lbs can be reached by incremental increases of 10 in-lbs at each drop with samples that have an initial single drop strength of less than 10 in-lbs. This treatment is a crude form of cold-working and it causes stress-whitening of the sample, which indicates that orientation and/or crazing occur. Either or both of these effects would be expected to increase the impact strength of the sample.

Mechanical Properties. The most notable differences from polystyrene in mechanical properties are the lower tensile, flexural modulus, and hardness values and the higher elongation and flexural strength for the BDS resin. All of these differences are due to the presence of butadiene in the resin. In fact, the mechanical properties are similar to those for the

conventional impact polystyrenes, which also contain butadiene but are opaque. Table V shows a comparison of the mechanical properties of these resins with some competitive commercial resins.

The density of the resin, which is about 1.02 g/cc, coupled with its moderate price, yields a favorable cost-volume ratio in comparison to most of the other clear plastics.

Hinge Flex Life. An unusual and very interesting property of these resins is the flexural hinge life (see Table VI)(2). The KR01 resin is superior to the KR03 resin in this property, but both contrast strongly with polystyrene which cannot be flexed. Although the hinge life of these resins does not equal that of polypropylene, it is more than sufficient to make practical certain types of packaging units with integral hinges, such as boxes for pills, hardware and fishing lures, which receive limited opening and closing.

The hinge life is dependent upon the thickness of the hinge as shown in Table VI. Electron micrographs of KR01-type hinges before and after flexing indicate the morphology to be a random array of polybutadiene domains in a polystyrene matrix in the unflexed state. However, after flexing, the polybutadiene domains show some orientation with the appearance of fine light lines between the arrays of polybutadiene. These are thought to be microcracks which would account for the good lifetime in flexure of the resins. A similar mechanism is thought to account for toughening in rubber-modified polystyrene and, therefore, seems logical that it might apply here too.

Chemical Resistance. The chemical resistance of these resins is similar to that of polystyrene (see Table VII). The resins are soluble in or highly swollen by most organic solvents; however, the resins are not affected by methanol, ethanol, or aqueous solutions containing these alcohols. In fact, it has been reported that one manufacturer is packaging an alcohol-based product in a bottle made of these resins. The environmental stress crack resistance (ESCR) of the BDS resins is better than that of polystyrene, and KR03-type resin is better than KR01. However, the ESCR of these resins still limits the type of food products which can be packaged in them. In general, dry foods, meat products, and gelatin products may be packaged with no problems, but oily products such as butter and margarine may not. Unsaturated oils cause more rapid failure than saturated oils. The type of container also affects the ESCR - thermoformed containers crack much more quickly than injection molded. For instance, a thermoformed tub containing margarine cracks in a few days while an injection molded tub will last more than a month. Containers made from general purpose polystyrene failed in a few hours in the same test.

TABLE V  
A COMPARISON OF THE MECHANICAL PROPERTIES OF VARIOUS RESINS

<u>Resin</u>	<u>Density</u> (ASTM D792-66) <u>g/cc</u>	<u>Tensile</u> (ASTM D638-68) <u>psi</u>	<u>Elongation</u> (ASTM D638-68) <u>per cent</u>	<u>Flexural</u> <u>Modulus</u> (ASTM D790-66) <u>psi</u>	<u>Flexural</u> <u>Strength</u> (ASTM D790-66) <u>psi</u>	<u>Hardness</u> (ASTM D2240) <u>Shore D</u>
<u>K-Resin</u>						
KR01	1.01	4000	10	240,000	6800	74
KR03	1.04	4000	100	225,000	6800	70
<u>Polystyrene</u>						
General Purpose	1.05	7600	4	480,000	1000	86
Medium Impact	1.04	4400	32	390,000	5800	82
High Impact	1.04	2600	43	220,000	6800	74
<u>Cellulose Acetate</u>	1.20	7100	47	241,000	7800	80
SAN	1.08	6900	6	480,000	15,200	88

TABLE VI  
HINGE FLEX LIFE\* OF K-RESIN BDS POLYMER

<u>Resin</u>	<u>Hinge Thickness, in.</u>	<u>Number of Flexes</u>
GP Styrene	0.005	1
	0.010	1
KRO1	0.005	235
	0.010	564
	0.015	605
	0.020	535
	0.025	307
KRO3	0.005	145
	0.010	200
	0.015	188
	0.020	110
	0.025	59

\*Flexed 180° with 1.5 kg load on a Tinius Olsen Folding Endurance Tester.

TABLE VII  
CHEMICAL RESISTANCE OF K-RESIN BDS POLYMER

<u>Chemical</u>	<u>Dissolve</u>	<u>Soften</u>	<u>Permeates*</u>
<u>Organic Solvents</u>			
Hydrocarbons	X		
Ketones	X		
Esters	X		
Ethers	X		
Light Alcohols		X	X
Heavy Alcohols	X		
Glycols		X	X
<u>Oils</u>			
Mineral		X	X
Vegetable		X	X
<u>Water Based</u>			
Water			X
Dairy Products			X
Syrups			X
Detergents			X
Salt Solutions			X

\*Permeation of 3% per year or more.

### Processability

These resins are very easily processed. Their rheological properties are shown in Figure 2 and as would be expected on the basis of its broader molecular weight distribution, the KRO3-type resin has a much lower viscosity. The viscosities of the KRO1 and KRO3-type resins bracket those of general purpose polystyrene and cellulose propionate which are also shown in Figure 2. In addition, the shear responses of all four resins are quite similar. Therefore, processing techniques suitable for these other resins are generally suitable for the BDS resins. In general, their processing characteristics most closely resemble medium impact polystyrene. The KRO1 and KRO3-type resins exhibit very low die swell, low warpage and shrinkage comparable to that of general purpose polystyrene (KRO1 > GPPS > KRO3).

These resins are stable during processing and do not present any major difficulties. Since they contain both polybutadiene and polystyrene, degradation can occur by two mechanisms: (1) visbreaking of polystyrene and (2) crosslinking of polybutadiene. Since both processes are promoted by heat and shear, the shear-heat input during processing should be minimized. Experience has shown that the crosslinking of the polybutadiene segments predominates as the major form of degradation. Figure 3 shows spiral flow data for these resins. For the KRO1 resin, an unstable condition is reached somewhere between 218 and 232 C; whereas, the KRO3 resin becomes unstable somewhere between 232 and 260 C. This is probably due in part to the lower viscosity of the KRO3 resin which minimizes the effect of shear on the resin.

The toughness of these resins makes some processing techniques possible that cannot be used with some competitive resins such as SAN and general purpose polystyrene. Intricate injection molds and deep draws in thermoforming are two examples.

Extrusion(3). These resins have been extruded on equipment used for high density polyethylene, polystyrene and cellulose. Single and two stage screws may be used. Metering screws for PVC may be used because they are designed for low shear-heat generation. To assure the best possible appearance of the product, the following three procedures are used: (1) the resin is hopper dried since it is slightly hygroscopic and the presence of water causes streaking; (2) the equipment is kept scrupulously clean and the dies are kept free of nicks and scratches, since surface imperfections are accentuated by the high clarity of the resin; (3) slitting is done on the hot sheet to avoid edge cracking.

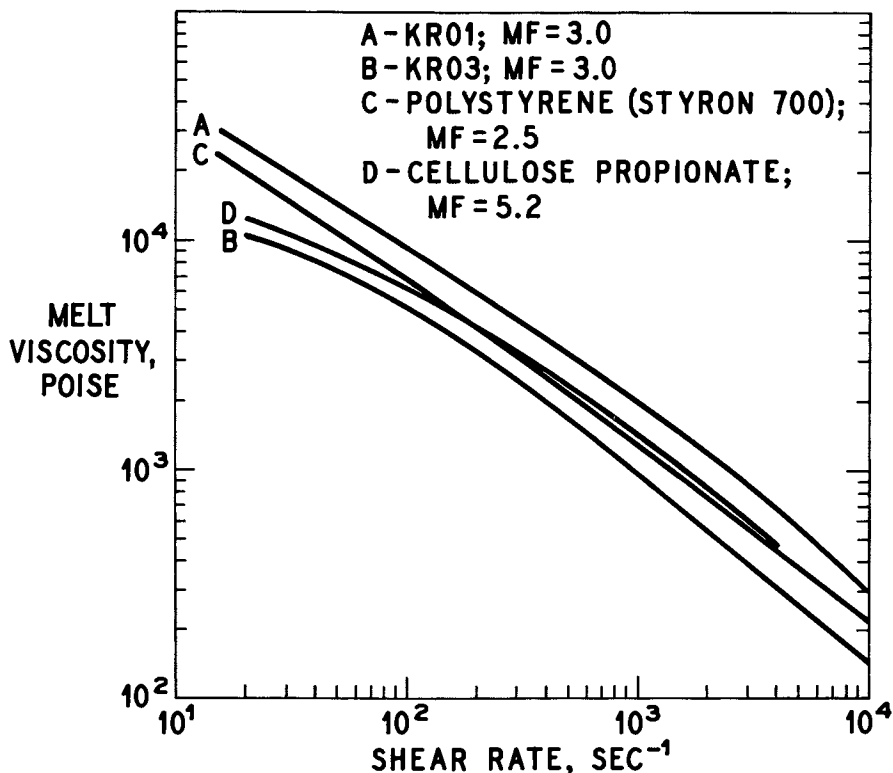


Figure 2. Rheological properties measured at 200°C (CIL data according to ASTM D1703-62)

Thermoforming. BDS Resins behave similarly to impact polystyrene in thermoforming, although a narrower temperature range (120-150 C) is used. Most thermoforming development work has been done on general purpose polystyrene equipment and in general any technique applicable to thermoplastic sheet can be used. Production rates of up to 20,000 parts/hour on multi-cavity machines have been achieved. Polished mold surfaces are a must for obtaining good clarity.

Blowmolding(4). Blowmolding equipment used for HDPE may be used with these resins with minor modifications to the dies and molds. Actually, PVC molds with low shrinkage allowances are more suitable than those for HDPE, because the shrinkage characteristics of these resins are similar to those for PVC.

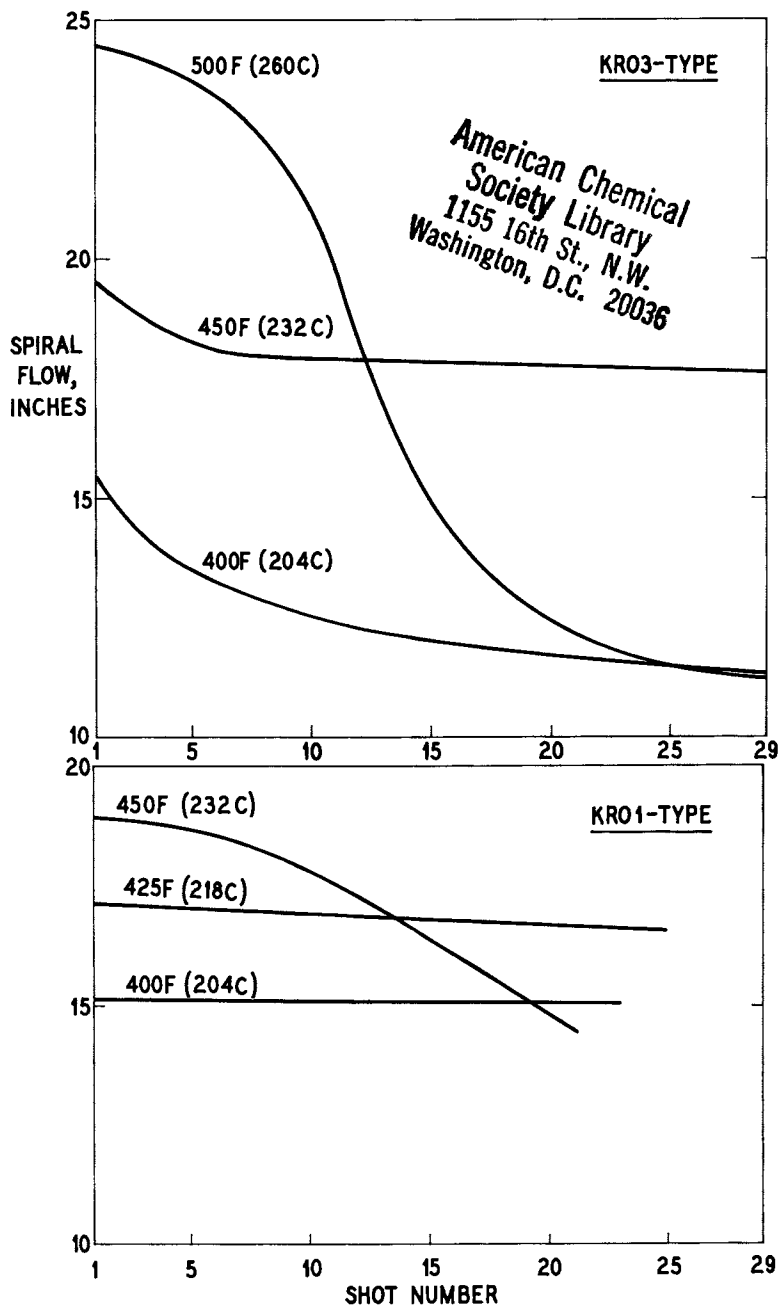


Figure 3. Spiral flow of k-resin polymers

Either reciprocating screw or continuous parison extrusion may be used. These resins have less diameter die swell than HDPE and have a higher melt temperature range (195-215 C).

Injection Molding(5). Injection molding conditions for these resins are similar to those for high impact polystyrene and polypropylene. A melt temperature of 218 C with mold cooling water at 10 C is recommended for the KRO1-type resin. The impact properties of the KRO3-type resin can be enhanced if the melt temperature is increased to 232 C and the mold cooling water to 38 C. At these conditions and using fast fills and high injection pressures, good properties can be obtained on relatively fast cycles. Molds made for general purpose polystyrene can be used and because of the toughness of these resins, many shapes unattainable with general purpose polystyrene can be made. Generally speaking, warpage is not a problem with KRO1 resin but uneven mold cooling may cause warpage in the KRO3 type resin.

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# Random Copolycarbonates: Characterization and Comparative Properties of Polymers Containing Tetrachlorinated Bisphenols

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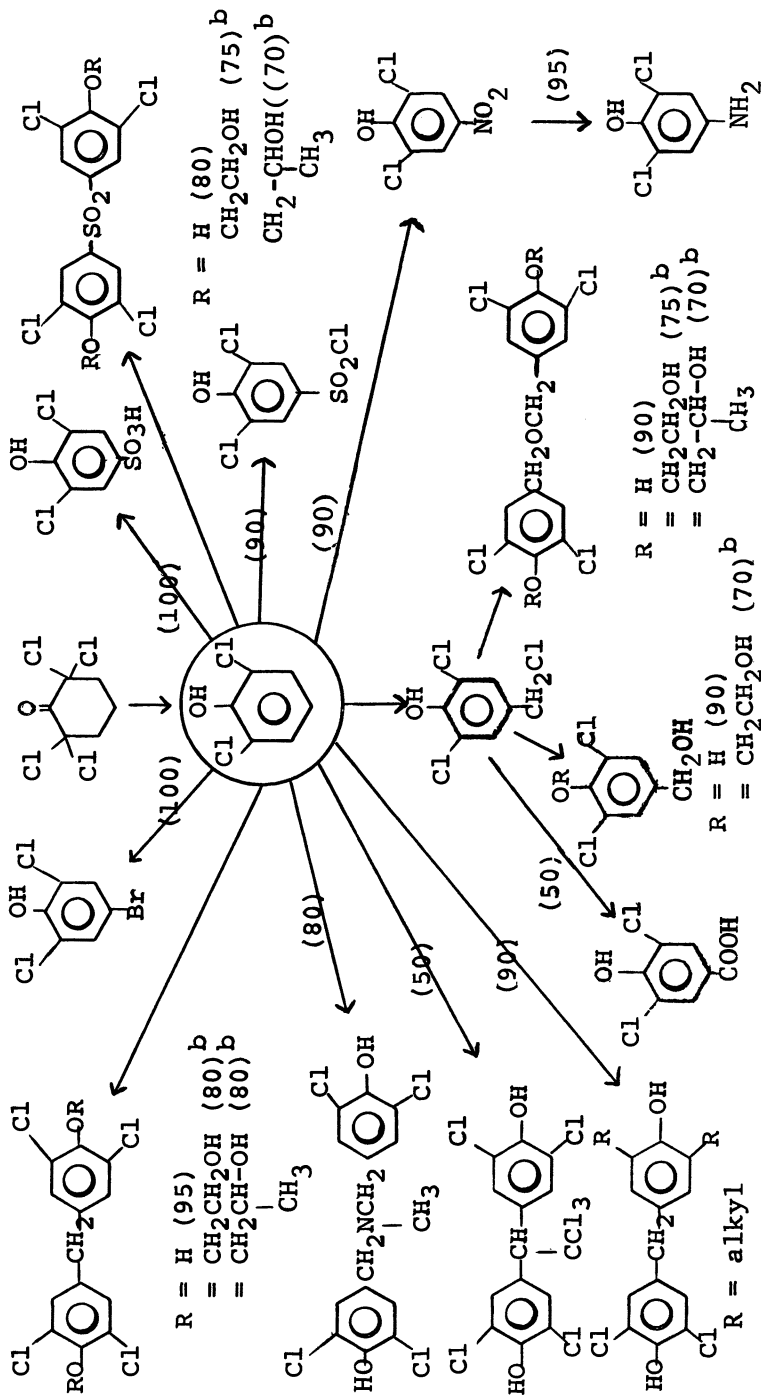
## Abstract

Several 2,2',6,6'-tetrachloro-4,4'-dihydroxy bisphenols were subjected to random copolymerization with bisphenol A at two levels of incorporation. Copolymerization of TCBF with isomeric chlorinated bisphenols was also carried out.

Original, as well as aged physicals, were obtained for all of the copolycarbonates except TCBF. The most interesting properties were obtained from copolymers of TCBF under the conditions studied. Copolymers containing TCBF possessed properties that in general were equal to or better than either bisphenol A or tetrachlorobisphenol A homopolycarbonates, e.g., the bisphenol A copolymer containing 70% TCBF was found to have a  $T_g$  of 190°C. This latter copolycarbonate, as well as that prepared from TCBF and a mixture of chlorinated isomers had significantly better stress cracking resistance to perchlorinated hydrocarbon solvents than either bisphenol A or tetrachlorobisphenol A homopolymers.

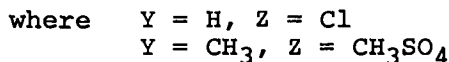
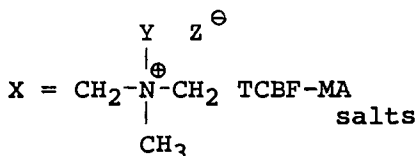
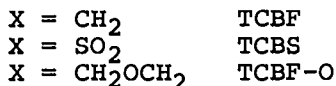
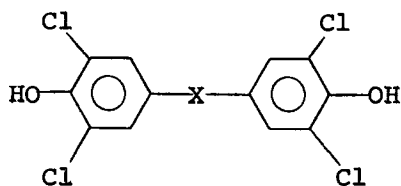
The recent discovery (1) of an improved synthesis of isomerically pure 2,6-dichlorophenol (2,6-DCP) in high yield from pyrolysis of 2,2,6,6-tetrachlorocyclohexanone inevitably led to the subsequent preparation of various monomers for use as building blocks in polymer synthesis; a representation of the type of intermediates possible is presented in Scheme I.

Several types of polymers based on 2,6-DCP and its derivatives have been previously prepared. These include polyphenylene oxides (2) from reaction of 2,6-dichloro-4-bromophenol, polysulfonates (3) based on 2,6-dichloro-4-benzene sulfonyl chloride, and polyesters (4) formed via condensation of 3,5-dichloro-4-

Scheme I. Intermediates based on 2,6-DCP<sup>a</sup>

hydroxybenzoic acid. More recently, poly(3,5-dichloro-4-methylenephénylene ether), a high temperature polymer based on 3,5-dichloro-4-hydroxybenzyl chloride, has also been synthesized and studied (5).

Foremost among the monomers prepared from 2,6-DCP, however, are the bisphenolic intermediates. Several of these, along with their appropriate chemical abbreviations, are illustrated below:



TCBF (6), TCBS (7) and TCBF-O (8) have been previously described; TCBF-MA and its salts, however, are new compositions.

A comparison of melting points of the above bisphenols to some which are more well known in the literature is presented in Table 1. Although melting points of monomers need bear no direct relationship to polymer morphology, they may with a knowledge of monomer structure, provide some insight concerning what may be expected in polymer systems in general. This is based on the thermodynamic equation,  $\Delta G_m = \Delta H_m - T \Delta S_m$ , which at the melting point leaves  $\Delta G_m = 0$ , since we have an equilibrium situation.  $T_m$  then is equal to  $\Delta H_m / \Delta S_m$ . If one assumes  $\Delta H_m$  to be constant for this series of compounds, the melting point will be a simple function of entropy change as the monomer proceeds from the solid to the liquid state (and vice-versa). Small entropy changes due to increased symmetry will result in higher  $T_m$ . One may then relate this to the ability of the molecules to pack together once incorporated in polymer chains and hence, make a priori predictions as to what to expect in such systems. While not foolproof, it is, nevertheless, a useful technique. From the melting point comparison, one may then predict that several of the new bisphenolic types will, if successfully incorporated,

impart significant crystalline character to both homopolymers and copolymers. This argument is further reinforced by steric (chlorine versus hydrogen) and polarity considerations which should tend to restrict rotation of the polymer chain and also, thereby, provide for higher Tg's.

TABLE I

Comparison of Melting Points for Various Bisphenols and Selected Derivatives

<u>Bisphenol</u>	<u>M.P., °C.</u>
TCBA <sup>a</sup>	130
TCBF-O	132
BA <sup>b</sup>	157
TBBA <sup>c</sup>	165
TCBF-MA	175
TCBF	195
TCBF-MA (DMS salt)	218
BS <sup>d</sup>	243-48
TCBF-MA (HCl salt)	245
TCBS	295

a Tetrachlorobisphenol A

b Bisphenol A

c Tetrabromobisphenol A

d Bisphenol S, Mixture of Isomers

Although the data concerning these polymers are quite limited, both TCBF and TCBS (as well as some of their appropriate derivatives) have been incorporated into thermoplastic and thermoset resin systems including polycarbonates (9,10,11), polysulfones (12), thermostable (aromatic) polyesters (13), alkyl polyesters (14), unsaturated polyesters (15,16) and epoxy resins (16).

While bisphenolic intermediates lend themselves in general to the preparation of several unique polymers, one of the more interesting from the standpoint of physical properties is the polycarbonate system based on bisphenol A. Although this polymer possesses many excellent characteristics, as for example, good dimensional stability and strength, good resistance to UV light, superior impact resistance, etc., it does suffer in the areas of susceptibility to stress cracking and chlorinated solvents (17,18). Polycarbonates, which are usually amorphous in nature, stress crack by an instantaneous crystallization mechanism (19).

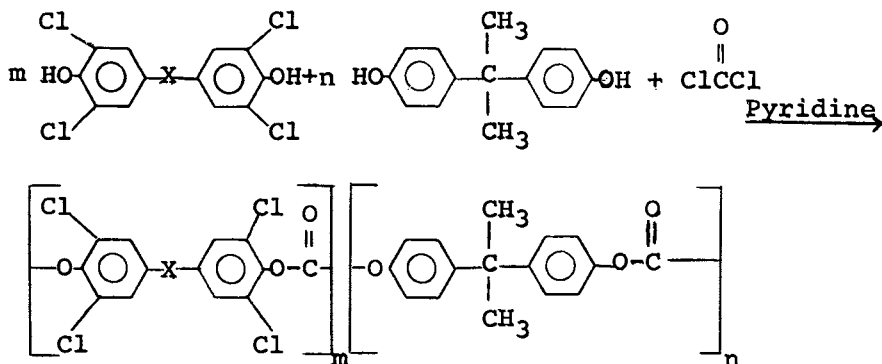
This is inherently due to an ordering of the low molecular weight polymer fractions which have a greater solubility in the diffusing solvent. As a result, very high shearing forces are created at the order-disorder interface leading to the formation of voids in the polymer. When the polymer is subjected to sufficient stress, the voids are thus allowed to propagate quite rapidly (and dramatically). As a result, use of bisphenols which would tend to impart more crystalline (and hence less soluble) character to the finished polymer, should allow for greater solvent and stress cracking resistance. (Less negative free energy for each of these two processes).

According to the literature, TCBF does not form useful polycarbonates due to excessive crystallinity in the polymer formed (20). The product polymer is of low molecular weight, exhibits melting points greater than 300°C. and is generally insoluble in most organic solvents. A proper use of the crystallinity inherent in this monomer by copolymerization with bisphenol A should allow for the formation of a copolycarbonate which performs significantly better in those properties in which bisphenol A homopolycarbonate is deficient, without seriously affecting most of its good properties. Impact resistance could be compromised, however. Copolymers in certain (preferred) concentration ranges should exhibit higher Tg's than bisphenol A homopolycarbonate and hence allow for a wider practical range of utility. Although copolymerization of TCBF and bisphenol A is not novel (9,10), essentially nothing has been published concerning the properties of such copolymers.

Stability of copolycarbonates of bisphenol A with both TCBS and TCBF-MA salts was held to be rather tenuous. Bisphenol S polycarbonate is approximately fifteen times less hydrolytically stable than bisphenol A homopolycarbonate (21). Chlorine substitution, as in the case of TCBS, however, could further decrease the stability of the system through an inductive effect (22), or enhance it through a steric effect to block hydrolysis (23). While it was not expected that the TCBF-MA salts would give premium polycarbonates because of the possible built-in instability due to the presence of the quaternary ammonium salt it was possible that this system could serve as a model, albeit crudely, for their potential utility in polymer systems. This was based on the partial steric inaccessibility of the ammonium salt grouping due to its being "buried" between the phenyl rings of the bisphenol. Suitable polymers incorporating these salts

(e.g., polyesters) could possess better dyeability and antistatic properties, as well as a stronger resistance to nonpolar solvents. Besides a possible sensitivity to acid, the characteristics of TCBF-O copolycarbonates with bisphenol A were not as predictable.

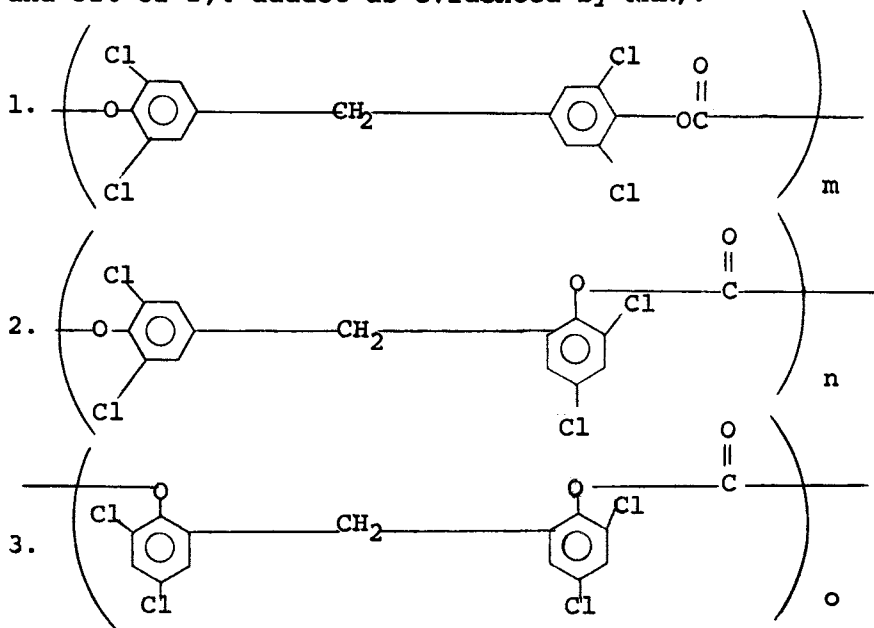
From this background, synthesis of copolymers of the various chlorinated bisphenols with bisphenol A was carried out at both high and low levels of incorporation in order to obtain a clearer overall assessment of their physical properties. In all cases, random copolymerization with bisphenol A was attempted via solution polymerization with phosgene in the presence of pyridine catalyst.



Copolymer	Low, % BA	High, % BA
BA + TCBF	30	70
BA + TCBS	30	70
BA + TCBF-O	30	70
BA + TCBF-MA salts	90	95

The excessive crystallinity in 4,4'-methylene bisphenols also lends itself to modification by another method, viz., disruption of the polymer chain with isomeric bisphenols in order to diminish symmetry and hence produce a workable, useful, polycarbonate. While employment of this technique with 4,4'-dihydroxydiphenyl methane (BF) was previously found to produce workable copolymers, they were not useful because of low glass transition temperatures (20). Other physical properties of the polymer were quite good, however. Use of the chlorinated analogs should produce respectable polymers possessing more reasonable Tg's. Although preparation of such a copolymer can be achieved

in several ways, only one formulation, namely that making use of a 50:50 mixture of pure 3,3',5,5'-tetrachloro-4,4'-dihydroxydiphenyl methane and a mixture of isomeric tetrachlorodihydroxydiphenyl methanes, prepared from the reaction of equal parts of 2,6- and 2,4-dichlorophenol with formaldehyde, was actually used in this study. (The reaction of the two phenols yielded product bisphenol containing 48% of 2,6-adduct and 52% of 2,4-adduct as evidenced by NMR).



### Polymer Synthesis and Characterization

Except in the case of the copolycarbonate of bisphenol A with the DMS salt of TCBF-MA, all polycarbonates and copolycarbonates were prepared via a recently published method making use of pyridine as catalyst and tetrahydrofuran as solvent (24). Due to insolubility of the dimethyl sulfate salt of TCBF-MA in THF, an older, but less convenient approach, making use of pyridine as both solvent and catalyst had to be employed (17,18).

The THF employed was dried and distilled over LiAlH<sub>4</sub>; pyridine was dried and distilled over potassium hydroxide. Bisphenol A was recrystallized from toluene (250 g/300 ml) to a melting point of at least 157°C.

Purification of phosgene was accomplished by bubbling the gas stream through concentrated sulfuric acid prior to addition to the reaction solution.

Commercially available bisphenol A polycarbonate (molding, extrusion grade—from General Electric Co., MW = 30,000) was used as external standard. To ensure proper application of the experimental method, bisphenol A polycarbonate was independently synthesized for comparative purposes.

Viscosity and gel permeation chromatography were used to monitor comparative molecular weight. Since instability of polycarbonates can be a serious problem, the polymers prepared in this study were checked in three ways: 1) testing with  $\text{AgNO}_3$  solution for free chloride ion, 2) monitoring of immediately precipitated polymer viscosity with that of polymer kept in solution overnight and then precipitated (conditions conducive to degradation in presence of amine or amine salt), 3) monitoring of polymer viscosity several weeks after precipitation. All of the polycarbonate samples used in the testing phase of this program gave negative results in the  $\text{AgNO}_3$  tests and showed no change in the differential viscosity studies; any breakdown of polymer in testing would thus be due to the polymer structure itself and not the presence of catalyst impurities. Degradation of the polycarbonate by chlorocarbonate end groups was obviated by end-capping with phenol after the polymerization was complete. All of the polycarbonates prepared for this study contained no additives. The content of the experimental polycarbonates was monitored either by NMR or % chlorine content. Basic physical data for the polymers prepared is presented in Table II.

### Physical Testing

Thin films (2 to 4 mils in thickness) were used for the majority of physical testing. All were heated at  $110^\circ\text{C}$ . for 1 week prior to testing to remove solvent. Polycarbonate films were cast from 20% solutions in methylene chloride. Molded pieces used to test stress cracking were molded at 450 to  $550^\circ\text{F}$ . and 10,000 psi.

Thin films of the polymers were subjected to tensile strength measurements making use of an Instron tester (minimum of 4 specimens per test). The initial tensile strengths observed served as a base to monitor degradation in films which were subjected to heat aging at 130 and  $160^\circ\text{C}$ ., hydrolysis testing at  $100^\circ\text{C}$ . and 95% R.H., UV aging at r.t., acid ( $\text{HCl}$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{HNO}_3$ —all as 20% solutions in water) and base ( $\text{NaOH}$ ,  $\text{NH}_4\text{OH}$ —



TABLE II  
 Basic Physical Data on Experimental Polycarbonates

Polycarbonate	$\bar{M}_w^a$	$\bar{M}_n^a$	$\bar{M}_w/\bar{M}_n^a$	% BA <sup>b</sup>	$\eta_{rel.}^c$
BA <sup>d</sup>	32,000	15,000	2.13	100	1.26
TCBA	-	-	-	-	1.45
30%TCBA/70%BA	-	-	-	70	1.25
70%TCBA/30%BA	-	-	-	32	1.26
30%TCBF/70%BA	40,000	22,000	2.05	72	1.27
70%TCBF/30%BA	45,000	21,000	2.39	35	1.28
30%TCBF-O/70%BA	35,600	16,000	2.25	67	1.26
70%TCBF-O/30%BA	-	-	-	36	1.27
Mixed TCBF (50:50)	54,200	17,000	3.15	-	1.21
5%TCBF-MA (DMS salt)	-	-	-	94	1.18
95%BA	-	-	-	94	1.26
5%TCBF-MA (HCl salt)	-	-	-	-	-
95%BA	-	-	-	-	-
10%TCBF-MA (HCl salt)	31,000	16,000	1.95	87	1.28
90%BA	-	-	-	-	-

a) Polystyrene used as molecular weight reference. An estimate of molecular wt. equal to 25 per angstrom was used.

b) NMR and elemental analysis.

c) 25°C., CH<sub>2</sub>Cl<sub>2</sub>, all solutions equal to 0.5% polymer and 99.5% solvent.

d) Low molecular weight peak (~2000) due to stabilizer not included in molecular wt. calculations.

as 5 and 20% solutions in water) resistance testing at r.t., stress cracking resistance testing (carbon tetrachloride, acetone and xylene at r.t., and finally solvent resistance testing in 22 common solvents (carbon tetrachloride, acetic acid, acetonitrile, ethyl ether, methanol, ethanol, hexane, cyclohexane, ethyl acetate, anisole, diphenyl ether, dioxane, chlorobenzene, nitrobenzene, chloroform, benzene, toluene, sym-tetrachloroethane, acetone, dimethyl formamide, cyclohexanone and epichlorohydrin), all at r.t.

### Results and Discussion

Polymerization of TCBF, TCBF-O and TCBF-MA (HCl salt) all proved successful at their respective high and low levels of incorporation with bisphenol A. The dimethyl sulfate salt of TCBF-MA was only successfully polymerized at the 5% level. Use of TCBS in a copolymer system was shown to be impossible due to the instability of the carbonate link. Commercial bisphenol A polycarbonate (MW = 30,000) was used as the external standard in this study. Homopolycarbonates of both bisphenol A and TCBA (3,3',5,5'-tetrachlorodiphenyl-2,2-propane) were independently synthesized as internal standards.

As a further control, copolymers of bisphenol A and TCBA were also polymerized to the proper molecular weight and the fact and extent of copolymerization was determined by NMR. All homopolycarbonates and copolycarbonates with the exception of the TCBA homopolymer were of comparable molecular weight (MW=30 to 45,000).

TCBF and Mixed TCBF Copolymers. Polymers incorporating TCBF at both levels as well as the mixed TCBF copolymers proved to be superior to bisphenol A homopolymer in practically every respect studied. Comparative testing results are presented in Table III.

It can be readily seen from the data in Table III that TCBF copolymers are superior to the bisphenol A homopolycarbonate in tensile yield strength, glass transition temperatures, hydrolytic resistance, thermal resistance at 130 and 160°C., resistance to UV light, base resistance, solvent resistance, and solvent stress cracking resistance. Copolymers at both high and low levels of TCBF were comparable to each other in hydrolysis resistance, UV resistance and thermal resistance at 130 and 160°C.; the 70% TCBF copolymer, however, was superior to the 30% TCBF copolymer in glass transition temperature, tensile

TABLE III  
COMPARATIVE TESTING RESULTS OF TCBF, TCBF-O, AND MIXED  
TCBF MODIFIED COPOLYCARBONATES VERSUS BA AND TCBA POLYCARBONATES

	TCBF		TCBF-O		MIXED TCBF	TCBA	
	30%	70%	30%	70%		30%	70%
MP, ° C.	230	255	205	199	270	265	100%
TG, ° C. <sup>(a)</sup>	155	190	140	-	150	-	180
Tensile Yield	11,500	13,000	9000	10,000	11,000	12,500	12,500
Hydrol. Resist. <sup>(b,c)</sup>	85%	75%	84%	80%	100%	75%	100%
UV Resist. <sup>(b,d)</sup>	96%	90%	33%	5%	100%	75%	95%
Thermal 130°C. <sup>(e)</sup>	96%	91%	66%	-	100%	76%	100%
Thermal 160°C. <sup>(f)</sup>	96%	100%	-	-	92%	84%	93%
Acid Resist. <sup>(g)</sup>	Good	Good	Good	Good	Good	Good	Good
Base Resist. <sup>(g)</sup>	Better	Better	Better	Better	Better	Better	Better
Solvent Resist. <sup>(h)</sup>	Better	Best	Better	Better	Best	Good	Best
Opt. Clarity	Trans-parent	Trans-parent	Trans-parent	Trans-parent	Trans-parent	Trans-parent	Trans-parent
Density <sup>(i)</sup>	1.20	1.40	1.30	1.40	1.49	1.37	1.40
Stress Cracking Resist. (CCl <sub>4</sub> )	Good	Better	None	None	Best	None	None

a) Measurements obtained via DTA.

b) % of original tensile yield remaining after timed exposure.

c) 95% R.H. at 100°C. for 10 days.

d) r.t. for 4 weeks, UV light suspended 10 inches above samples placed on a turntable.

e) 4 weeks.

f) 10 days.

g) r.t. for 2 weeks.

h) r.t. for 24 hours.

i) 25°C.

yield, resistance to sodium hydroxide, solvent resistance and solvent stress cracking resistance.

In general, not a great deal of difference was noted between the TCBF copolymers and either homopolymer or copolymers of TCBA in a direct comparison of the results obtained in the heat aging and hydrolytic resistance testing in neutral and basic media. With the exception of the 30% TCBA copolymer, the same was essentially true for the polycarbonates subjected to UV aging as well. Of all the polymers tested only the mixed TCBF copolymer showed some resistance to attack by ammonium hydroxide. The 70% TCBF copolymer possessed the highest glass transition temperature (190°C.) of any of the polycarbonates studied.

Solvent resistance was measured in 22 solvent systems. In 18 of these, the bisphenol A polymer and TCBF copolycarbonates behaved similarly. In 3 of them, viz., carbon tetrachloride, acetic acid, and acetonitrile, the TCBF copolycarbonates were definitely better. In only one case, namely that of ethyl acetate, was bisphenol A polycarbonate superior. While the TCBF copolymers and TCBA homopolymers were equally resistant to carbon tetrachloride, the TCBA copolymers were definitely inferior. Resistance to acetic acid was best accomplished with the TCBF copolymers. Both the mixed TCBF copolycarbonate and TCBA homopolycarbonate showed by far the best resistance to acetonitrile solvent.

Stress cracking resistance was measured qualitatively on both films and molded pieces of identical thickness under equal stress using carbon tetrachloride, acetone and xylene. With carbon tetrachloride as solvent, the bisphenol A and TCBA homopolymers and the TCBA copolymers all cracked immediately; the mixed TCBF and 70% TCBF copolymers, however, showed a definite resistance to stress cracking under these conditions. The 30% TCBF copolymer film did stress crack, but significantly less easily. Molded pieces of both the 30 and 70% TCBF copolycarbonates (1/8 inch thickness) showed stress cracking resistance to carbon tetrachloride under moderate stress; the mixed TCBF copolycarbonate did not crack even under strong stress. Molded pieces of all the other polycarbonates prepared cracked immediately upon exposure to carbon tetrachloride. Acetone and xylene were found to indiscriminately attack both stressed films and molded pieces of all the polycarbonates tested.

TCBF-O Copolymers. The 30 and 70% TCBF-O

copolycarbonates were superior to bisphenol A homopolycarbonate in tensile yield strength, hydrolysis resistance, resistance to base, and solvent resistance. They were inferior to it, however, in glass transition temperature, thermal stability at 130 and 160°C., and UV resistance. In 18 of the 22 solvents studied, the BA homopolymer and TCBF-O copolycarbonates seemed to behave similarly. The TCBF-O polycarbonates were also shown to be superior to BA homopolymer in carbon tetrachloride, acetic acid, and acetone. Only in the case of acetic acid, however, was the solvent resistance close to that exhibited by the TCBF copolymers. In the case of ethyl acetate, BA homopolycarbonate was better. Stress cracking resistance was negligible. In most cases, the TCBF-O copolymers were inferior to the TCBA polycarbonates.

TCBF-MA Copolymers. These copolymers were shown to be highly inferior to all other tested polycarbonates in practically every respect. The amine salt apparently does, indeed, serve to help degrade the polymer with time.

### Conclusions

Polycarbonates containing TCBF possess several interesting properties. In essentially all of the tests carried out, these polymers were found to be significantly better than bisphenol A homopolycarbonate. While the three TCBA-containing polycarbonates were equal to TCBF copolycarbonates in many respects, they were found to be inferior in glass transition temperature (70% TCBF) and stress cracking resistance in the presence of perchlorohydrocarbons. On an equal basis of 30% incorporation with bisphenol A, TCBF gave better UV resistance than TCBA. Finally, only the mixed TCBF polymer showed some degree of resistance to ammonium hydroxide.

More generally, this study shows how modification of polymers with TCBF may be achieved so as to extend their range of utility while not sacrificing some of their other key properties. Since the compositions studied were not optimized, systems possessing even better properties are quite likely.

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# Polyethersulphone—A New High Temperature Engineering Thermoplastic

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## Introduction

The polysulphones are a family of engineering thermoplastics (1) and in some cases can be used continuously under loadbearing conditions to temperatures in excess of 400°F. They are tough, rigid materials of high thermal stability and can be converted into products particularly by injection moulding or extrusion techniques. This paper outlines the technical development of the polysulphones; and the methods available for their synthesis; it also provides an appreciation of structural considerations, and an appraisal of the properties, processing characteristics and application areas for Polyethersulphone, the polysulphone made by ICI.

The search for thermoplastic materials which can be used for long periods at 300°F and above led logically to polymers composed of linked aromatic rings, since high thermal and oxidative stability would be expected from polymers of this structure (2). The aim was to select these links so that good stability would be retained, and the polymer backbone would be sufficiently flexible to show thermoplasticity below the decomposition temperature but well above 300°F. The sulphone linkage was investigated because the stability of the diaryl sulphones was well known, but it became evident that a polymer chain consisting only of phenylene groups linked via sulphone groups, ie poly(phenylenesulphone) was too rigid to show thermoplasticity (3). Fortunately the synthetic procedures devised for preparing high polymer containing aryl sulphone linkages as the main structural feature led inevitably to the inclusion of other more flexible chain bonds, particularly ether linkages (4,5,6).

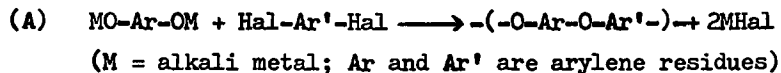
Routes to aromatic polysulphones were discovered independently and almost simultaneously in the early 1960's in the laboratories of the 3M Corporation (5) and Union Carbide Corporation (6) in the USA and at the Plastics Division of ICI in the UK (4). All three companies have since commercialised their discoveries. In 1965 Union Carbide introduced 'Udel' Polysulfone which is rated to have a continuous use temp-

erature of 300°F and an upper maximum use temperature of 340°F, and yet can be fabricated easily on conventional equipment. By contrast 3M's introduced their 'Astrel' Polyarylsulphone in 1967, which is an especially high performance material claimed to be capable of use up to 500°F. Although still classified as a thermoplastic 'Astrel' is generally considered rather difficult to process and often requires specialised equipment with extra heating and pressure capabilities. More recently, in 1972 ICI started development marketing of a family of Polyethersulphones in the UK and Europe, and during the past few months our US operating company ICI America Inc has started assessing market prospects in the USA prior to a decision to build a commercial plant. Resin is available on an imported basis at present and ICI America Inc is actively investigating the opportunities for a domestic manufacturing operation. Polyethersulphone can be used up to 400°F, and has a temperature performance between that of the Union Carbide and 3M's polysulphones, and yet can be processed on entirely conventional moulding or extrusion equipment. The structure of these polysulphones are shown in Fig 1.

#### Synthetic Procedures for Making Polyarylsulphones

A priori, there are two possibilities for synthesising the polyarylene sulphones. Either a polyether synthesis could be used to join up the aryl sulphone intermediates with ether linkages or a polysulphonylation process employed to link up aryl ethers. In practice either method can be used and will give polymers of high molecular weight provided that the intermediates are selected within certain structural limitations and the reaction conditions are closely controlled. The methods are quite different chemically and a polymer structure made by one route cannot usually be made by the other, although some structures can be made by either process.

Polyetherification - A polyether synthesis according to equation (A) was first described by Union Carbide Corporation (6). In this process ether bonds



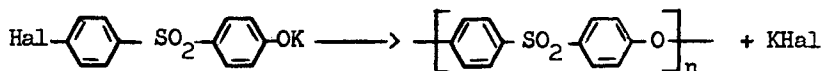
are formed via displacement of halogen by phenoxide anions with removal of the halogen as alkali metal halide and, to obtain polysulphones, one or both of the arylene residues must contain the sulphone group. In fact the sulphone group is an essential constituent of the dihalide, as it plays a vital part in the reaction by activating the halogens to attack by the phenoxides. Aromatic halides which do not contain powerful electron-with-



Figure 1. Structures of polysulphones

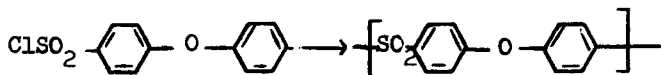
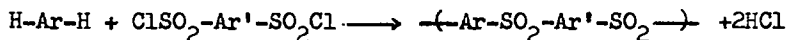
PRODUCT	POLYMER REPEAT UNIT(S)	SOFTENING BEHAVIOUR
"Astrel" 360 (3M Corp)	$\text{--} \left[ \text{--} \text{C}_6\text{H}_4 \text{--} \text{SO}_2 \text{--} \right] \text{--}$ and $\text{--} \left[ \text{--} \text{C}_6\text{H}_4 \text{--} \text{O--} \text{C}_6\text{H}_4 \text{--} \text{SO}_2 \text{--} \right] \text{--}$ first unit predominates	Tg 550°F injection moulds in specially modified machines.
Polyethersulphone 720P (ICI)	$\text{--} \left[ \text{--} \text{C}_6\text{H}_4 \text{--} \text{SO}_2 \text{--} \right] \text{--}$ $\text{--} \left[ \text{--} \text{C}_6\text{H}_4 \text{--} \text{O--} \text{C}_6\text{H}_4 \text{--} \text{SO}_2 \text{--} \right] \text{--}$ second unit predominates	Tg 490°F; injection moulds with some difficulty in conventional equipment
Polyethersulphone 200P (ICI)	$\text{--} \left[ \text{--} \text{C}_6\text{H}_4 \text{--} \text{O--} \text{C}_6\text{H}_4 \text{--} \text{SO}_2 \text{--} \right] \text{--}$	Tg 446°F injection moulds in conventional equipment
"Udel" Polysulfone (Union Carbide Corporation)	$\text{--} \left[ \text{--} \text{C}_6\text{H}_4 \text{--} \text{CMe}_2 \text{--} \text{C}_6\text{H}_4 \text{--} \text{O--} \text{C}_6\text{H}_4 \text{--} \text{SO}_2 \text{--} \text{C}_6\text{H}_4 \text{--} \text{O--} \right] \text{--}$	Tg 375°F injection moulds in conventional equipment

drawing groups like sulphone are unreactive and, in the absence of such groups, the reaction is not suitable for the synthesis of high polymers. The polycondensation reactions can be performed in dimethyl sulphoxide or sulpholane and the dipolar aprotic solvent plays an important part in the reaction as it dissolves both the reactants and the polymers and also gives a greatly enhanced rate of reaction (8). Both of the functional groups required for the polyether synthesis can be included in a single polycondensation intermediate. For example:



These intermediates polycondense rapidly on melting and polymers of high molecular weight can be obtained using the intermediates such as the potassium 4-(4-chlorophenylsulphonyl)phenoxide.

Polysulphonylation - The second important route to polyarylsulphones is a polysulphonylation process in which sulphone linkages are formed by reaction of arylsulphonyl chlorides with aromatic nuclei (4).



This is a typical electrophilic aromatic substitution in which the aromatic substrate is attacked by some form of the arylsulphonylium cation and hydrogen displaced as a proton. The attacking reagent is formed by interaction of the sulphonyl chloride with a Friedel Crafts catalyst; the catalyst should be selected from  $\text{FeCl}_3$ ,  $\text{SbCl}_5$  or  $\text{InCl}_3$  since with these halides only catalytic quantities are required, in contrast to the equimolar quantities usually recommended for Friedel Crafts condensations with acid halides (9). This choice of catalyst is important as it eliminates side reactions and helps considerably with the problem of catalyst removal from the polymers.

Polysulphonylation can be carried out either in the melt or in solution and both functional groups can also be built into a single intermediate.

### Effect of Structure

The toughness of the polysulphones is very dependent on structure (10) and is easily spoilt by the inclusion of bulky side groups or by departing substantially from all para-orientation of groups forming the links between aromatic rings (Fig 2).

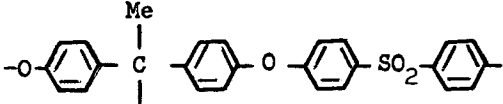
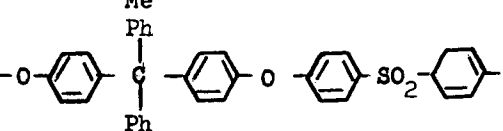
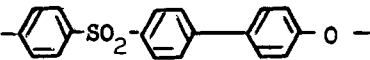
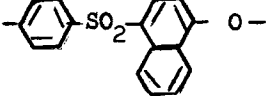
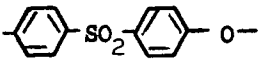
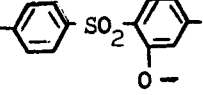
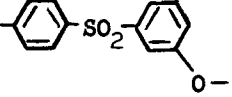
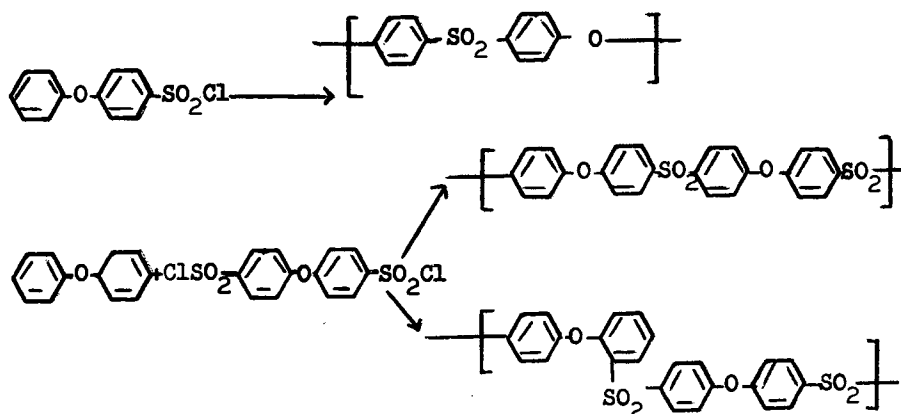
STRUCTURE	IMPACT BEHAVIOUR
 <p style="text-align: center;">Me   -O-C-   Me</p>	Tough
 <p style="text-align: center;">Me   -O-C-   Ph</p>	Brittle
	Tough
	Brittle
	Tough
	Brittle
	Brittle

Figure 2. Effect of structure on impact behavior

The effect of deviation from the all para-structure is very marked, and is discernible when a small proportion of the all para-repeat units are replaced by ortho/para ones (Fig 3). Fig 3 show the results of impact tests performed on a series of copoly-(ethersulphones) in which the proportion of ortho/para-repeat units varied from zero to 50%. The all para-homopolymer is a tough material, specimens of which do not break in a Charpy type impact test unless they are notched to make the test more severe. However, the copolymers become increasingly more brittle as the proportion of ortho/para-repeat units is increased, and are brittle unnotched if the proportion of these units is 20% or more. This effect was first noticed when testing polyethersulphones prepared by the polysulphonylation reactions; the virtually 'all para' polymer made from the monosulphonyl chloride gave specimens which required notching before they would break whereas polymer from the disulphonyl chloride/diphenyl ether system which was shown by nmr examination to contain 10-20% of ortho/para repeat units, gave specimens which were brittle unnotched.



The data in Fig 3 show that the presence of ca 20% of ortho/para-repeats is sufficient to account for this marked change in toughness, but the presence of branched chains in the product from the disulphonyl chloride/diphenyl ether system could be a contributing factor.

A copolymer containing 50% of ortho/para repeats has a low impact strength and breaks before yielding in a tensile test at any temperature up to  $T_g$ ; this behaviour is in marked contrast with that of the 'all-para'-homopolymer which yields in tensile tests at all temperatures from  $T_g$  down to  $-112^\circ\text{F}$ . The brittleness shown by the 50% ortho/para-copolymer ruins its performance in a creep test conducted at  $300^\circ\text{F}$  where the specimen fails in a brittle fashion after 1 hour, before it has had time to creep.

### The Temperature Performance of Polysulphones

To put the temperature performance of the polysulphone family into perspective and to see how the polysulphones fit into the spectrum of engineering thermoplastics; consider Fig 4 (11). This diagram shows the accepted limits of temperature to which various thermoplastics can be used continuously whilst still retaining a good proportion of their useful properties. Some of these materials have satisfactory mechanical and electrical properties to higher temperatures than those indicated, particularly when reinforced with glass, but lifetimes at these temperatures tend to be short. Broadly speaking, for applications requiring continuous use above 280°F which is considered just about the upper limit for the polycarbonates and PTMT's, polysulphones are some of the few thermoplastic materials that can be considered.

There are of course many plastics materials which have better high temperature performances than the polysulphones, for example the polyimides and fluorocarbon polymers, but most of these materials are thermosetting resins and all require somewhat specialised techniques for handling; eg sintering or thin layer coating techniques (12).

The remainder of this paper will be confined to the properties, processing characteristics, and applications of the polyethersulphones (PES) of which there are already four different grades available each with significantly different properties. Unless otherwise stated all the data subsequently presented refers to the standard grade of PES (300P).

### Mechanical Properties

Creep Behaviour - The more important mechanical properties of PES are now summarised (13). Fig 5 illustrates two examples of the effect of a continuous loading on PES at ambient temperatures, and shows that for a loading of 2900 psi a strain of 1% is produced after a 3 year period and that with the very high stress of 6500 psi a strain of only 2.6% results after this loading time. This very low rate of creep, which is coupled with a good resistance to failure by static fatigue, makes PES superior in these respects to any other unfilled thermoplastics so far investigated in the laboratories of ICI.

The creep performance of PES at 300°F is shown in Fig 6. At this temperature an applied stress of 1450 psi produces a strain of 1% after 3 years and that a strain approaching 2.5% is produced by an applied stress of 2900 psi. The creep of PES at 300°F is less than the creep of many other engineering plastics materials at room temperature. Although its load-bearing capability is reduced above 300°F, PES can still be considered for loadbearing applications up to 360°F. PES has a

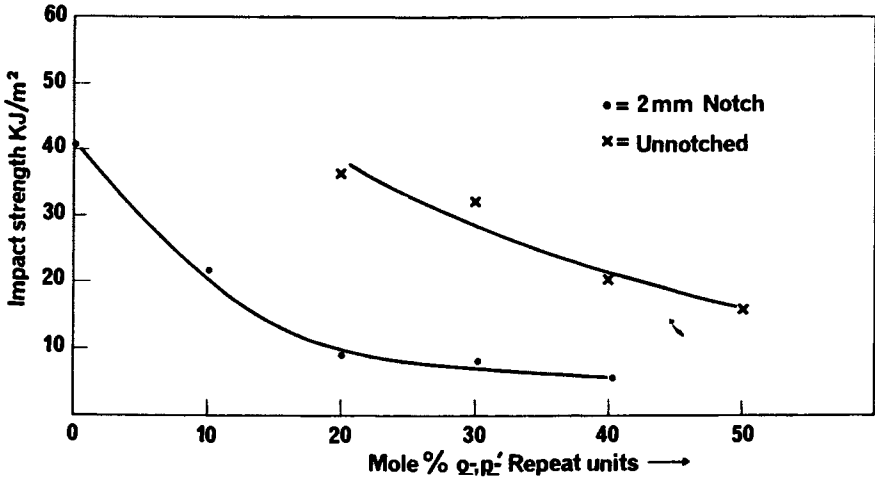


Figure 3. Impact strength of o-, p'-copolymers

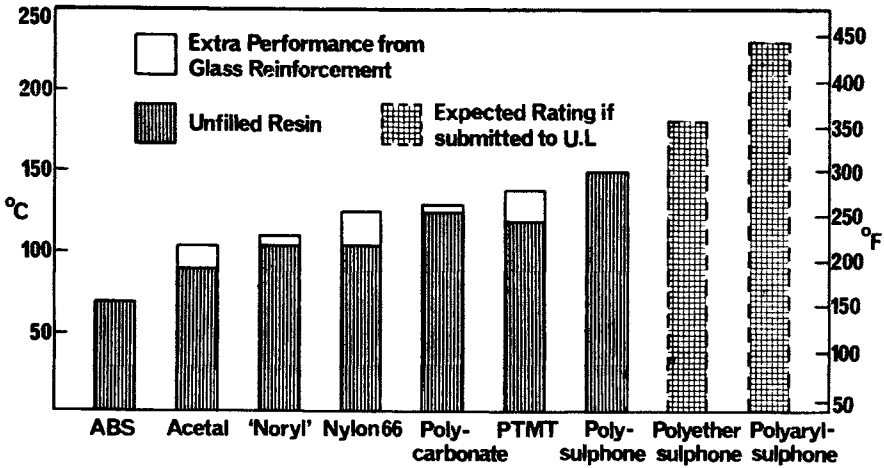


Figure 4. Maximum continuous use temperatures of some engineering thermoplastics based on Underwriters Laboratories ratings

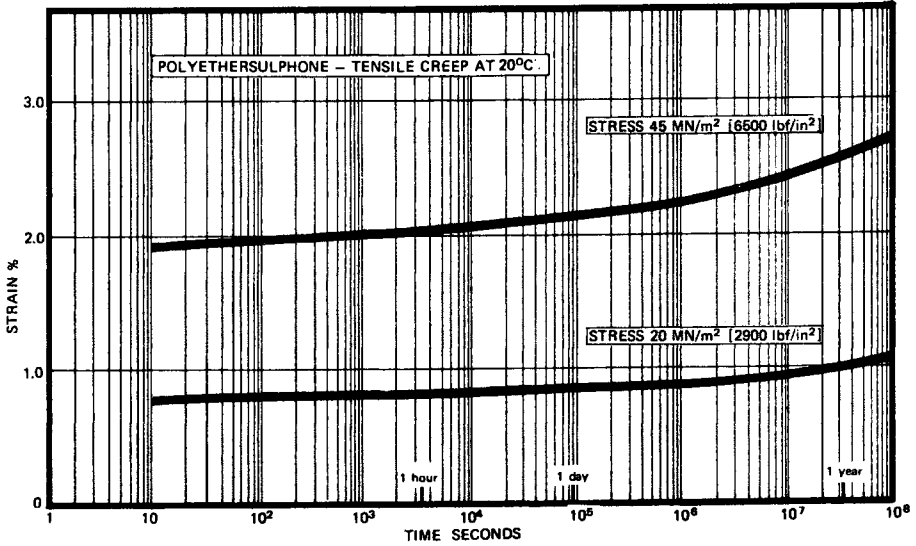


Figure 5. *Polyethersulphone : tensile creep at 20°C*

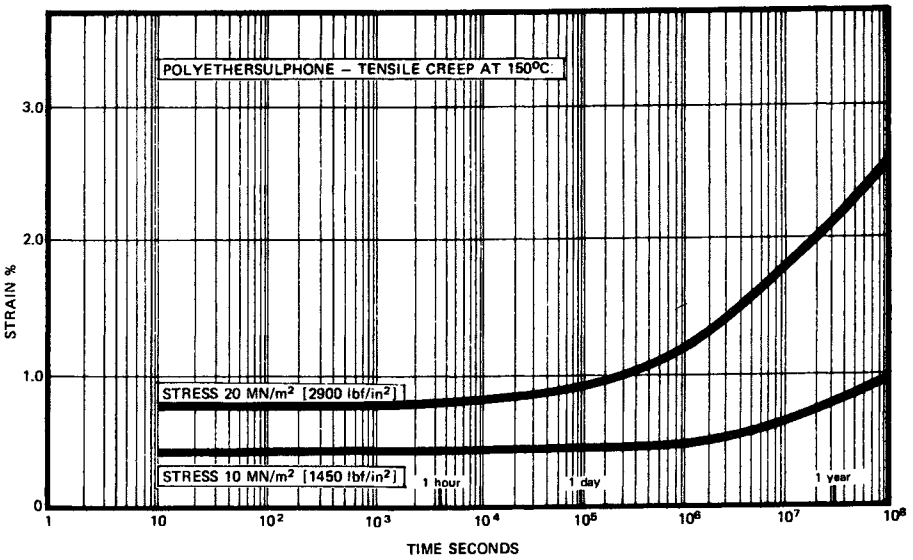


Figure 6. *Polyethersulphone : tensile creep at 150°C*

heat deflection temperature of  $397^{\circ}\text{F}$  at 264 psi (ASTM D 637) and a glass transition temperature ( $T_g$ ) of  $446^{\circ}\text{F}$ . Temperatures in the region of  $600\text{--}735^{\circ}\text{F}$  are required for processing the material, and there is a comfortable margin between these processing temperatures and those temperatures at which rates of decomposition become significant.

Mechanical Strength - Polyethersulphone is a strong and a tough material. The tensile yield strength of PES is 12,200 psi which is 20-30% higher than that shown by the more familiar 'engineering type' thermoplastics such as polycarbonates and nylons. When considering a material for high temperature use its retention of tensile strength at high operating temperatures is an important factor, and Fig 7 shows the variation of tensile strength of PES with temperature. At  $360^{\circ}\text{F}$  PES still has a tensile strength in excess of 9000 psi, a value typical of the strength of many engineering plastics at ambient temperatures; at  $360^{\circ}\text{F}$  these other materials have yield strengths approaching zero. But what is perhaps of even greater importance for a high temperature material is its retention of strength after periods of use at the high temperature, and Fig 8 shows that heat ageing PES at  $300^{\circ}\text{F}$  for 1 year in fact increases its tensile strength slightly.

Impact Strength - The impact behaviour of PES is good; it is not as outstanding as that of Polycarbonate but it shows better impact performance than that of nylons or acetals. PES cannot be broken in the unnotched Izod test, and a notched Izod (ASTM D 257) has a value of 1.6 ftlb/in notch; it is particularly resistant to crack initiation; and PES is even tougher after it has absorbed its equilibrium amount of water.

### Environmental Properties

Dimensional Stability - Like many other thermoplastics, PES is slightly hygroscopic and will absorb moisture when exposed to a wet atmosphere, but to a much less extent than nylon 66. The resulting changes in dimension are small (of the order of 0.15%) and are predictable. Complete immersion in water at  $68^{\circ}\text{F}$  for 24 hours (ASTM D 570) gives an uptake of 0.43% and an equilibrium moisture content of 2.3% is reached after 2 weeks. PES has a low and uniform mould shrinkage during injection moulding so it can be moulded to close tolerances. Furthermore, the coefficient of expansion is  $5.5 \times 10^{-5}$  which is half that of many other thermoplastics and this fact, together with low creep ensures that good dimensional stability is retained over a wide range of temperatures.



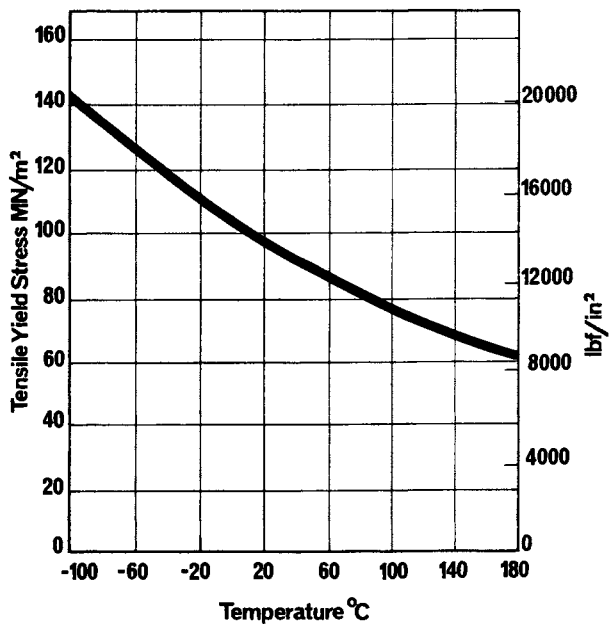


Figure 7. *Polyethersulphone 300P: tensile yield stress/temperature*

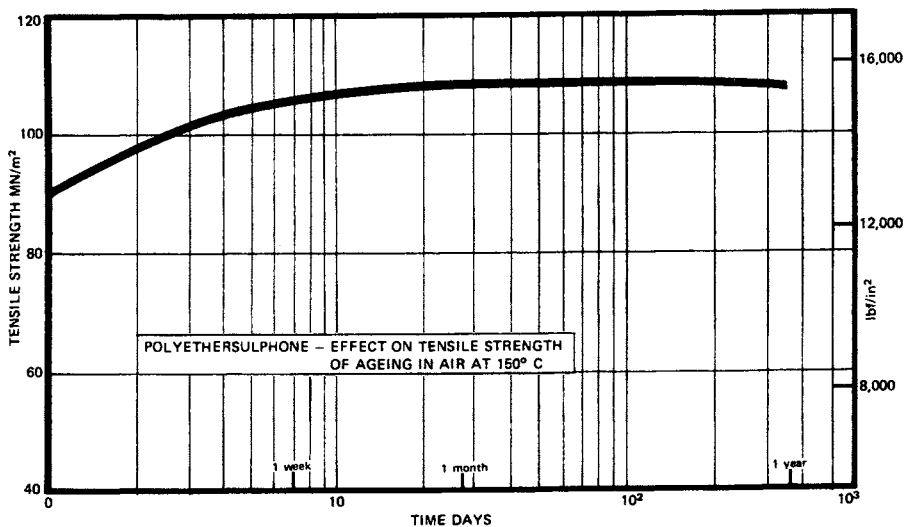


Figure 8. *Polyethersulphone: effect on tensile strength of aging in air at 150°C*

Thermal Endurance - Polyethersulphone has a high oxidative and thermal stability and it is therefore capable of being used for very long periods of time at high temperatures. Fig 9 plots the results of accelerated heat ageing tests made under conditions specified by the International Electrotechnical Commission, the British Standards Institution and the American Society for Testing Materials (15). The graph shows that PES has a predicted useful life of 20 years at 360° F. (The expression 'useful life' is defined as the time taken for a material to lose 50% of its tensile strength measured originally at room temperature). PES can therefore be considered for some Class H electrical applications.

Chemical Resistance - PES is an amorphous aromatic polymer and as such tends to be stable towards aqueous solutions but susceptible to attack from certain polar organic solvents. PES resists attack from acids, alkalis, oils, fats, greases, petroleum and aliphatic hydrocarbons and alcohols. It does however suffer from stress cracking in certain ketones, esters and aromatic hydrocarbons, and dissolves in the more polar solvents such as dimethyl formamide and some chlorinated hydrocarbons. Because of the solubility of the material it can be applied as a lacquer or solvent cast into thin film.

Flammability - PES has an Oxygen Index of 38 and according to the ASTM D 635 flammability test is classified as 'non-burning' this means that although the material burns when in contact with flame the flame is extinguished immediately when the source of ignition is removed. There is considerable confidence that PES is well within VE-0 on the Underwriters Laboratories flammability ratings. Even in thin section, PES film remains self extinguishing, and this factor will influence its choice for a number of electrical uses in particular.

### Electrical Properties

The retention of properties at high temperatures is seen in the electrical behaviour of PES, and its low power factor, good permittivity and high resistivity all remain reasonably constant up to high temperatures.

The volume resistivity of PES (ASTM D 150) at ambient temperatures is high at around  $10^{17}$  -  $10^{18}$  ohm cm and, although the resistivity decreases as the temperature rises a value of  $10^{15}$  is retained at 400° F. Such behaviour is unusual in thermoplastics because many thermoplastics severely deform or are molten at these very high temperatures.

A material which is intended for use as the dielectric of a capacitor should retain fairly uniform values for capacitance

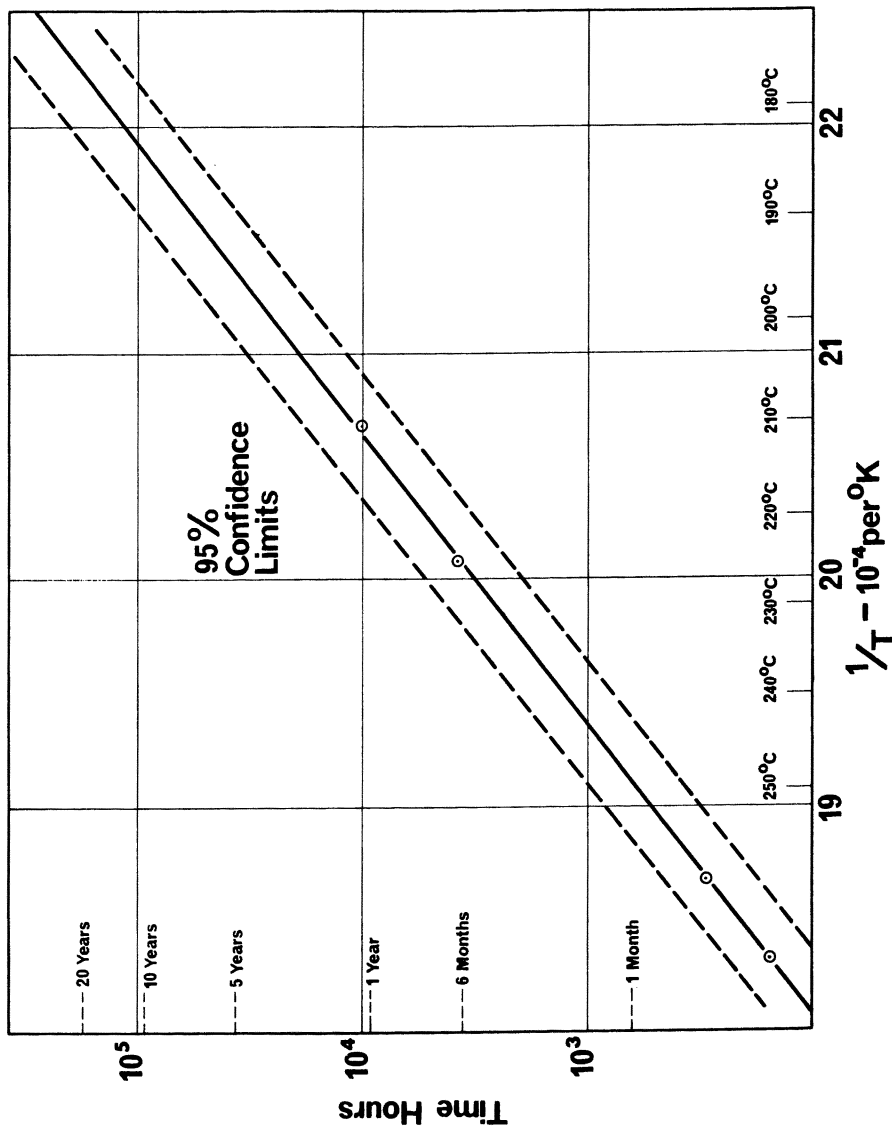


Figure 9. Polyethersulfone 300P : thermal life curve

throughout the operating temperature range of the capacitor. Polyethersulphone is particularly good in this respect, showing a change of about 1% over the temperature range 70°F to 400°F (Fig 10).

Power factor, which is sometimes called loss factor or  $\tan \delta$  is a measure of the electrical losses which occur when an electrical potential is applied across the material, and these losses usually manifest themselves in the form of heat. The variation of loss tangent with temperature is shown in Fig 11, the loss tangent remaining low at around 0.001 up to 400°F, above 400°F the losses begin to increase significantly and these loss characteristics resemble those of polyimide H film.

The dielectric strength of PES, as measured in oil by the short term tests ASTM D 149, is 800 KV/cm for a 0.25 mm section and 158 KV/cm for 3.25 mm. The tracking behaviour of PES when subjected to high voltages is very complex and this phenomenon is currently under investigation. There are indications that electrical breakdown associated with carbonisation tends to occur across the surface of the material. However, results obtained are similar to those found for other amorphous aromatic polymers like polycarbonate.

### Processing Properties

Polyethersulphone is a true thermoplastic and can be processed by all the traditional techniques we associate with thermoplastics. These include injection moulding, blow moulding, extrusion of rod and sheet, and vacuum forming sheet into complex shapes. PES requires slightly higher processing temperatures than those needed for most other thermoplastics but these temperatures are well within the capabilities of most modern screw injection moulding and other machines. Set temperatures of 660°F are usual, but temperatures as high as 735°F may be necessary where there are long and narrow flow paths. Mould temperatures should also be fairly high, above 195°F and as close to 300°F as possible.

Even at these high processing temperatures PES is still a viscous melt similar in many respects to a polycarbonate melt, and is far less viscous than PVC at its recommended melt temperature. PES has flow properties similar to those of 'Udel' polysulphone and PPO except that slightly higher melt temperatures are required. There are also certain mould design features which minimise problems due to flow; these include the avoidance of long and narrow flow paths and the use of full runners and large gates.

Polyethersulphone can be machined, ultrasonically welded and solvent welded using standard techniques. Components can also be vacuum metallised, electroplated and painted.

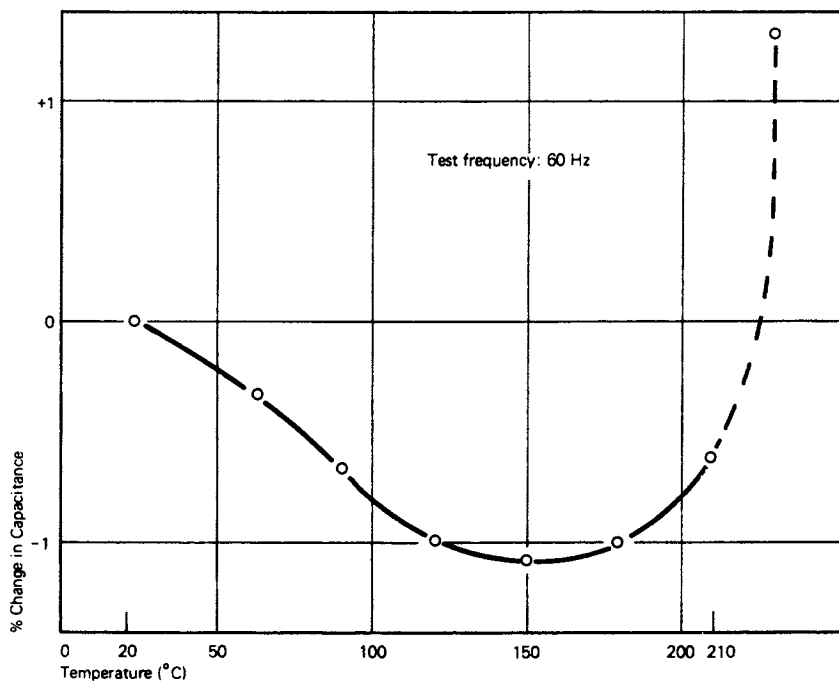


Figure 10. *Polyethersulphone 300P* : temperature dependence of capacitance

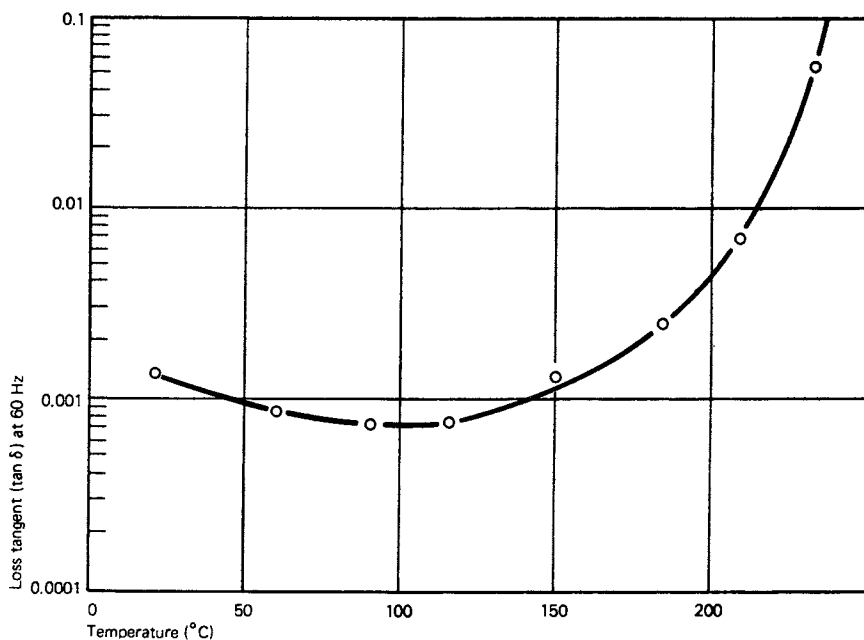


Figure 11. *Polyethersulphone 300P* : dependence of loss tangent on frequency

### Grades of Polyethersulphone

There are two standard grades of PES currently available; 200P and 300P. The 200P grade is the general purpose injection moulding resin which shows an optimum combination of mechanical performance and ease of processing. The 300P grade is of higher molecular weight and is for use where creep resistance is of major importance, and this superior mechanical performance is at the expense of the ease of processability as the 300P is slightly more viscous in the melt.

Although Polyethersulphone is itself a good melt adhesive (16) a special grade coded 100P has been developed specifically for use in adhesive formulations for metals and glass, as a lacquer for coatings, and in the impregnation of glass and carbon fibres. A commercial application for this grade is described later in this paper.

Another recent development has been the introduction of Polyethersulphone with performance at temperatures higher than that of the 300P grade. One of these high performance grades, PES 720P, has a use temperature 35°F higher than that of the 300P grade and can be used therefore for applications which require performance at 400°F and above. These high performance grades are considerably more expensive than the basic homopolymer grades and will therefore be used in specialised applications; they can, however, still be processed on entirely conventional injection moulding equipment.

### Applications for Polyethersulphone

PES has been available commercially for just over one year, and a year is too short a time for any new and specialised plastics material to become fully established. However PES is already being used in many commercial applications, and a very large number of other uses are currently under active development.

It is useful, therefore to describe a number of these possibilities and to outline the product properties which lead to PES being selected as that most likely to succeed in the particular applications. In many cases PES is being evaluated for applications which were considered too hot for plastics to handle.

PES is mainly replacing metals - sometimes because there is a saving in materials costs as, for example, in the replacement of stainless steel or brass, but more often PES is used because of its ability to injection mould complex shapes, and so avoid costly machining and finishing operations which are often necessary with die case metal.

In general terms it is likely that the three commercially available polysulphones will not compete with each other for

specific end uses. The main reason for this is that their properties and prices are significantly different, and so for example PES would not be considered for an end use for which 'Udel' Polysulfone was entirely satisfactory. However, some overlap could occur where, for example, the safety factor provided by one material is small and where there is a desire for a wider margin, or where one polysulfone provides a specific property advantage which justifies its use.

The lighting industry is an area where the use of a plastic with the temperature performance of PES means that existing plastic parts can be re-designed to be located closer to the heat source; alternatively, parts which have up until now been made of metal because no plastic could offer the necessary performance can now be considered in PES. For instance, there is considerable interest in the practicability of replacing the metal end of incandescent lamp bulbs with PES. The advantages of using PES are that the bulb base is a one-piece injection moulding which can be fixed to the bulb using ultrasonic welding, and to which the solder contacts can be applied direct to the moulding without the use of traditional brass inserts. Whether PES is used in this particular application depends, of course, upon its technical suitability and economic feasibility. Both aspects are currently being evaluated.

In some applications in the electrical and electronics industries PES is being used because its properties are necessary in the manufacture of the component rather than its in-service requirement. For example, in one established application PES is used for the coil formers of a line output transformer that is used in a colour TV set to produce the 27 Kv for operation of the electron beam. During normal use, temperatures above 175°F are rarely reached and therefore on this basis alone several materials were contenders, with PES an expensive option. PES was selected eventually because the former must withstand the 340-360°F baking temperature required to shrink the stretched polycarbonate interleaving film on the windings, and because it offered satisfactory electrical performance during use. The 'non-burning' characteristics of PES are an added bonus for this type of application.

Other coil formers are made from PES because the mouldings do not deform when tags are dip soldered, and this ability to withstand solder temperature is leading to some very interesting applications.

PES can be readily extruded into film and foil, and this opens up possibilities for its use in flexible printed circuitry where performance up to 360°F for prolonged periods is required. When using PES it is also possible to dip solder the whole board, as long as the film is not too thin and the immersion time in the bath fairly short. A further advantage of using PES is that

the foil can be electroplated readily.

The use of PES as a dielectric for miniature capacitors is a particularly interesting development. PES can be solvent cast into two or three micron film which can then be metallised and wrapped into a capacitor. The combination of a permittivity of 3.5 and low loss factor of around 0.001 makes PES a very useful dielectric, particularly if the temperature is likely to be high. The main advantages of PES over competitive materials in this application are the thinness of the film and the good physical and electrical properties at the manufacturing and in-service temperatures of the components. It has a high permittivity (3.5) and so the capacitance per unit volume is high. This means that capacitors made from PES are more compact for a given value of capacitance than they would be if other polar dielectrics were used. For example a capacitor made from PES would be 6% smaller than one made from-PET film of the same thickness, and 13% smaller than an equivalent polycarbonate capacitor. In this age of miniaturisation such advantages are important. One of the few drawbacks at present with PES in this application is that it takes up a small amount of water which causes a slight change in capacitance. Ways of eliminating this problem are being investigated.

In many respects PES is an ideal material for use in electrical connectors as it can be moulded to close tolerances and maintains structural and electrical integrity to high temperatures. Multipin connectors based on a plastic dielectric retention system for use in supersonic aircraft and where a 10,000 hour lifetime at 400°F is required, are a possible application for the high performance grade 720P.

PES has other applications in aircraft. One of these is more mundane than the multipin connector but is nevertheless an obvious application for a polymer which boasts high temperature resistance. PES is used for the door frame of an oven used in aircraft for reheating cooked meals and holds the inner and outer aluminium casing together. Temperatures in this oven can reach 400°F in places and PES was chosen because it can be injection moulded into complex shapes and continually withstands the high reheat temperatures without giving off toxic fumes. Applications for PES in other parts of domestic and commercial ovens are also being developed.

One of the first applications for the adhesive grade of PES is as a structural adhesive to upgrade the temperature performance of epoxy resins (17). Mixtures of PES with epoxy resin are used to stick the aluminium outer skin on to aluminium honeycomb and such structures are designed for a 10,000 hr lifetime at 300°F which is typical of the performance requirements of some supersonic aircraft. This adhesive grade can also be used as a matrix for making carbon fibre composites which show high



interlaminar shear strengths. Composites based on PES are tough and maintain higher strengths to higher temperatures than composites based on conventional epoxy resin systems.

PES is being evaluated for a number of automotive applications because of its resistance to battery acids, heat and transmission fluids. In the automatic car gearbox, for instance, temperatures as high as 340<sup>o</sup>F can be reached and this has up until now restricted the use of plastics in this area of the car. PES shows particularly good resistance to lubricating oils at these high temperatures, and several manufacturers are currently evaluating PES for a number of components inside gear boxes. These include bearing cages, auxiliary gears for operating items such as the speedometer cable, adapter plugs to locate the filler tube to the gearbox casing and many others.

Car headlamp reflectors - particularly those which use quartz iodine lamps can reach very high temperatures during use and PES offers for the first time the design freedom to make complex shaped reflectors and housings which were either impossible or very expensive to machine from metals. PES is also being evaluated for a variety of small components such as commutator supports and parts of alternators and switch gear.

PES is undergoing extensive trials for use in medical equipment where its ability to withstand repeated steam or dry heat sterilisation or chemical sterilisation is important. The use of PES for parts of respirators, anaesthetic equipment, and flow control devices are all being actively developed.

The high temperature properties of PES and the ease with which a single layer can be extruded on to wire make it potentially suitable for some speciality uses. One UK manufacturer has put PES insulated wire on to his range of products. However, PES wire covering should be used only in environments which are not likely to be contaminated with highly polar fluids or solvents. For instance it is not likely to be suitable as a high temperature aircraft wiring because of possible stress cracking by 'Skydrol' hydraulic fluid.

A way of upgrading the performance of PES wire covering is to cross-link it. This improves resistance to solvents and increases cut-through temperature. The 100P grade of PES can be applied as a lacquer and undergoes cross-linking when baked at over 572<sup>o</sup>F.

### Conclusion

Although Polyethersulphone has been available commercially for only a short time it seems likely that its inherent mechanical and electrical properties will prove useful in a very wide variety of end uses. Furthermore Polyethersulphone belongs to a family of materials, variants of which can be readily made, and

this adaptability for particular end uses extends even further its potential usefulness.

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## Polyphenylene Sulfide: A New Industrial Resin

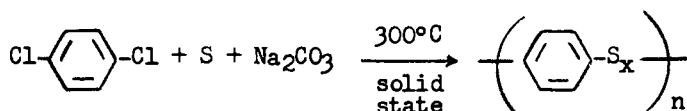
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### Synthesis and Structure

Polyphenylene sulfide resins may have been made as by-products in the research of Friedel and Crafts (1888) and later workers studying the preparation of diphenyl sulfide and related aromatic sulfur compounds. This early work has been reviewed and referenced in summaries by Lenz, (1) Gaylord (2) and Smith. (3) However, it was not until 1948 that Macallum (4) prepared the resins by a method that defined their structure with reasonable certainty and yielded sufficient quantity to study some of their properties.

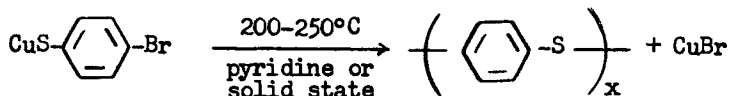
Macallum reacted *p*-dichlorobenzene with sulfur and anhydrous sodium carbonate in a sealed vessel at 300-340°C.



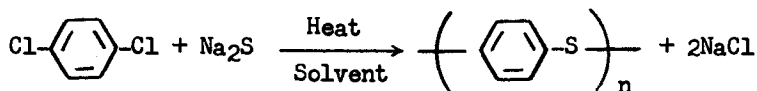
The inorganic products were carbon dioxide, sodium chloride, sulfate and thiosulfate. In the resin formula *x* stands for one or more atoms of sulfur. Macallum's work is reported in more detail in U. S. patents. (5, 6) He showed that resins could be made from a variety of nuclearly chlorinated aromatic compounds and mixtures of them. Adding monochlorobenzene to *p*-dichlorobenzene resulted in a lower molecular weight resin; whereas, the inclusion of trichlorobenzene gave a stiffer resin. He reported that his higher molecular weight resins were good thermoplastic molding materials that had good tensile strength and toughness. He also recognized their unusual thermal stability and chemical resistance.

In 1954 Dow Chemical Company purchased the Macallum patents because they made *p*-dichlorobenzene and had an interest in thermally stable plastics. (7) The Dow workers made a detailed study of the Macallum polymerization system, (1) and the structure of the polymers. (8) They found that the process would be

difficult to control because the yields and polymer properties were very unpredictable. Consequently, they launched a detailed study of other synthesis methods. (7, 9, 10, 11) Considerable attention was given to condensation polymerization of metal salts of p-halo thiophenol. Of the compounds studied cuprous p-bromothiophenoxide gave by far the best yield and the highest melting point product so this reaction and the product were the most extensively studied but considerable difficulty was encountered in removing the by-product, copper bromide, from polymers made by this process.



In 1967 a patent by Edmonds and Hill (12) was issued to Phillips Petroleum Company for a new synthesis of arylene sulfide polymers. The patent describes the production of polymers from polyhalo-substituted aromatic compounds and alkali metal sulfides in a polar organic solvent.



This reaction is quite general and many variations of reactants and conditions can be used. The addition of monochlorobenzene to the reaction mixture decreases the molecular weight of the polymer. The molecular weight can be increased by post-treatment with a small amount of sulfur (13) or recycling some of the polymer to the reactor. (14) The addition of trichlorobenzene to the system acts as a cross-linking agent. This discovery opened the way for a commercially feasible synthesis from readily available raw materials, and led to extensive efforts to characterize and develop applications for the materials. The operation of a semi-works facility was followed by the commercial production of Ryton® polyphenylene sulfide resins in a 6 million pound per year plant late in 1972.

### Properties

Polyphenylene sulfide (PPS) is obtained from the polymerization mixture as a fine off-white powder which after purification can be used directly in some coating applications. It is not soluble in any known solvent below about 200°C, but above that temperature it is soluble to a limited extent in some aromatics, chloroaromatics and heterocyclic compounds. The inherent viscosity, measured at 206°C in 1-chloronaphthalene is typically 0.16, indicating only moderate molecular weight. The annealed polymer is highly crystalline as shown by X-ray diffraction, (15) and the

crystalline melting point determined by differential thermal analysis is near 285°C. (16)

An important characteristic of polyphenylene sulfide is the change caused by heating it in air. When heated to a sufficiently high temperature (350-400°C) it melts to a relatively fluid liquid. On continued heating it becomes progressively more viscous and eventually gels and solidifies. This solid, "cured" polymer, is believed to be crosslinked because it is insoluble in all solvents tested, even at elevated temperatures. The changes that occur can be followed by differential thermal analysis (DTA). Figure 1 presents DTA curves for quenched samples of uncured and cured polyphenylene sulfide. The uncured sample A shows a sharp premelt crystallization at 135°C and crystalline melting point at 285°C. These peaks are just visible for the cured sample B, and will disappear completely for more highly cured polymer. The break at 85°C is the glass transition temperature.

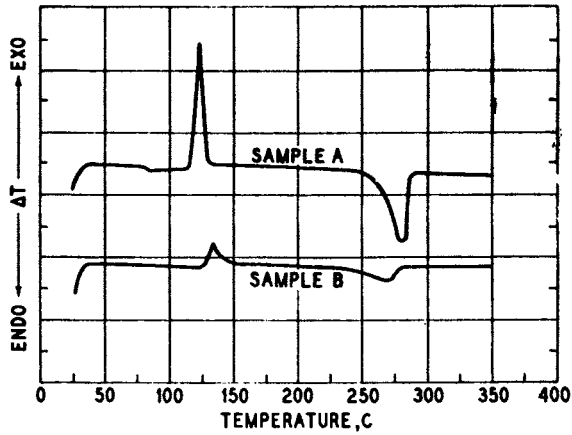
Under controlled curing conditions polymers having progressively higher melt viscosities can be produced. These are marketed as different grades as desired for special coating applications, injection or compression molding. Curing the resin increases its toughness, ductility and resistance to solvents and chemicals.

Thermogravimetric analysis of polyphenylene sulfide in nitrogen or in air indicates no appreciable weight loss below about 500°C. In air, degradation is essentially complete at 700°C, but in an inert atmosphere approximately 40% of the polymer remains at 1000°C. Comparative thermogravimetric data shown in Figure 2 demonstrate that polyphenylene sulfide displays a greater resistance to weight loss at elevated temperatures than either the conventional thermoplastics or the heat-resistant polytetrafluoroethylene.

Thermogravimetric analysis is a short-term weight loss measurement and the thermal stability shown by it may not translate directly to retention of properties on long-term high-temperature exposure. Figure 3 shows the effect of such exposure on 40% glass filled molded specimens of polyphenylene sulfide. After 30 weeks at 204°C the flexural modulus is unaffected and the tensile strength reduced by only about 50%. The degradation after 16 weeks at 232°C as indicated by the triangle points does not appear significantly more rapid.

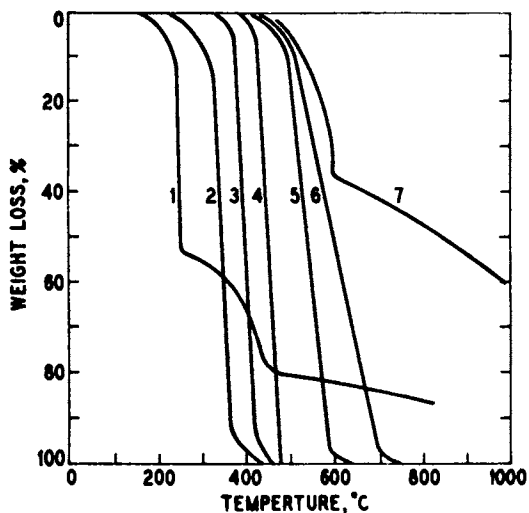
Polyphenylene sulfide is rated as "non-burning" by industry flammability tests. As shown in Table I, it has a higher Limiting Oxygen Index than many of the other engineering plastics.

The retention of mechanical properties at elevated temperatures is unusually good. Figures 4 and 5 show the effect of temperature on tensile strength and flexural modulus for both the unfilled resin and resin containing 40% glass fiber.



**SAMPLE A: MELTED UNDER NITROGEN AND QUENCHED BEFORE DTA;  
SAMPLE B; HEATED AT 370°C IN AIR 4 HOURS AND QUENCHED  
BEFORE DTA. HEATING RATE, 10°C/MINUTE**

*Figure 1. Differential thermal analysis of polyphenylene sulfide in nitrogen*



KEY: 1 - POLYVINYLCHLORIDE; 2 - POLYMETHYLMETHACRYLATE; 3 - POLYSTYRENE;  
4 - POLYETHYLENE; 5 - POLYTETRAFLUOROETHYLENE; 6 - POLYPHENYLENESULFIDE  
IN AIR ATMOSPHERE; 7 - POLYPHENYLENESULFIDE.

Figure 2. *Comparative thermogravimetric analysis (nitrogen atmosphere)*

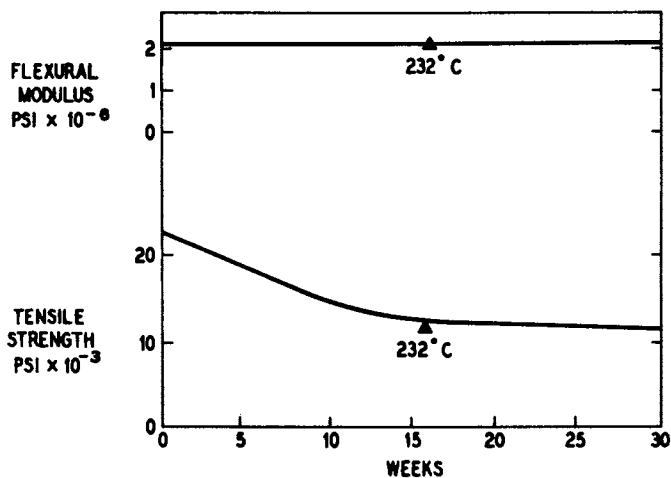


Figure 3. *Polyphenylene sulfide: 40% glass filled aging at 204°C in air*

TABLE I  
POLYPHENYLENE SULFIDE RESIN FLAMMABILITY

<u>Material</u>	<u>Limiting Oxygen Index, %</u>
Polyvinyl Chloride	47
Polyphenylene Sulfide	44
Nylon 6-6	28.7
Polycarbonate	25
Polystyrene	18.3
Polyolefins	17.4
Polyacetal	16.2

Polyphenylene sulfide possesses unusual chemical resistance as shown in Table II. More extensive data on chemical resistance can be found in the literature. (17, 18) It is slightly attacked by some chlorinated organics, certain amines and a few other compounds. It is most severely attacked by concentrated nitric and sulfuric acids or strong oxidizing solutions such as chromic acid and sodium hypochlorite.

TABLE II  
CHEMICAL RESISTANCE  
(% Tensile Retained After 24 Hours @ 93°C)

<u>Reagent</u>	<u>Poly-phenylene Sulfide</u>	<u>Poly-carbonate</u>	<u>Modified Phenylene Oxide</u>	<u>Poly-sulfone</u>	<u>Nylon 6-6</u>
30% H <sub>2</sub> SO <sub>4</sub>	100	100	100	100	0
37% HCl	100	0	100	100	0
Glacial acetic acid	98	67	78	91	0
30% NaOH	100	7	100	100	89
Acetic anhydride	100	0	55	0	74
10% NaCl	100	100	100	100	94
Bromine water	64	48	87	92	8
10% NaOCl	84	100	100	100	44
Ethylene chloride	72	0	0	0	65
Chlorobenzene	100	0	0	0	73
Chloroform	87	0	0	0	57
Toluene	98	0	0	0	76
Cyclohexane	100	75	0	99	90
Gasoline	100	99	0	100	80
Diesel fuel	100	100	36	100	87
Amyl alcohol	100	48	62	100	87
2-Aminoethanol	100	0	100	100	93
Butyl amine	49	0	0	0	91
Aniline	96	0	0	0	85
Pyridine	93	0	0	0	74
Methyl ethyl ketone	100	0	0	0	87
Amyl acetate	100	46	0	0	88



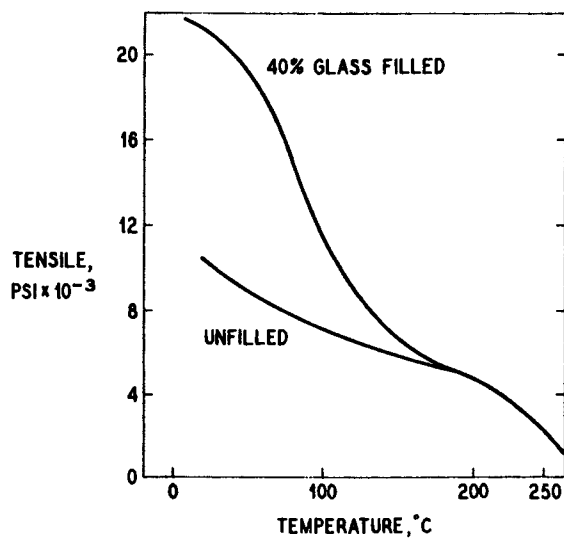


Figure 4. *Polyphenylene sulfide tensile vs. temperature*

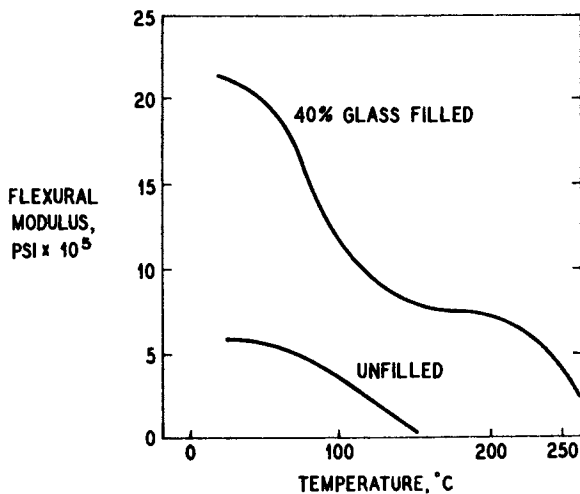


Figure 5. *Polyphenylene sulfide flexural modulus vs. temperature*

Table III lists typical mechanical properties of polyphenylene sulfide moldings both with and without 40% glass filler for comparison with other engineering plastics.

### Coatings

Polyphenylene sulfide coatings can be applied by spraying liquid slurries on hot or cold metal surfaces, dry powder spraying of hot pieces, electrostatic spraying on either hot or cold surfaces, or immersing hot parts in a fluidized bed. The resin is available in different grades which vary in the amount of crosslinking and resultant melt flow. The most fluid grade is used for thin coatings; whereas, the more viscous grades are used for heavier coatings to prevent sagging during the coating and curing operations. In all cases the coatings must be baked at a minimum of 370°C for sufficient time to produce a tough, flexible, adherent film. The time ranges from 45 minutes for 1-3 mil coatings up to 3 hours for 40 mil coatings. When multiple coats are applied it is preferable to bake each one thoroughly before adding the next.

Proper surface preparation of the part to be coated is important in order to obtain adherent coatings. In general, the surfaces should be grit-blasted, degreased, and coated as soon as possible with a minimum of handling. Iron and steel should be oxidized at 370°C temperature to a blue-gray color. Galvanized iron, some zinc alloys, and other metals that will not stand the 370°C temperature cannot be coated with polyphenylene sulfide.

Liquid slurries for spraying are usually made with water containing a small amount of wetting agent, and compounded to contain 30-35% solids. Reinforcing agents or pigments can be added if they will withstand the 370°C curing temperature. Chrome oxide and iron oxide pigments can be used to make greens, reds and browns. Titanium oxide gives a light tan colored coating. Polytetrafluoroethylene may be added to increase the non-stick properties of the coating. To provide a smooth coating the slurry must be thoroughly mixed in efficient equipment such as a ball mill. The slurry can be sprayed with most industrial type spray guns by adjusting the nozzle to provide a fine mist. Slurry coats are usually 1-2 mils thick. After spraying, the parts must be handled with care because the dried coating before melting is weak and is easily damaged or scraped off. Heavy metal objects which will retain heat above the melting point of the resin (290°C) may be coated while hot. By this technique heavier coatings 10-20 mils thick can be obtained in one spray application.

For dry powder spraying from a flocking spray gun the formulation must be sprayed onto a surface preheated to about 370°C. Electrostatic powder spraying can be done on either hot or cold metal surfaces. Thicknesses when sprayed cold are usually limited to about 5 mils but coatings as heavy as 40 mils can be built up on hot parts.

TABLE III. TYPICAL PROPERTIES OF POLYPHENYLENE SULFIDE COMPARED TO OTHER ENGINEERING PLASTICS

	PPS	PPS/Glass (60/40)	Polysulfone	Polyimide	Poly- carbonate	Modified PPO
Density, gms/cc	1.34	1.64	1.24	1.43	1.20	1.06
Tensile, psi	10,800	21,400	10,200	10,500	9,000	9,600
Elongation, %	3	3	50-100	6-7	110	60
Flex. Mod., psi x 10 <sup>-5</sup>	6.0	22.0	3.9	4.6	3.4	3.6
Flex. Strength, psi	20,000	37,000	15,400	15,000	13,500	13,500
Tens. Modulus, psi x 10 <sup>-5</sup>	4.8	11.2	3.6	4.5	3.45	3.55
Hardness, Shore D	86	92	84	-	83	82
Compression Strength, psi	16,000	21,000	13,900	24,000	12,500	16,400
Notched Izod Impact, ft-lbs/in.*						
@ 24°C	0.2	1.0	1.2	0.9**	2.3	0.7
@ 150°C	1.0	1.8	-	-	-	-
Unnotched Izod Impact, ft-lbs/in. @ 24°C	3	9	-	-	No break	No break
Heat Deflection Temp. @ 264 psi, °C	137	220+	174	360	132	130
Max. Rec. Svs. Temp., °C	230	230	150-170	260	121	-
Therm. Exp., 10 <sup>-5</sup> in./in.°C	5.4	4.0	5.6	4.5-6.1	6.8	5.9
Water Abs. (24 hrs), %	0.02	.01	0.22	0.32	0.15	0.066
Mold Shrinkage, in./in.	.010	.002-.006	.0076	-	0.005-	0.005-
Material source	Ryton R-6	Ryton R-4	Udel P-170C	Vespel SP-1	Lexan 100	Noryl 731

\*On 1/4" specimens

\*\*On 1/8" specimens

Fluidized bed coating is limited to heavier parts that will retain heat long enough to accumulate the desired thickness of melted resin. The part is preheated to 370°C then removed from the oven and immersed in the bed of fluidized powder as quickly as possible. One to three seconds contact time is usually sufficient to deposit 5-10 mils.

The outstanding characteristics of cured coatings are their combination of toughness, flexibility, thermal and chemical resistance. Coatings will withstand a reverse impact of greater than 160 inch-pounds (ASTM D2794-69) and a 180° mandrel bend on a 3/16 mandrel (ASTM-1737-62).

### Injection Molding

Polyphenylene sulfide may be used for injection molding with or without added fillers depending upon the desired properties of the finished part. Any of a wide variety of fillers that are stable at the 315-370°C processing temperature can be used. Examples are glass fiber, milled asbestos, and Fybex inorganic titanate fiber. Reinforcing fillers such as glass fibers are of considerable interest because they provide the greatest improvement in mechanical properties at the lowest cost. Molding compounds are prepared by dry blending the filler with the precured molding grade of polyphenylene sulfide in suitable equipment such as a cone blender or drum-tumbler. Although the dry blends can be injection molded directly, it is generally desirable from the standpoint of handling and feeding to extrude and pelletize the compound before molding. Pelletized molding resins are now available commercially either uncompounded or filled. One filled grade contains 40% glass fibers. The maximum amount of filler that can be used in injection molding is limited by processability and ranges from about 20% for asbestos to about 45% for glass fibers.

Polyphenylene sulfide resins are preferably molded in reciprocating screw machines. Molding is very similar to other resins such as polyolefins except that higher stock temperatures are needed, 300-360°C. Polyphenylene sulfide has a slight tendency to gas at molding temperatures. To prevent void formation the lower stock temperature along with high injection and hold pressures are recommended. Typical conditions which produce well-formed parts free of voids and sink marks are 315°C stock temperature, 65°C mold temperature, 15,000 psi injection pressure and 5,000 psi hold pressure. Higher mold temperatures (120°C) favor higher tensile strength and better surface appearance with some loss in impact strength. Compounds have been reground and remolded through three cycles with only 10% loss in tensile strength. Properties of a variety of filled compositions have been described in Hill, Werkman and Carrow. (19)

### Compression Molding

Compression molding is used to fabricate certain types of parts that cannot be injection molded. Such pieces are usually more massive or are stock shapes for machining into finished parts. The resin in them is more highly crosslinked and often has a high loading of fillers. The crosslinking, or curing, is done before molding by exposing the resin to air at elevated temperature which reduces the melt flow so the resin can be handled in molding operation. Practically any filler that can withstand the 370°C curing and molding temperature can be used. Thorough blending of the filler with the resin is important, but many of the commercial blenders are suitable. Curing conditions depend upon the amount and kind of filler and upon the grade of polyphenylene sulfide used. For example, to prepare a 50% asbestos feedstock the high melt flow uncured coating grade powder should be used. After thorough mixing it is cured for about 1 hour above the melting point at 370°C. This grade of polymer wets the filler better than the precured coating grades. Unfilled polyphenylene sulfide powder and many blends with powders and pigments need to be partially cured first below the melting point at 265-280°C, and then finished at 370°C. Curing is usually done in shallow pans in a circulating air oven. The cure below the melting point prevents coalescence at 370°C permitting air contact and circulation through the mass. The final product is a porous sheet that is granulated before molding. A rather careful sequence of filling, heating, compression, and cooling operations is necessary to obtain the highest quality molded objects. It will suffice here to say that the molding is carried out at 340-400°C with 1,000-4,000 psi pressure. Molded polyphenylene sulfide exhibits excellent machinability in typical operations of turning, milling, drilling, and tapping. However, at high glass loadings some wear on machine tools is encountered. Carbide tools are recommended. Optical finishes are possible with grinding and lapping.

### Applications

Polyphenylene sulfide resin is a new material with a new combination of desirable properties. Because of this, the list of applications is growing steadily and it is not possible to foresee all of them.

Polyphenylene sulfide coatings are finding wide application because of their good adhesion, hardness, chemical resistance, thermal stability and flexibility. The incorporation of small amounts of polytetrafluoroethylene in the polyphenylene sulfide coating formulation provides hard, scratch resistant release coatings. (20, 21) The use of release coatings of this type in food contact service is permitted by Section 121.2621 of the Food Additives Regulations. The properties of two typical polyphenylene sulfide coatings are summarized in Table IV.

TABLE IV  
PROPERTIES OF POLYPHENYLENE SULFIDE COATINGS

<u>Property</u>	<u>PPS/TiO<sub>2</sub> Coating (3/1)</u>	<u>PPS/TiO<sub>2</sub>/PTFE Coating (3/1/0.3)</u>
Hardness, pencil	2H	2H
Mandrel bend, 180°, 3/16"	Pass	Pass
Elongation (ASTM D 522), %	>32	>32
Reverse impact, inch-pounds	160	160
Abrasion resistance, Taber mg loss/100 rev, CS-17 wheel	50	57
Chemical resistance	Superior	Superior
Thermal stability	Superior	Superior
Color	Light Tan	Light Tan

Polyphenylene sulfide release coatings are finding application in coating cookware for non-stick use. Another interesting application for PPS release coatings involves the coating of tire molds to aid in the release of the finished tire from the mold. (22) When this release coating was employed, more than 8,000 tires were produced without cleaning the mold; whereas, cleaning was required after producing only 500-600 tires using a conventional silicone mold release agent. In addition the need for a blemish paint was eliminated, tire rejects were reduced and an improved surface finish resulted.

Polyphenylene sulfide coatings are also finding acceptance as corrosion resistant, protective coatings for oil field pipe, valves, fittings, couplings, thermocouple wells and other equipment in both the petroleum and chemical processing industries. Coated parts of this type have been operating satisfactorily for extended periods of time in media such as: liquid ammonia, crude oil, refined hydrocarbons, brine, dilute hydrochloric and sulfuric acids, dilute caustic and many other chemicals. In particular, PPS is providing protection when both corrosive environments and elevated temperatures are involved. Thus parts of carbon steel coated with PPS formulations are replacing parts previously fabricated from expensive alloy metals.

Polyphenylene sulfide coatings offer a combination of properties that include: good thermal stability, outstanding chemical resistance, low coefficient of friction, useful electrical properties, and precision moldability. In turn, these properties lead to a variety of applications not available to many other plastics. For example, a number of pump manufacturers are using polyphenylene sulfide compounds as sliding vanes, impellers, impeller cases, gauge guards and seals in corrosive service involving materials such as 60% sulfuric acid, liquid ammonia and various hydrocarbons.

Polyphenylene sulfide is establishing itself as a basic engineering material for bearing applications and other types of anti-friction, low-wear uses. When solid lubricants such as molybdenum disulfide, polytetrafluoroethylene, etc., are incorporated, formulations with an interesting range of anti-friction characteristics result. An extremely low friction coefficient and low wear rate makes possible self-lubricated journal rolling element and sliding bearing components from these PPS formulations. The need for self-lubrication becomes extremely important in those bearing applications where the bearing is so inaccessible that proper servicing is difficult or the bearing is exposed to environmental extremes that make ordinary lubricants ineffective.

Anti-friction formulations containing PPS resin and three other available anti-friction compounds were evaluated in journal bearing test configurations. Journal test bearings of the PPS formulation were compression molded into steel spherical bearing seats and then bored to fit the test shafts. The commercial bearing materials were machined into sleeve bearings from flat stock and press fitted into steel spherical bearing seats. The test data recorded in these evaluations included load, speed, PV (product of load, psi; and speed, fpm) wear, test duration, friction coefficient, and bearing temperature. (23)

Table V shows a typical comparison of the test data recorded of the various anti-friction compounds at one shaft speed and one loading. Probably the most outstanding characteristic of the PPS formulation is its extremely low friction coefficient. The effect of this very low friction coefficient is clearly shown in its extremely low bearing temperature build-up at various loads compared to the other materials.

Prevention of excessive bearing temperature is most important in achieving low wear rates, particularly in plastic bearing systems where thermal conductivity is usually low and dissipation of heat build-up is not nearly as efficient as in metal bearings. Temperature build-up can reach a critical temperature at which the cohesive strength of the plastic matrix is so reduced that it fails as a binder for the self-lubricating additives and results in excessive wear and bearing failure. The wear for the PPS formulation is relatively low. Polyphenylene sulfide compounds with low friction and low wear properties have been evaluated as cages for non-lubricated ball bearings at 177°C (350°F) and 50 psi load. These materials have operated in excess of 600 hours where other materials fail in less than 20 hours. In another application a 10.5-inch diameter piston for a non-lubricated gas compressor has been in service for over 6 months and is performing better than the aluminum piston that it replaced. The piston was machined from a 35-pound compression molded block of polyphenylene sulfide.

TABLE V  
COMPARATIVE JOURNAL BEARING DATA\*

<u>Material Designation</u>	<u>Radial Wear, in.</u>	<u>Test Duration, hrs.</u>	<u>Friction Coefficient, <math>\mu</math></u>	<u>Maximum Bearing Temp., °F</u>	<u>Maximum Shaft Temp., °F</u>
PPS/MoS <sub>2</sub> /Sb <sub>2</sub> O <sub>3</sub>	0.0060	162.5	0.02-0.05	155	<200
PTFE/MoS <sub>2</sub> /fiberglass	0.0025	125	0.23-0.26	316	347
PTFE/glass/iron oxide	0.0084	117.5	0.20-0.30	340	>500
Polyimide/PTFE/graphite	0.0078	55	0.08-0.18	205	277

\*Measurements made at 60 psi load and 1800 revolutions/minute, corresponding to a PV of 17,640 (load in psi times speed in feet/minute). Test shaft was 5/8" with a surface finish of 6-10 microinches, root mean square.



West and Senior (24) have reported an evaluation of several polyphenylene sulfide compositions as journal bearings. The preferred composition was 25% polytetrafluoroethylene, 10% graphite, 10% lead monoxide and 55% polyphenylene sulfide. This was compared directly at various temperatures with a commercially available journal bearing lined with an epoxy composition. The epoxy bearing failed catastrophically at 170°C, but at that temperature the coefficient of friction of the polyphenylene sulfide bearing reached its minimum and the wear factor was still similar to that of polyimides at ambient temperature. The polyphenylene sulfide bearing was still stable at a temperature of 220°C.

Electrical properties of polyphenylene sulfide compounds are summarized in Table VI. The dielectric constant is low in comparison with other plastic materials. Similarly the dissipation factor is low. Dielectric strength is quite high ranging from 500-600 volts per mil for the various compounds. Thus, both filled and unfilled polyphenylene sulfide materials are useful electrical insulators.

TABLE VI

ELECTRICAL PROPERTIES OF POLYPHENYLENE SULFIDE COMPOUNDS

<u>Property</u>	<u>Unfilled PPS</u>	<u>40% Glass- filled PPS</u>
Dielectric constant, 25°C -		
10 <sup>3</sup> Hertz	3.2	3.9
10 <sup>10</sup> Hertz	3.1	3.6
Dielectric constant, 120°C -		
10 <sup>3</sup> Hertz	3.1	3.9
10 <sup>10</sup> Hertz	3.1	3.6
Dissipation factor, 25°C -		
10 <sup>3</sup> Hertz	0.0004	0.0010
10 <sup>10</sup> Hertz	0.004	0.006
Dissipation factor, 120°C -		
10 <sup>3</sup> Hertz	0.003	0.004
10 <sup>10</sup> Hertz	0.007	0.02
Dielectric strength, volts/mil	585	490

The electric properties of polyphenylene sulfide and the ability to injection mold very small parts with great precision have led to the use of a variety of connectors, coil forms, etc., in the electronics industry. For example, a pin cushion connector coil terminal support used in color television is now being volume produced from PPS in a multiple unit.

In conclusion it can be said that polyphenylene sulfide is unique by having high flexural modulus, resistance to solvents and chemical degradation, good electrical insulating properties, a high melting point, yet with sufficient thermal stability so that it can be readily molded or applied by certain coating techniques. This list of applications will continue to grow as the design engineer becomes familiar with the properties and possibilities that this new plastic has to offer.

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# 8

## Polyimides: Chemistry, Processing, Properties

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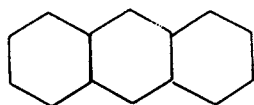
High temperature polymers may be defined as those macromolecules which retain useful physical properties for periods >10,000 hours at 450°F or for >1,000 hours at 500-550°F. Stated alternately, these polymers perform satisfactorily at temperatures above the limits of epoxies or phenolics: Implicit in the designation "high temperature" or "thermostable" polymer are two basic criteria:

- 1) thermo-oxidative stability - the ability to withstand degradation of properties over long periods at high temperatures in air.
- 2) thermophysical profile - specimen must retain a substantial percentage of room temperature strength and modulus at elevated use temperature. Plasticity or creep should not limit the utility to temperatures below the thermo-oxidative limit. Workers new to the field, particularly those with chemical rather than engineering background, tend to emphasize the first criterion at risk of neglect to the second. It is evident that both must be given weight, since either can be utility limiting.

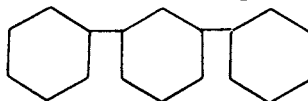
Although the point will be stressed later in this paper, it must be stated at the outset that requirement for rigidity at 550°F necessitates chemical structures of chain stiffness sufficient to place severe constraint on achieving facile processability.

### The Structures

To achieve the thermal performance just described requires, generally polymer chains possessing several fused rings.



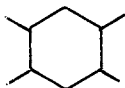
Fused rings



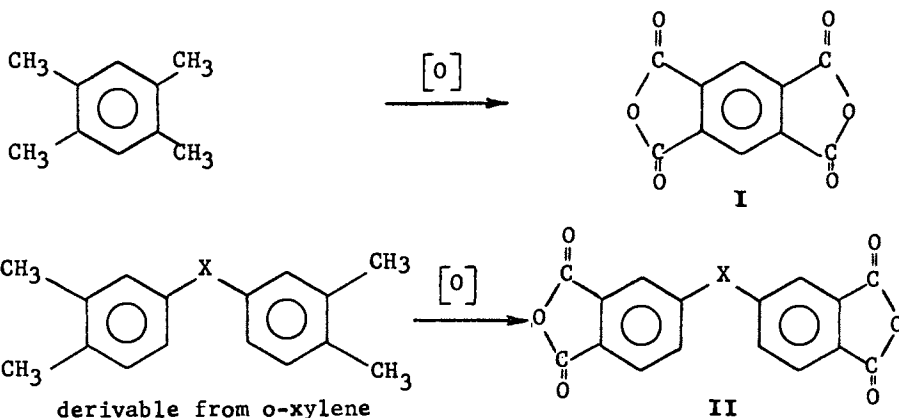
Non-fused chain of rings

\*Paper prepared when both authors were members of the CIBA-GEIGY

Focusing attention on the center member of the fused ring structure, we see that four chemical bonds extend:

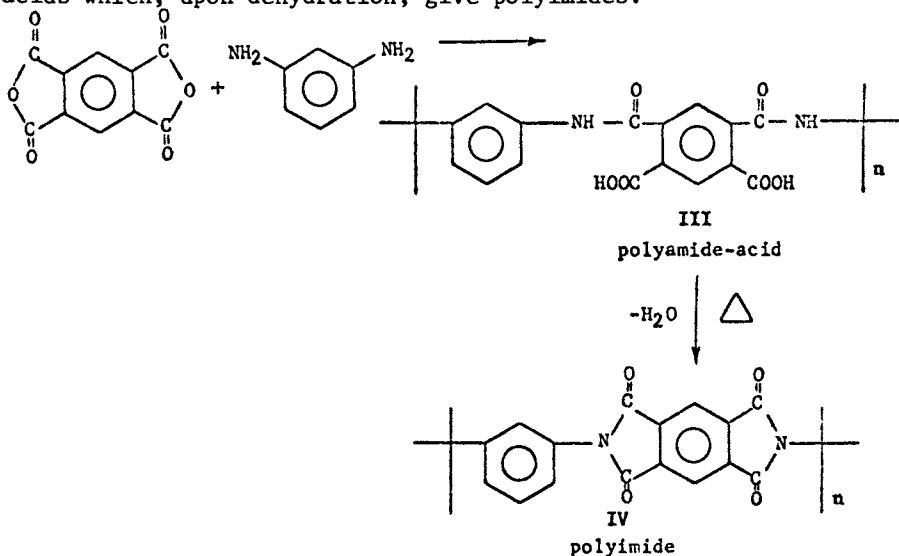


Thus, to build structures with reasonable concentrations of fused rings, at least one tetrafunctional monomer is required. Such materials are generally more costly than mono- or difunctional compounds. Notable exceptions are those tetrafunctional materials obtainable by oxidation of methyl groups.

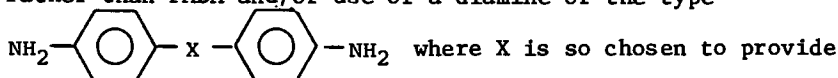


Compound (I) is pyromellitic dianhydride (PMDA) and (II), when  $X = \text{C}_6\text{H}_4$ , is benzophenonetetracarboxylic dianhydride (BDTA).

Reaction of dianhydrides with diamines affords polyamide-acids which, upon dehydration, give polyimides.



The structure may be made more tractable by employment of BTDA rather than PMDA and/or use of a diamine of the type



greater molecular mobility.

Of all thermostable polymers, polyimides are the cost-effective candidates, due to combination of thermal stability, processing characteristics and, most particularly, low cost - due to derivability from the only available inexpensive tetrafunctional monomers.

### The Processing Dilemma

The initial applications of polyimides were as varnishes and overcoat enamels as wire insulation. Polyimides provided significant improvement in high temperature cut through resistance as well as excellent dielectric properties. They continue in use today both as homopolymers and copolymers with amides and ester moieties. Paralleling this technology was the development by duPont of Kapton<sup>®</sup> polyimide film. Kapton enjoys a strong position as a class 220+ organic film. These applications represent the major portion of polyimide consumption.

Applications to engineering end uses have been slower to develop due to greater demands in processing. The remainder of this discussion is developed to such engineering applications typified by laminates, composites and molded articles.

Processing considerations overshadow all others in competition for attention by current workers in this field. Two key problems are at the root of the frustration. The first was alluded to earlier, namely that of chain stiffness, required for satisfactory thermophysical profile and adequate stability, places a constraint on processability. Engineers desire polyimide materials which can be processed under low pressure at temperatures between 350-400°F. This is mandated by autoclave procedures in the industry which employ equipment, bagging materials, tooling, seals and the like designed for use with epoxies and phenolics. The problem is real, not merely the stubborn whim of a few possessing too much inertia for change, but necessity being the mother of invention has provided for the development of improved bagging systems capable of higher temperatures.

However the constant effort of polyimide suppliers is to provide materials which will flow during fabrication of parts below 400°F, but which will retain structural stiffness in use of that part at 550°F. The polymer chain stiffness which affords 550°F physicals wrecks havoc with 350-400°F processing. Even low molecular weight prepolymers which can build during cure to higher molecular weight crosslinked structures often do not flow below 400°F unless a species is chosen which sacrifices 550°F thermo-physical properties.

The second source of frustration stems from the condensation reactions employed to build macromolecular polyimides from polyamide-acids, prepolymers, or monomer mixtures. Condensation reactions eliminate one small molecule (e.g. water, alcohol, acetic acid) for every bond formed. Yet the great majority of practical reactions leading to stable rings with aromatic character are formed by condensation. This means while imide formation is taking place, volatiles (one mole per mole of ring formed - one mole of gas occupies 40 liters at 400°F) are eliminated. These gases give rise to voids in the fabricated part which reduce drastically the physical properties obtainable and sacrifice thermo-oxidative stability. More recently polyimides possessing solubility in their ring closed, imidized, form have been made available, however, other polyimide characteristics are compromised and shall be discussed in more detail in a later section.

### The State of the Art

The constraints upon processing described above have not been fully resolved, but progress has been made which permits employment of polyimides in engineering composites, molded articles and to a very limited extent, structural adhesives. The principal avenues employed are discussed below.

a) Compromise. Facile processability can be readily achieved by backing away from all aromatic chain-stiff structures through incorporation of aliphatic moieties. Early in the development of high temperature polymer science, these avenues were investigated, but have been largely discarded. The attendant sacrifice of thermo-oxidative stability and thermophysical profile pushes performance down to the phenolics range, a class of polymer with which polyimides cannot compete economically.

b) Processing under severe conditions. Patents issued to duPont teach that the high molecular weight reaction product of oxydianiline and PMDA can be formed under severe conditions of temperature and pressure into certain simple shapes. Products marketed under the trade-name Vespel are believed fabricated by such techniques. Complex articles are machined from the basic shapes.

Carborundum Co. has announced availability of a high temperature aromatic polyester, Ekonol. This material, too, requires processing under conditions deemed severe by conventional plastics industry standards, although more processable versions have recently been introduced.

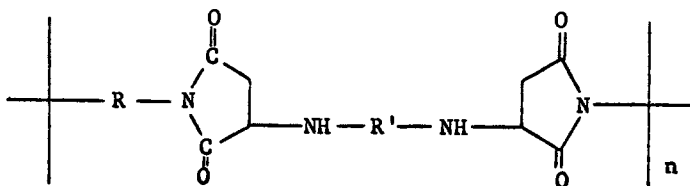
c) Processing polyamide-acids vs polyimides (state of the art). As stated earlier, the initial reaction product of a dianhydride with a diamine is a polyamide-acid, ordinarily soluble in highly polar solvents such as dimethyl formamide (DMF) and N-methylpyrrolidone (NMP). Advantage may be taken of such solutions to fabricate thin (non-engineering) items such as fibers, films and wire-enamels. While polyimide fibers are not

commercial, film (Kapton, duPont) and wire enamel (Pyre-ML, duPont) are. However, problems inherent to removing copious quantities of solvent preclude efficient manufacture of laminated or molded articles via this route. Prepregging, B-staging and laminating with such varnishes generally gives disappointing results due to lack of flow with dry prepreg and serious volatiles problems with wet.

d) Approaches based on processing of monomers. (1) Patents issued to Monsanto Company teach that diesters of BTDA can be mixed in solution with aromatic diamines to afford high solids varnishes stable for long periods. Reaction of the BTDA diester with diamine begins during B-staging, but the resin remains sufficiently non-advanced to permit facile flow under mild vacuum bag-autoclave conditions. However, volatiles generated during completion of the reaction can give rise to voids as described above.

(2) Acylated diamine technology. A polyimide system QX-13, has been marketed by ICI of the United Kingdom. This composition is reported<sup>2</sup> to be a mixture of diacetylmethylenedianiline with BTDA. Upon cure, acetic acid is liberated. Processing conditions employed and physical properties obtained are generally similar to other condensation polyimide resins.

(3) Polyaminobismaleimide resins. Patents issued to Rhone-Poulenc teach a novel approach to attainment of low temperature processing without volatiles evolution. Commercial resins based on this technology are described by M.A.J. Mallet<sup>3</sup> as mixtures of methylenedianiline (MDA) with the bismaleimide of methylenedianiline chain extend and crosslink upon thermal treatment to afford excellently consolidated parts under modest processing conditions. Strictly speaking, the thermal reaction product of such a monomer mixture is a polymaleimide, which structure is not fully aromatic. This contrast with the fused ring aromatic polyimide structures described (illustrated on page 101.



polymaleimide  
(idealized structure)

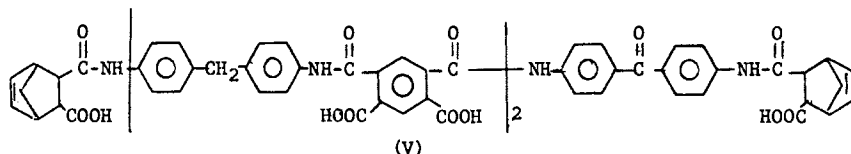
Accordingly, a price is paid in thermo-oxidative stability to attain low temperature and pressure volatiles-free curing to composites of excellent initial physical properties.

(4) TRW/CIBA-GEIGY technology. Under contract from NASA-Lewis, TRW Systems Group, developed an addition polyimide resin

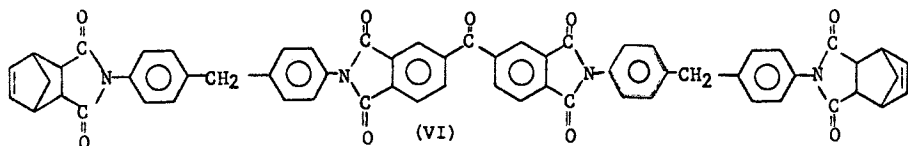


named P13N.

P13N is a true polyamide-acid prepolymer of molecular weight 1300, end capped with Nadic anhydride to permit addition cure, precluding volatiles elimination and void formation. The varnish is supplied as a 40% solids solution in DMF containing the following idealized species (V).



B-staging on the reinforcement can be carried to full imidization if desired to afford a non-volatiles generating prepreg for use in press molding (VI).



Idealized structure of B-staged P13N

Chain extension (curing) occurs between 475–575°F by addition reactions of the nadic end groups to afford articles of excellent thermal stability and physical properties. Since the product is predominantly aromatic polyimide, thermal stability lies close to that obtained with the all aromatic compositions and well above polymaleimides. However, due to volatiles-free processing, physical properties, as with the latter, are much easier to develop than with condensation systems.

P13N resin is an excellent base for the formulation of both particulate and reinforced molding compounds. Three avenues can be employed.

- 1) Dry blending of P13N powder (commercially available) with fillers.
- 2) Slurrying of P13N varnish with fillers, followed by drying, B-staging and crushing.
- 3) Impregnation of a fiber tow with P13N varnish, followed by drying, B-staging and chopping.

The polyimide molding compound prepared by any of the above techniques is processed in a preheated mold at 550–600°F, followed by post cure to 625°F for 2–8 hours for development of maximum physical properties. Absence of volatile by-products permits facile production of sound moldings having thick sections, while the modest (1300) molecular weight of the prepolymer permits flow at reasonable temperatures.

P13N laminating varnish, while excellently suited for press laminating, is not recommended for autoclave laminate processing.

Gelation, which sets in at temperatures below that required for flow at slow heat-up rates, does not permit consolidation prior to cure during the gradual temperature rise of commercial autoclaves (contrast press-molding in which a press preheated to 550°F is recommended).

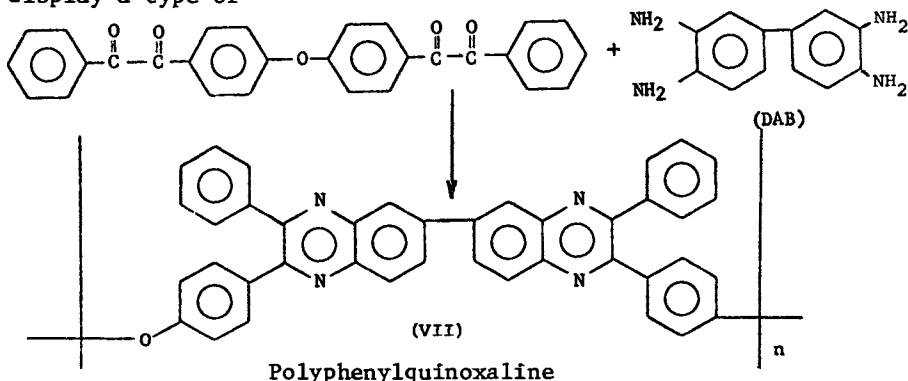
To overcome the lack of autoclavability of P13N laminating varnish both TRW and CIBA-GEIGY, who acquired technology rights in 1970, have been working both jointly and independently to provide modified versions possessing the requisite flow. One system is P105A. In this variant, 20% of the methylenedianiline was replaced by thiodianiline (TDA) and the molecular weight was dropped to 1050. In contrast to P13N which demands rapid heat rise for processing, the modified resin cures virtually independent of heat-up rate, values as low as 1°F/minute being acceptable. Facile autoclavability is thus obtained, while the volatiles free cure of the system is retained. The requirement for processing at 550°F remains, however.

Such resins offer similar "forgiveness" in molding applications. Requirement for employing a preheated mold to ensure rapid heat-up is obviated, and transfer molding can be easily achieved.

Studies employing the Brabender PlastiCorder reveal that P105A and developmental variants higher in TDA content can be held in the melt stage at elevated temperatures upwards of one hour prior to cure. Such performance suggests a variety of impregnation and extrusion applications, which processes are currently under investigation.

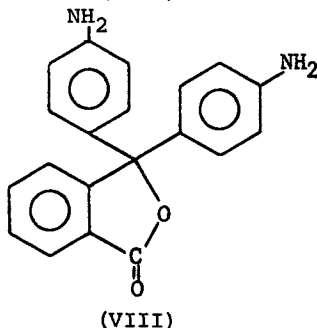
It is our opinion that pyrolytic polymerization technology provides an optimum balance of processability and property retention.

5) Soluble polyimides. As previously mentioned most recent activities have centered about soluble polyimides. Though solubility would not be expected with polymers having a fused ring backbone, promise of solubility was indicated by the peculiar properties of polyquinoxalines (VII) which have been shown to display a type of



behavior which is not possessed by compositions described previously. Polymers such as VII demonstrate both solubility and melt flow in the fully ring-closed form. Thus, processability can be achieved in a wholly aromatic system free of complications from reaction volatiles. To be sure, to obtain a thermophysical profile in the range of Skybond or P13N systems requires choice of a structure with very high "T<sub>g</sub>" (>600°F), and this results in very high processing temperatures. Nonetheless, it is possible to obtain sound, void-free laminates and moldings employing these techniques. Unfortunately, the tetrafunctional monomers required are costly. However, there are reports that one of these, diaminobenzidine (DAB) may become available at reasonable cost due to potential volume use in polybenzimidazole fibers for the Air Force.

The indication that fully aromatic polyimides could exist with both flow and solubility in the closed-ring form came from the Russian scientist, Korshak, who developed the polyimide based upon anilinephthalein (VIII) and BTDA.



Unfortunately, thermal stability of this system was modest.

During the past two years, there has been considerable activity with soluble polyimides, the Upjohn Company offering several candidates commercially, while both CIBA-GEIGY and duPont revealed developmental compositions. Patent literature indicates related activity in Japan and Germany as well.

High molecular weight soluble polyimides are indeed "polyquinoxaline"-like in their physical properties. Unfortunately the complete elimination of solvent in molding powders and prepreg was not easily achieved in our laboratories and thus, the formation of void free functional articles has proven difficult. Also their requirement for high processing temperatures and somewhat diminished thermophysical profile is expected to limit commercial acceptance into engineering end uses.

### Properties and Applications

Composite Structures. Polyimides have been utilized for the fabrication of composites of quartz, glass, boron, graphite and

	BORON		GRAPHITE		GLASS	
	Room Temp.	600°F	Room Temp.	600°F	Room Temp.	600°F
<u>Press Molded</u>						
Flexural ST	$2.45 \times 10^5$ psi	$2.48 \times 10^5$ psi	HM-S $1.54 \times 10^5$ psi	$0.91 \times 10^5$ psi	$80-90 \times 10^3$ psi	$50-65 \times 10^3$ psi
Flexural Mod.	$2.49 \times 10^7$ psi	$2.02 \times 10^7$ psi	$2.70 \times 10^7$ psi	$2.20 \times 10^7$ psi	$3.5-4.0 \times 10^6$ psi	$2.8-3.0 \times 10^6$ psi
SBS.	13,100 psi	10,400 psi	9,3000 psi	6,100 psi	8,000 psi	3200-3500 psi
			BT-S $2.20 \times 10^5$ psi	$1.12 \times 10^5$ psi		
			$2.3 \times 10^7$ psi	$2.10 \times 10^7$ psi		
			13,800 psi	7,700 psi		
<u>Autoclave Molded</u>						
Flexural ST	$2.45 \times 10^5$ psi	$2.22 \times 10^5$ psi	HT-S $2.00 \times 10^5$ psi	$1.36 \times 10^5$ psi		
Flexural Mod.	$2.20 \times 10^7$ psi	$1.90 \times 10^7$ psi	$1.40 \times 10^7$ psi	$1.33 \times 10^7$ psi		
SBS.	10,500 psi		11,225 psi			
			Type A $2.26 \times 10^5$ psi	$1.55 \times 10^5$ psi		
			$1.26 \times 10^7$ psi	$1.04 \times 10^7$ psi		
			11,000 psi	6,400 psi		

Figure 1. Physical properties

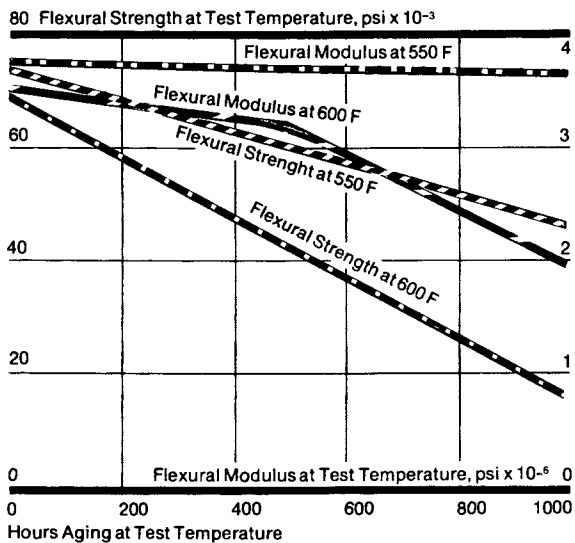


Figure 2. Typical flexural properties of E glass reinforced PI3N laminates as a function of aging in air at elevated temperatures

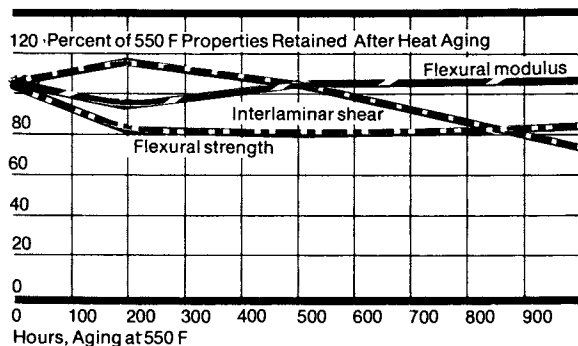


Figure 3. Flexural strength, flexural modulus, and short beam shear at 550°F of non-post cured PI3N/boron specimens after aging at 550°F

Property	Value	ASTM Test Method
Specific Gravity, g/cc	1.33	D-792, Method A
Hardness, Shore D	90.5-91.5	D-790
Flexural Strength, psi		D-790
25 C (77 F)	10,000-12,000	
260 C (500 F)	6,000-8,000	
288 C (550 F)	5,000-8,000	
Flexural Modulus, psi x 10 <sup>6</sup>		D-790
25 C (77 F)	4.6-4.9	
260 C (500 F)	3.0-3.3	
288 C (550 F)	2.6-3.0	
Tensile Strength, psi		D-657
25 C (77 F)	7,260	
260 C (500 F)	5,700	
Tensile Modulus, psi x 10 <sup>6</sup>		D-657
25 C (77 F)	5.56	
260 C (500 F)	3.46	
Elongation at Failure, %		D-657
25 C (77 F)	1.37	
260 C (500 F)	1.82	
Compressive Strength, psi		D-695
25 C (77 F)	37,000	
260 C (500 F)	—	
Compressive Modulus, psi x 10 <sup>6</sup>		D-695
25 C (77 F)	4.19	
260 C (500 F)	—	
Compressive Strain at Failure, %		D-695
25 C (77 F)	14-17	
260 C (500 F)	—	
Deflection Temperature		D-648
Before Post cure	> 300 C	
After Post cure	> 300 C	
Heat Resistance, Aged, % Weight Loss	<b>316 C (600 F)</b> <b>266 C (500 F)</b>	
100 hours	2.3	1.4
250 hours	3.7	1.2
500 hours	6.9	2.5
750 hours	8.2	2.5
Coefficient of Linear Thermal Expansion in./in./C at 25 C to 225 C	2.3 x 10 <sup>-5</sup>	D-696
Water Absorption, immersion at	<b>23 C</b> <b>100 C</b>	D-510
24 hours	0.4%	1.9%
7 days	1.3%	—
Molded Shrinkage (in./in.)	1.26 x 10 <sup>-2</sup>	D-256
Specific Heat, cal/°C/gm	0.287	
Thermal Conductivity BTU-in./hr.-ft. <sup>2</sup> -°F	1.56	Cenco-Fitch
Flammability, Limited Oxygen Index	31.6	D-2863-70

Figure 4. Physical data for PI3N polyimide molding powder

Figure 5. Summary of typical properties (machined and direct formed parts)\*\*

PROPERTY	TEMP. °F.	ASTM METHOD	UNITS	DU PONT POLYIMIDE COMPOSITION													
				SP-1 (Base resin)			SP-21 (15% Graphite)			SP-22 (40% Graphite)			SP-31 (15% acetylenesum dust/Phs)			SP-6 (50% glass fibers)	
				M <sub>⊥</sub> <sup>a</sup>	M <sub>∥</sub> <sup>a</sup>	D-1 <sup>b</sup>	M <sub>⊥</sub>	M <sub>∥</sub>	D-1 <sub>⊥</sub>	M <sub>⊥</sub>	M <sub>∥</sub>	D-1 <sub>⊥</sub>	M <sub>⊥</sub>	M <sub>∥</sub>	D-1 <sub>⊥</sub>	M <sub>⊥</sub>	M <sub>∥</sub>
<b>MECHANICAL</b>																	
Tensile Strength (ultimate)	73	D1708	psi × 10 <sup>3</sup>	14.5	11.0	10.5	11.5	6.3	9.0	8.7	6.5	7.3	14.2	9.5	10.2	7.1	3.7
	572			6.3	4.8		6.0	4.4		4.3	2.8		7.2	5.3			
Tensile Elongation (ultimate)	73	D1708	%	8.0	5.0	6.5	4.5	2.0	4.5	2.8	1.8	2.5	9.4	4.8	6.5	0.8	0.5
	572			3.0	2.5		3.0	1.8		1.3	0.9		6.3	3.6			
Tensile Modulus	73	D1708	psi × 10 <sup>3</sup>	485	450	380	630	540	470	730	620	720	945	440		1350	895
	572			300	275		450	385		440	310		315	285			
Flexural Strength (ultimate)	73	D780	psi × 10 <sup>3</sup>	18.5	15.5	11.0	18.0	11.4	7.5	15.4	9.8		22.0	16.0		12.0	6.0
	572			10.5	8.4		9.9	6.2		7.9	5.2						
Flexural Strain (ultimate)	73	D780	%	12.7	9.8	8.3	7.1	3.5	2.3	2.0	2.1		8.6	6.1		1.2	1.5
	572			4.9	4.1		4.0	2.4		1.8	1.6						
Flexural Modulus	73	D780	psi × 10 <sup>3</sup>	480	440	420	670	585	480	800	630		534	485		1000	620
	572			275	250		380	308		560	385						
Compressive Strength (ultimate)	73	D635	psi × 10 <sup>3</sup>	35.7*	45.0*	18.7	29.0	34.0	17.4	18.2	18.5						
	572			18.5*	19.3*		9.3	9.9		10.0	10.8						
Compressive Strain (ultimate)	73	D635	%	>50*	>60*		33.0	30.0		13.3	18.2						
	572			>50*	>60*		14.0	13.0		11.3	11.4						
Compressive Modulus	73	D635	psi × 10 <sup>3</sup>	569	615		630	640		600	600						
	572			276	235		300	290		380	430						
<b>ELECTRICAL</b>																	
Dielectric Constant at 10 <sup>3</sup> Hz	33	D180			3.41			7.80									
	506				3.01												
Dissipation Factor at 10 <sup>3</sup> Hz	73	D180			.0052			.0040									
	506				.0011												
Dielectric Strength - short time 80 mils thickness		D143	vols/mil					250									
Volume Resistivity	73	D267	ohm-cm.		10 <sup>14</sup> -10 <sup>17</sup>			1.5 × 10 <sup>13</sup>									
Surface Resistivity	73	D267	ohms/square		10 <sup>12</sup> -10 <sup>16</sup>												
Arc Resistance		D485	seconds		230												
<b>WEAR AND FRICTION</b>																	
Wear Rate (unlubricated) in nitrogen (PV = 25,000) in air (PV = 25,000)			mil/1800 hrs.		.010-.015 .25-1.2			.004 .09					.05 .26				

NOTES: (a) M designates specimens machined from molded billets. ⊥ and ∥ denote direction of specimen orientation relative to direction of molding (perpendicular and parallel respectively). Most values for polyimide parts produced from rod and tube forms are between the M<sub>⊥</sub> and M<sub>∥</sub> values.

(b) D-1 designates direct-formed specimens measured only in the ⊥ direction due to thickness limitations. Direct-formed parts have a fractional percentage of TEFLON TFE fluorocarbon resin added to facilitate processing.

(\*) For SP-1, these are compressive stresses at 50% strain, not ultimate strengths. Specimens did not fail.

\*\*Du Pont Vespel Design Handbook A 72582

PRD-49. The two principal applications of today are jet engine noise suppression devices and radomes for supersonic aircraft. These applications employ polyimides excellent property retention at elevated temperature and long term oxidative stability. In the radome application use is also made of their excellent dielectric properties and the desirable flat profile of these properties versus temperature.

More recently polyimides are attracting attention in combination with graphite fiber; less the result of the high temperature properties than insensitivity to moisture. Experience<sup>4</sup> has shown the deterioration of conventional composites during ambient storage to be the result of absorption of moisture. The infiltrated water apparently plasticizes conventional matrices causing significant deterioration of elevated temperature (300°F or higher) strength. The insensitivity of polyimides<sup>5</sup> to moisture and their extra margin of thermal performance (to 600°F) has made their potential utility attractive. Typical properties of these engineering laminates are presented in Figures 2 and 3.

A second area of potential and perhaps the largest is molding compounds. Applications are virtually unlimited since almost any property achieved with conventional molding compounds such as phenolic and epoxy can be realized with the polyimides, accompanied by extension of the desired properties to 550°-600°F. Required is identification of those applications which require the temperature capability; albeit cost effectiveness is the prime consideration. It is difficult to do justice to the myriad of matrix/reinforcement combinations; accordingly, properties obtainable are summarized in Figures 4 and 5.

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# 9

## Polyaminobismaleimides

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### 1. Introduction

Polyimide resins constitute a family of plastics possessed of dramatically superior properties when compared to more conventional plastics. Of particular importance is their ability to maintain useful mechanical properties after extreme thermal exposures for prolonged periods of time. The genesis of this attribute is two-fold --the highly aromatic nature of the polymer backbone, which confers the heat stability, and the imide moiety, which imparts stiffness to the macromolecular chain. The facile oxidation at elevated temperature of aliphatic polymer systems and the necessity for fused rings to achieve high resin glass transition temperatures and concomitant elevated temperature polymer mechanicals are well recognized and amply documented.

Two fundamentally different approaches to the molecular architecture of polyimides can be employed:

- The historically-first synthetic method consists in constructing tractable, high molecular weight precursors, called polyamic acids, which are imidized during the cure cycle, with loss of water, to the intractable, insoluble, infusible condensation polyimides.

- The more recent synthetic route preimidizes short molecular segments, similar in nature to those of condensation polyimides. Cure is by polymerization



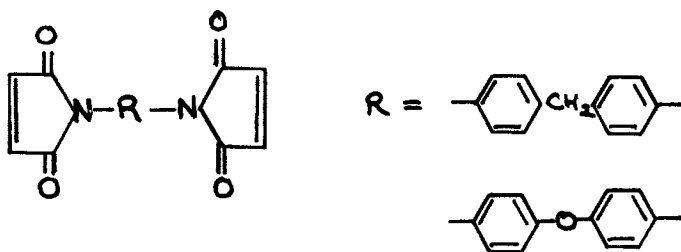
of the reactive termini of the "prepolymers" without loss of volatiles. These are the addition polyimides.

While condensation polyimides afford the most heat stable polymers, they are generally difficult and expensive to process and afford voidy parts. Epitomal of the heat resistance properties of condensation polyimides are the 20,000+ and 9,000 hour service lives of NOLIMID A380 adhesive for titanium bonds at temperatures of 500° and 575°F, respectively.

By contrast, addition polyimides allow the reproducible and facile preparation of large and void-free parts at only a modest sacrifice in end article thermal stability. Polyamino-bismaleimides (PABM's) are members of the additive polyimide class of resins.

## 2. Polyaminobismaleimide Chemistry

Multitudes of researchers have investigated the high reactivity of the activated double bonds of bismaleimides, as shown below.



Maleimide double bonds can react by either homolytic or heterolytic scission. In the former case, homopolymerization with a second maleimide group is observed; in the latter event, nucleophilic addition is possible.

Irradiation at 240°C, and at reduced pressure, of 1,4-dimaleimidobenzene affords 50% yields of poly-bismaleimides, which remain unaffected by temperatures as high as 600°C (Ivanov; Russian Patent #164,678). Similarly, heating of 4,4'-dimaleimidodiphenylmethane affords polymers which are heat stable to 460°C. These infusible and intractable products suffer from extreme brittleness, which severely restricts their practical utility (Sambeth & Grundschober; French Patent #1,455,514).

Working in the area of elastomers, Kovacic (U. S. Patent #2,818,407; Dec. 31, 1957) reported the Michael addition of amine capped prepolymers to bis-maleimides. Similarly, Sheremeteva and co-workers found that reaction of stoichiometric amounts of bis-maleimides and primary aromatic diamines in refluxing ethanol afforded polymers, which thermally degraded so rapidly that they could not be considered heat resistant.

Recent work in Rhone-Poulenc's laboratories, summarized in U. S. Patent #3,562,223 (July 13, 1967), has shown that by judicious selection of a bis-maleimide to aromatic diamine ratio between these two reaction extremes, it has proven possible to develop a class of polyimide resins with outstanding physicals and controlled crosslink density. (Figure 1).

While side-reactions of the primary aromatic amine with the maleimide moiety were to be feared, none are in fact observed. Thus, N-butylamine aminolyzes succinimides readily in a modification of the time-honored (1887) Gabriel synthesis of amino acids; by contrast, aniline does not react with succinimides, even in hot DMF. This contrast in behavior between primary aliphatic and aromatic amines is ascribable to their vastly different basicities ( $pK_b$ 's of 3.3 and 9.3, respectively).

Finally, maleimides are traditionally prepared by a two-step synthesis (e. g. Searle; U. S. Patent #2,444,536; May 14, 1946). Reaction of maleic anhydride with an amine at room temperature, in either NMP, DMF or acetone, affords the intermediate maleamic acid, which is then cyclodehydrated by acetic anhydride at 60°C in DMF.

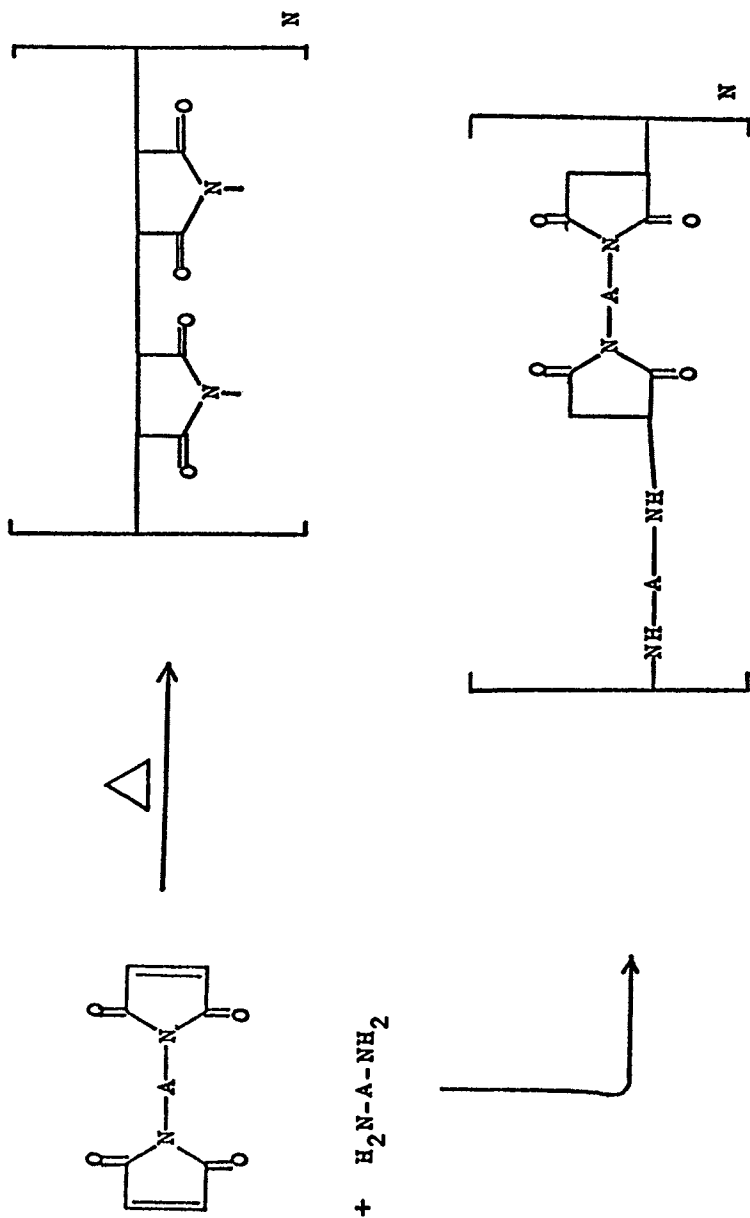


Figure 1. PABM chemistry

Figure 2a. TGA curves of PAEM's in air

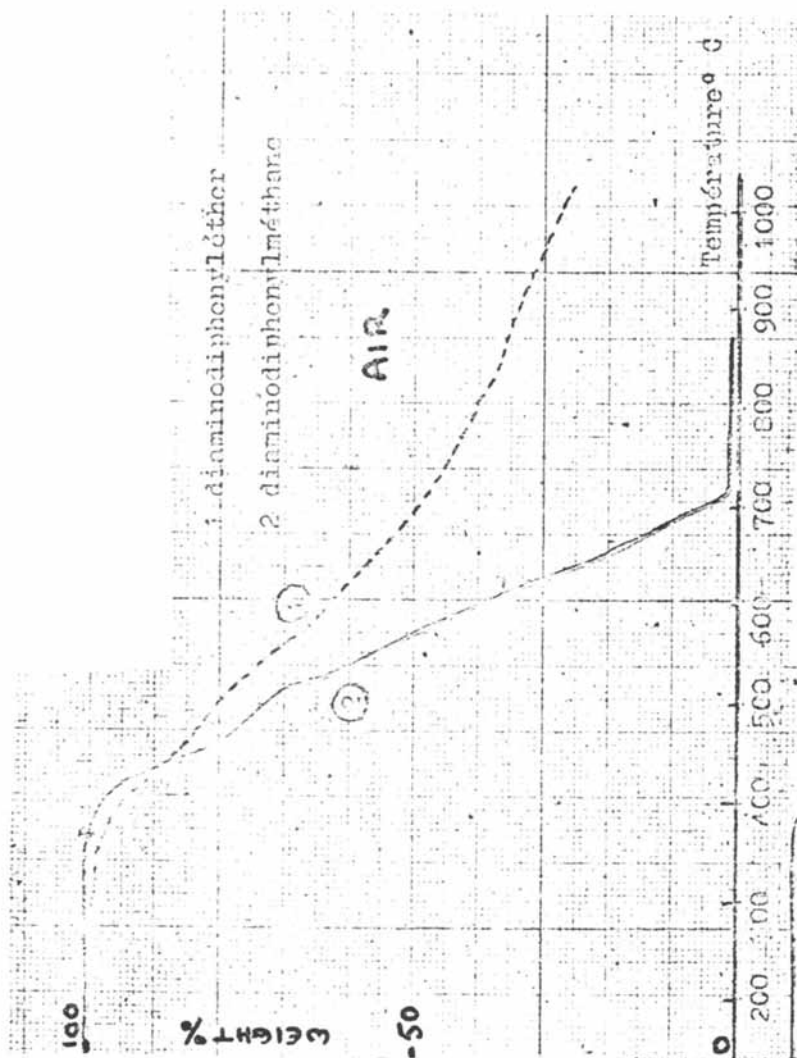
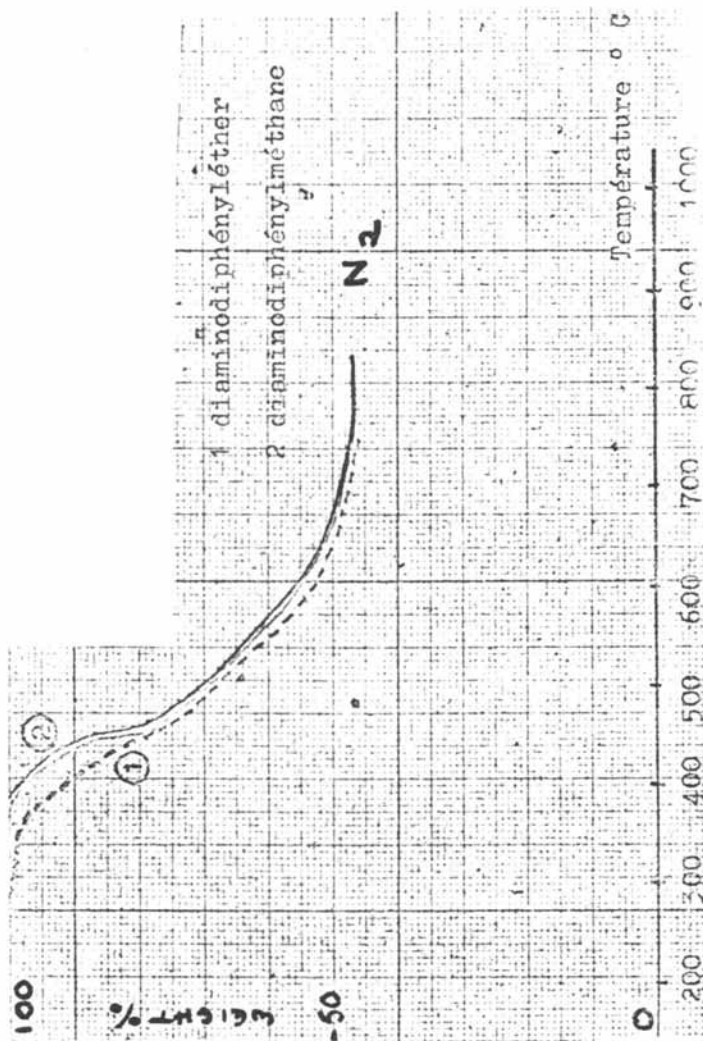
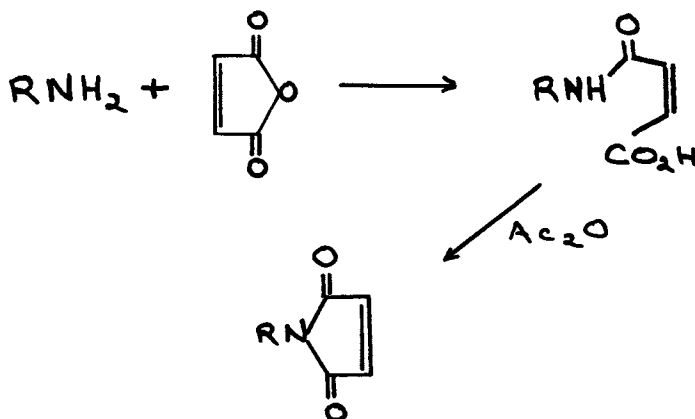


Figure 2b. TGA curves of PABM's in nitrogen





### 3. Polyaminobismaleimide Properties

The thermal resistance of polyaminobismaleimides may be evaluated by three criteria -- thermogravimetric analysis, thermophysical profile, and thermooxidative resistance.

3.1 Thermogravimetric Analysis. Figure 2 shows the TGA curves obtained for PABM's derived from methylenedianiline and oxydianiline under air and nitrogen atmospheres. In both cases, scan rates of 20°F/min were employed. These curves reveal that:

- the TGA main breakpoint, under either air or nitrogen, is 360°C for MDA-derived PABM's and 290°C for ODA-derived PABM's;
- until 500°C, curves obtained in air and nitrogen are identical;
- char yield is ca. 47% for both PABM systems.

The conclusion to be drawn from this information is that ODA or MDA based PABM's behave almost identically on thermal exposure. This is not totally unexpected, as the dominant factor, or alternatively the weak link, in oxidative degradation of these

polymers is the aliphatic prepolymer termini, which are identical for both resins.

**3.2 Thermophysical Profile.** Typical 181 E-glass (A-1100 finish) PABM laminate mechanicals are shown in Table I. Room temperature flexural strength and modulus are 70,000 psi and 4,000,000 psi, respectively. These laminates retain 70% and 80%, respectively of their room temperature flexural strength and modulus at 480°F.

To allow a more meaningful comparison of PABM's with competitive resin systems, typical room temperature, 400°F, and 480°F laminate flexural strengths are tabulated below. Percentage figures in parenthesis represent the retention of room temperature properties.

	Flexural Strength at:		
	R.T.	400°F	480°F
PABM	70 KSI	60 KSI (85%)	50 KSI (70%)
EPOXY NOVOLAC	70 KSI	32 KSI (45%)	20 KSI (30%)
EPOXY	80 KSI	20 KSI (25%)	15 KSI (20%)
SILICONE	37 KSI	20 KSI (55%)	18 KSI (50%)

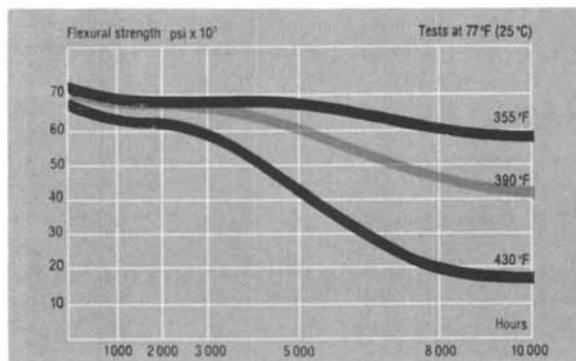
**3.3 Thermooxidative Stability.** Figures 3-6 detail the retention of PABM laminate (A-1100 finish) flexural strength and modulus after extended aging periods at temperature varying from 355° to 480°F. 85% of initial flexural strength (either room or elevated temperature) is maintained after 10,000 hours of aging at 355°F. Using as laminate half-life criterion, 50% retention of initial flexural strength, the following values are obtained for PABM's:

- 10,000 hours at 400°F; and
- 4,000 hours at 480°F (CS-290 finish).  
Comparable 480°F half-life values are:
- 2,000 hours for Freidel-Crafts phenolic resins (source: Albright and Wilson); and
- 250 hours for unmodified phenolic resins.

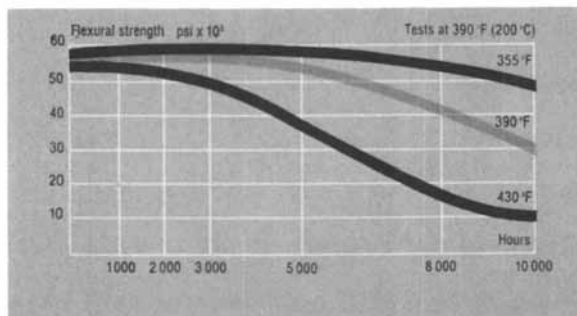
**TABLE I. PABM/181 E-Glass Laminate Physicals**

	ASTM Standard	Unit		
Flexural strength	D 790	psi × 10 <sup>3</sup>		
• at 77 °F (25 °C) .....			about	70
• at 390 °F (200 °C) .....			—	60
• at 480 °F (250 °C) .....			—	50
Flexural Modulus	D 790	psi × 10 <sup>3</sup>		
• at 77 °F (25 °C) .....			about	4,000
• at 390 °F (200 °C) .....			—	3,800
• at 480 °F (250 °C) .....			—	3,200
Tensile strength	D 638	psi × 10 <sup>3</sup>		
• at 77 °F (25 °C) .....			about	50
Compressive strength	D 695	psi × 10 <sup>3</sup>		
• at 77 °F (25 °C) .....			about	50
Delaminating strength	D 2345	psi		
• at 77 °F (25 °C) .....			about	2150
Izod impact strength	D 256			
• at 77 °F (25 °C) .....				
— notched .....		ft × lb/in	about	13
— unnotched .....		ft × lb/in	—	15





*Figure 3. Changes in flexural strength during thermal aging at 355°, 390°, and 430°F (180°, 200°, and 220°C)*



*Figure 4. Changes in flexural strength during thermal aging at 355°, 390°, and 430°F (180°, 200°, and 220°C)*

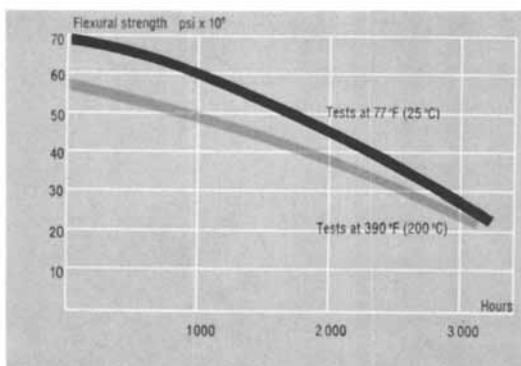


Figure 5. Changes in flexural strength during thermal aging at 480°F (250°C)

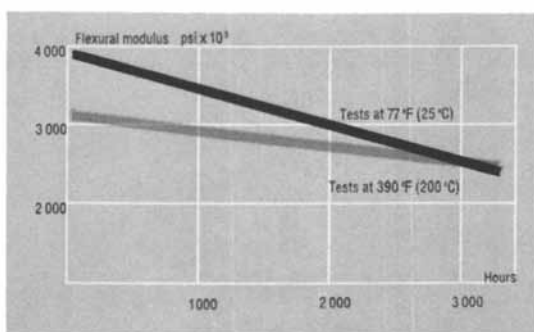


Figure 6. Changes in flexural modulus during thermal aging at 480°F (250°C)

#### 4. Polyaminobismaleimide Processing

Commercial variants of polyaminobismaleimide resins have been formulated to process similarly to conventional phenolics, epoxies, and polyesters. Constituent monomers of the formulation are B-staged to a degree of advancement such that classical rheological studies on PABM's yield Brabender Plasticorder curves whose shape is reminiscent of those of phenolics.

To further quantify these statements, let us note that PABM's have melting points of 100-120°C and gel times which are very temperature dependent. Viscosity increases from 100 to 10,000 poises in 30 min. at 150°C and in 5 min. at 170°C!

In practice, polyaminobismaleimide parts are processed on conventional thermoset transformation equipment (compression, transfer, and injection molding) at 350-400°F, in 5-20 minute cycles, and at 3,000-15,000 psi.

#### 5. Summary

The polyaminobismaleimide resins we have reviewed exhibit many interesting attributes. Among these are their:

- rheology, comparable to that of classical thermo-setting resins;
- moldability at modest temperatures, in conventional presses, and at low cost;
- mechanical properties, superior to those of several metals on a weight basis;
- excellent dimensional stability;
- fire, radiation, cryogenic temperature, and solvent resistance;
- utility in electrical, friction, and ablative applications.

Taken as a whole, these factors suggest that PABM's will fill many 500°F applications in the aircraft, air compressor, aerospace, automotive, bearings, electronic, electrical, and nuclear industries.

# 10

## Processable Polyimides

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### 1. Introduction

Since the discovery of polyimides in the early 1960's, engineers have sought to prepare composite parts where maximum use could be made of their exciting properties. Typical attributes include: high heat resistance (500° F and up), good mechanical properties, wear resistance, low friction, chemical inertness, low outgassing, radiation and cryogenic temperature stability, and inherent non-flammability. These attempts were frequently thwarted, however, by discouraging resin processability. Indeed, extensive and complex cure and post-bake cycles were required and strict adherence to fabrication parameters was demanded.

The historically-first condensation polyimides have recently been complemented by a second class of resins - addition-type polyimides. KINEL compounds and KERIMID 601 laminating resin are members of this new family of polyimides. Chemically they are designated polyaminobismaleimides (PABMs).

Condensation polyimides are predicated on the reaction of an aromatic diamine with an aromatic dianhydride. The resultant, tractable polyamic acid is converted during cure to the infusible, insoluble and intractable polyimide with loss of water.

Addition polyimides are based on short, preimide segments very similar in nature to those of condensation polyimides. These segments are capped by termini which polymerize thermally without loss

of volatiles. Processing is simple; only a slight sacrifice, as compared to condensation polyimides, is noted in cured matrix thermal stability.

The minor decrease in PABM part thermooxidative resistance, as compared to competitive polyimides, is very advantageously compensated for by the:

- ability to mold PABM compounds in conventional thermoset transformation equipment (compression and transfer molding, extrusion, free-sintering) to void-free, multi-pound parts in rapid cure cycles;
- very high compatibility of all particulate and fibrous reinforcements with PABM resin allowing the easy preparation and fabrication of a wide diversity of molding compounds;
- excellent long-term economics—comparable to epoxy molding compounds—which will serve to insure numerous large-volume applications for PABMs.

## 2. PABM Resin

2.1 Chemistry. KINEL/KERIMID 601 chemistry was reviewed in detail in the previous talk on polyaminobismaleimides.

The total absence of volatile generation during cure serves to explain the reproducible and facile preparation of void-free composites and the total insensitivity of molded parts to thermal shock.

2.2 Processing. PABM unfilled resin and molding compounds are generally processed at 380-480°F and 3000 psi in 2-30 minute cycles. Cycle times depend upon the specific reinforcement used and the size of the final part. Typical graphite powder reinforced PABM bearings are molded in 2-5 minutes.

Transfer molding times run 1-5 minutes.

PABM free-sintering is achieved at 15,000 psi in a 15 sec. cold-mold cycle time.

Large (2 to 5 pounds) fiber-glass reinforced PABM parts are cured more rapidly than comparable epoxy moldings owing to the absence of exotherm (5-10 minute cycles).

Post-cures, for maximum development of part mechanicals and heat resistance, are conducted at 450-480°F for 2-16 hours. Step post-cures are unnecessary.

2.3 Properties. PABM parts are capable of operating continuously at 500°F for 1-2000 hours.

PABM pieces possess the room and elevated temperature mechanicals and electricals, the fire, cryogenic

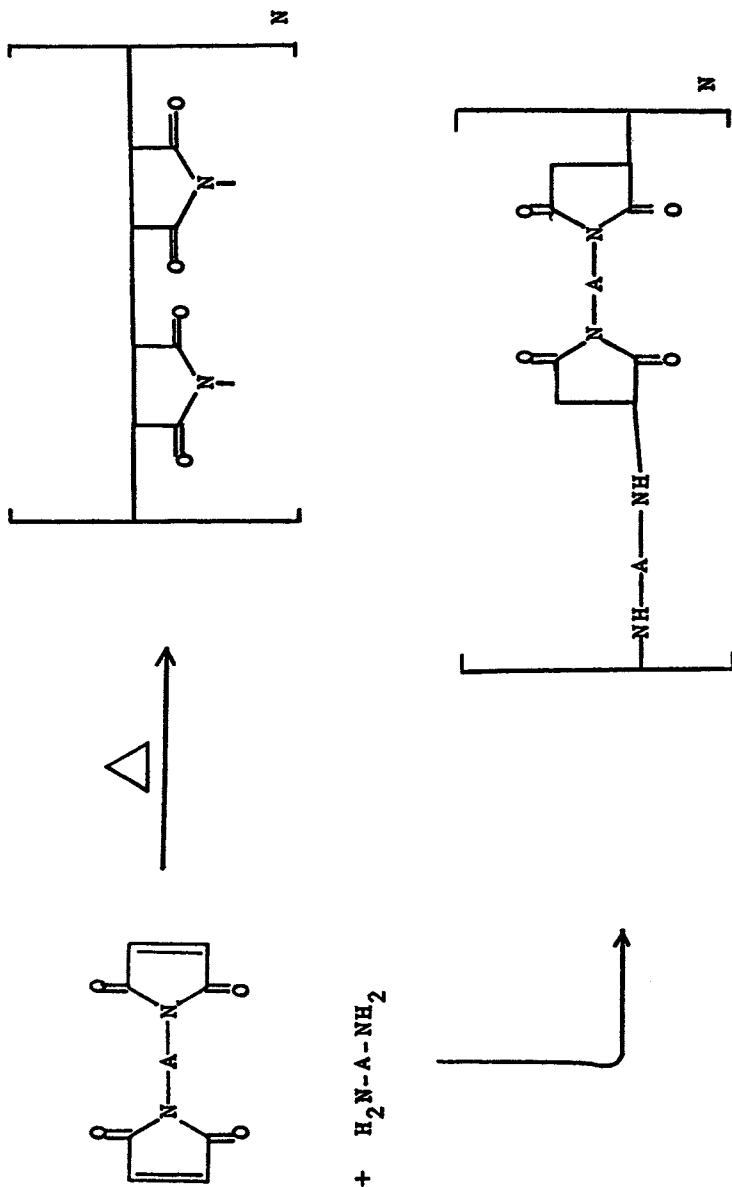


Figure 1. PABM chemistry (U. S. Patent 3,562,223)

temperature, solvent, moisture, and steam resistance traditionally expected of polyimides.

Heat distortion temperatures run 660°F and over for glass-fiber reinforced compositions.

Polyimide part properties are custom tailored by judicious selection of fillers. Typical fillers and engineering end-uses of resultant parts include:

- chopped glass fibers for jet engine parts and electrical connectors;
- graphite powder, molybdenum disulfide, or PTFE for bushings, bearings, thrust washers, valve seats, face seals and piston rings;
- chopped graphite fibers for zero-coefficient of expansion rotary air compressor vanes;
- asbestos fibers for brake linings and vanes;
- diamonds, Borazon, silicone carbide, or aluminum oxide for abrasive wheels; and
- mica or silica powder for potted and encapsulated electronic components.

Specific properties of these compositions will be discussed in subsequent sections.

### 3. Structural KINELS

3.1 Description. Two major families of PABM compounds have been developed to satisfy the needs of two distinct types of end-uses. The first series of PABMs is directed to applications where mechanical properties are of prime import; these PABMs are fiber-glass reinforced.

KINEL 5504 is 65% filled with quarter-inch glass fibers, exhibits the highest mechanical properties of any KINEL (49,500 psi flexural strength and 3.25 MSI flexural modulus at room temperature), and is generally compression molded. Current commercial end-uses include jet engine parts; typical of these are the blocker doors used for retro-thrust in the Rolls-Royce RB.211 engines of the Lockheed L-1011.

KINEL 5514 is 50% filled with eighth-inch glass fibers and is specially formulated for thin wall moldings. Typical end-uses include high-temperature electrical connectors and high precision moldings.

KINEL 5515 is a modified version of 5514, which is particularly suited for transfer molding applications. KINEL 5515 may be cured in 1-5 minutes at 380°F.

3.2 Initial Properties. Representative mechanical, thermal, and physical properties of three structural

TABLE 1  
KINEL 5504 AND 5514 PROPERTIES

	ASTM	KINEL 5504	KINEL 5514
<u>MECHANICAL PROPERTIES*</u>			
Flexural Strength, psi	D 790		
- at 77°F ( 25°C)		49,500	21,300
- at 392°F (200°C)		42,700	18,500
- at 482°F (250°C)		35,500	17,700
Flexural Modulus, psi	D 790		
- at 77°F ( 25°C)		3,250,000	1,980,000
- at 392°F (200°C)		2,980,000	1,710,000
- at 482°F (250°C)		2,420,000	1,490,000
Tensile Strength, psi	D 638		
- at 77°F ( 25°C)		27,000	6,400
- at 482°F (250°C)		22,700	5,400
Compressive Strength, psi	D 695		
- at 77°F ( 25°C)		32,500	34,000
- at 482°F (250°C)		18,400	19,800
Impact Strength, ft x lb/in.	D 256		
Notched Izod at 77°F		17	5.6
Specimen width: 0.5 in.			

\* Measurements were made on molded test specimens.



TABLE I (continued)  
KINEL 5504 AND 5514 PROPERTIES

	KINEL 5504	KINEL 5514
<u>THERMAL PROPERTIES</u>		
Heat Distortion temperature, °F	ASTM D 648 660	660
Flammability	AIR 0978/A	nonflammable
Coefficient of linear expansion from 25 to 300°C in/in/°C from 77 to 572°F in/in/°F	ASTM D 696 15x10 <sup>-6</sup> 8x10 <sup>-6</sup>	13x10 <sup>-6</sup> 8x10 <sup>-6</sup>
Thermal conductivity Btu. in/ft <sup>2</sup> .hr.°F	3.48	2.46
<u>PHYSICAL PROPERTIES</u>		
Specific gravity, g/cm <sup>3</sup> lb/cu.ft.	ASTM D 792 1.9 119	1.7 106
Mold shrinkage, %	ASTM D 1299 0.1	0.2
Hardness	ASTM D 785	

KINELs are shown in Tables I and II.

Particularly outstanding, for all three KINELs, is the very low mold shrinkage—0.1% for 5504, 0.2% for 5514, and 0.1-0.3% for 5515.

KINELs additionally possess good electrical properties over a wide range of temperatures and frequencies. These are shown in Table III.

3.3 Elevated Temperature Properties. KINELs 5504, 5514, and 5515 retain a very large percentage of their room temperature physicals at elevated temperature. The thermophysical profiles of KINELs 5504 and 5514 are graphically shown in Figures 2-4 for flexural strength, flexural modulus, and tensile strength. Values for comparable filled epoxies and phenolics are included for comparison.

% retention of room temperature properties at 480°F are shown below.

	KINEL 5504	KINEL 5514	KINEL 5515
Flexural Strength	72%	83%	79%
Flexural Modulus	74%	75%	67%
Tensile Strength	84%	85%	-
Compressive Strength	57%	58%	-

Finally the low flexural creep of KINEL 5504 at 392°F and under 2,500 psi pressure is shown over 100 hours in Figure 5.

3.4 Thermal Aging. In addition to their high heat distortion temperatures and retention of properties at elevated temperatures, PABMs exhibit outstanding thermooxidative stabilities.

Figures 6 to 9 show the variations in flexural strengths and moduli of KINELs 5504 and 5514, after aging in air at temperatures of 392°F (200°C) and 482°F (250°C) for several thousand hours. All agings were conducted on pre-cut test specimens.

Taking as half-life criterion the retention of 50% of initial flexural strength (measured at room temperature), the following thermal ratings are obtained for KINEL 5504:

Aging Temperature	Half-life
482°F (250°C)	1,300 hrs.
392°F (200°C)	10,000 hrs.
365°F (185°C)	20,000 hrs.

TABLE II.  
KINEL 5515 PROPERTIES

MECHANICAL PROPERTIES

Flexural Strength, psi	ASTM D 790	
- at 77°F (25°C)		16,300
- at 390°F (200°C)		15,000
- at 480°F (250°C)		12,800

Flexural Modulus, psi	ASTM D 790	
- at 77°F (25°C)		1,170,000
- at 390°F (200°C)		890,000
- at 480°F (250°C)		780,000

Impact Strength, ft x lb/in.	ASTM D 256	
Notched Izod at 77°F		1.5 - 2.0

PHYSICAL PROPERTIES

Specific gravity, g/cm <sup>3</sup>	ASTM D 792	1.6
Mold shrinkage	ASTM D 1299	
- perpendicular to transfer axis		0.1 - 0.3%
- parallel to transfer axis		0.2 - 0.3%
Hardness	ASTM D 785	
- Rockwell M		126
Water absorption		
- Change in weight after 24 h immersion in water at 77°F, %		+0.6

TABLE III  
KINEL ELECTRICAL PROPERTIES

	KINEL 5504	KINEL 5514	KINEL 5515
Dielectric Strength at 1MHz (V/mil) - ASTM D 149			
- at 77°F	500	450	525
- at 390°F	---	---	450
- after 24 hr water immersion	375	425	475
Dielectric Constant at 1MHz ASTM D 150			
- at 77°F	4.7	4.5	5.2
- at 390°F	4.8	4.6	---
- after 24 hr water immersion	---	---	5.2
Dissipation Factor at 1MHz ASTM D 150			
- at 77°F	0.007	0.017	0.003
- at 390°F	0.006	0.017	---
after 24 hr water immersion	0.009	0.016	0.012
Volume Resistivity at 1MHz (ohm.cm) ASTM D 257			
- at 77°F	5 x 10 <sup>15</sup>	1 x 10 <sup>16</sup>	1.5 x 10 <sup>15</sup>
- at 212°F	---	---	9 x 10 <sup>14</sup>
- after 24 hr water immersion	1.5x10 <sup>14</sup>	2 x 10 <sup>14</sup>	7.3 x 10 <sup>14</sup>

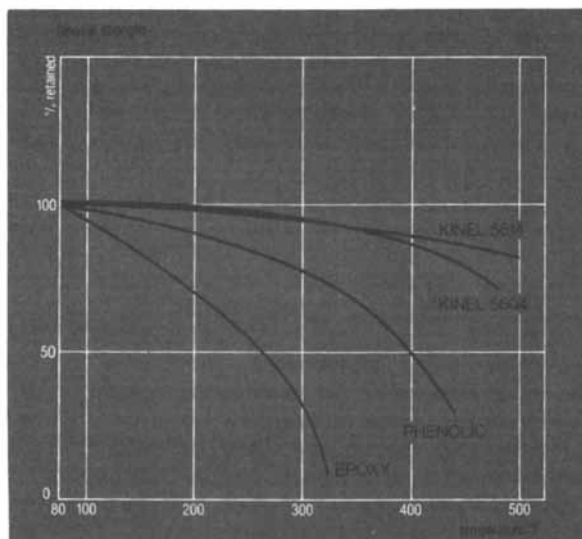


Figure 2. Flexural strength vs. temperature

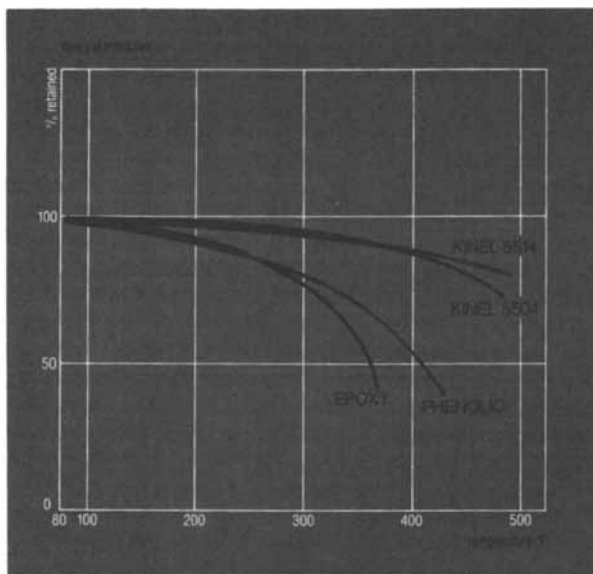


Figure 3. Flexural modulus vs. temperature

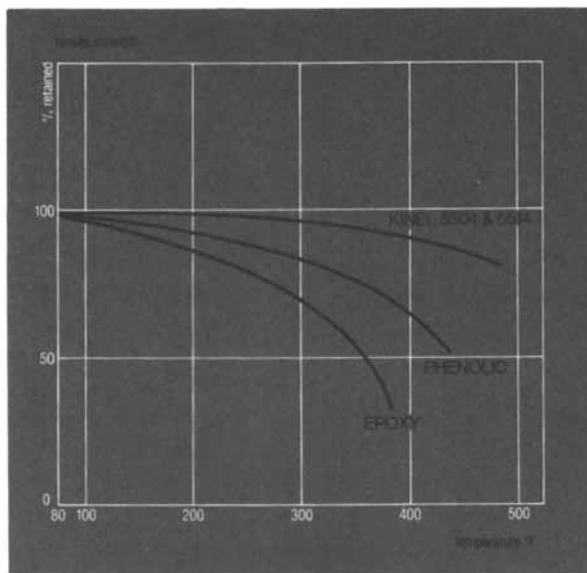


Figure 4. Tensile strength vs. temperature

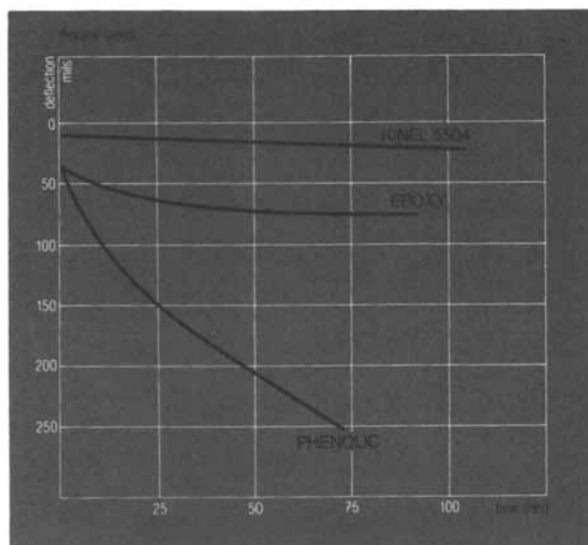


Figure 5. Flexural creep of Kinel 5504 vs. time at 392°F (200°C) and under a 2500 psi (175 bars) stress

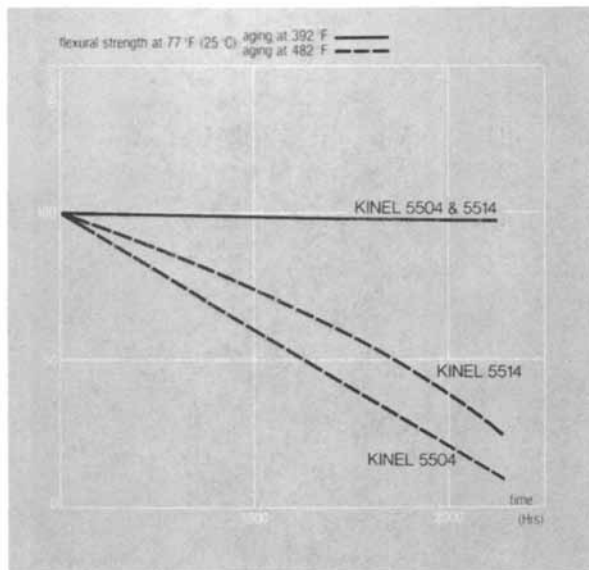


Figure 6. Flexural strength vs. aging time at 392°F (200°C) and 482°F (250°C), tested at 77°F (25°C)

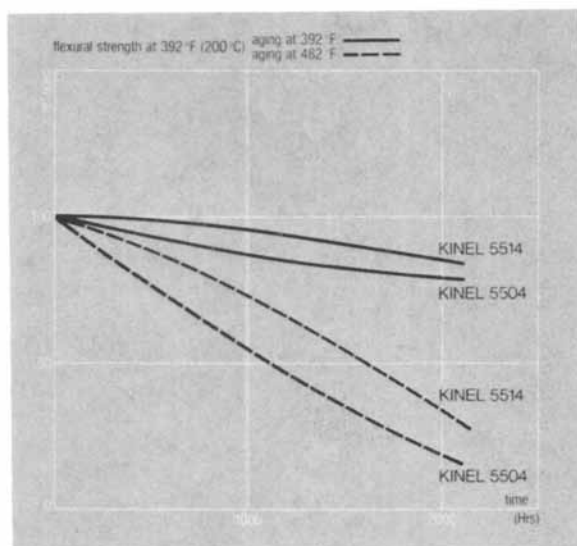
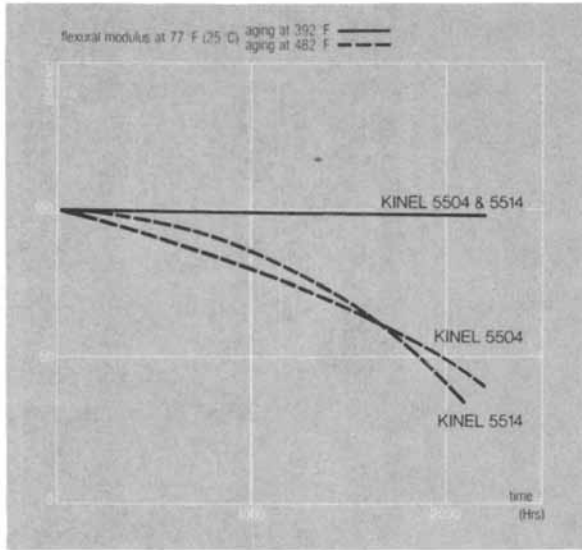
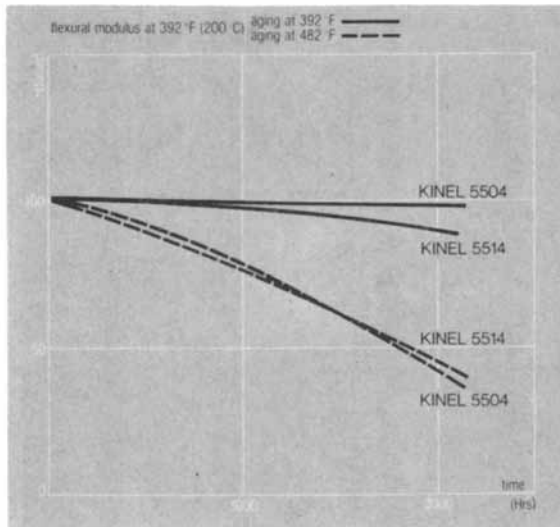


Figure 7. Flexural strength vs. aging time at 392°F (200°C) and 482°F (250°C), tested at 392°F (200°C)



*Figure 8. Flexural modulus vs. aging time at 392°F (200°C) and 482°F (250°C), tested at 77°F (25°C)*



*Figure 9. Flexural modulus vs. aging time at 392°F (200°C) and 482°F (250°C), tested at 392°F (200°C)*



3.5 Coefficient of Linear Thermal Expansion. The coefficients of linear expansion of KINELs 5504 and 5514 are quite low:

$$8 \times 10^{-6} \text{in/in/}^{\circ}\text{F} (15 \times 10^{-6} \text{cm/cm/}^{\circ}\text{C}) \text{ for KINEL 5504}$$
$$7 \times 10^{-6} \text{in/in/}^{\circ}\text{F} (13 \times 10^{-6} \text{cm/cm/}^{\circ}\text{C}) \text{ for KINEL 5514.}$$

They are of the same order of magnitude as those of many metals and alloys.

The dimensional stability of parts molded from PABMs is exceptional.

3.6 Fire Resistance. PABMs exhibit outstanding fire resistance. They are the only ones to meet AIR 0978/A Specification (French Aircraft Standard). This exceptional fire resistance makes their use possible in fireproof aircraft interior panels and ducts. Specific LOI values are: KINEL 5504—43.3; KINEL 5514—36.4.

3.7 Radiation Resistance. Parts molded in PABMs are unaffected by exposure to  $10^{10}$  rads. PABMs are therefore ideally suited for applications, such as electrical supports and insulators, in the hot zones of nuclear accelerators and reactors.

#### 4. Self-Lubricating KINELs

4.1 Description. The second major family of PABM compounds is directed to applications where low wear rates, low coefficients of friction, and good dimensional stability under load are sought. For these end-uses, graphite, molybdenum disulfide, and PTFE filled PABMs have been developed.

KINELs 5505 and 5508 are graphite filled compounds (25% and 40%, respectively). The first affords higher mechanicals, the second better wear and lubricity properties. Typical applications for KINELs 5505 and 5508 include: face seals and thrust washers; slip-on piston rings for air compressors; low speed, high load journal bearings (speeds less than 100 fpm); replacement for carbon/graphite mechanical goods.

KINEL 5511 is an asbestos fiber/graphite powder filled compound. Asbestos fibers impart resilience to the formulation. End-uses include: valve seats; seals; snap-on piston rings and vanes for rotary pumps.

KINEL 5517 is graphite and molybdenum disulfide filled. Wear, frictional properties, and applications are similar to those of 5505. 5517 is the most cost-

TABLE IV  
SELF-LUBRICATING KINEL PROPERTIES

	KINEL 5505	KINEL 5508	KINEL 5511	KINEL 5517	KINEL 5518
<u>MECHANICAL PROPERTIES</u>					
Flexural strength, psi					
77°F (25°C)	12,800	11,400	15,500	12,800	7,100
392°F (200°C)	10,000	8,500	13,000	10,000	6,500
482°F (250°C)	7,800	7,800	11,300	9,200	5,500
Flexural modulus, psi					
77°F (25°C)	750,000	1,050,000	1,850,000	900,000	390,000
392°F (200°C)	680,000	1,010,000	1,690,000	770,000	350,000
482°F (250°C)	640,000	1,000,000	1,600,000	750,000	320,000
Tensile strength, psi					
77°F (25°C)	5,700	4,700	5,000	5,700	5,000
392°F (200°C)	5,000	3,800	4,200	4,250	4,300
482°F (250°C)	4,200	3,100	3,800	3,600	3,600
Elongation at break, %	<1	<1	<1	<1	<1
Compressive strength, psi					
77°F (25°C)	22,200	15,700	15,700	20,000	20,000
392°F (200°C)	14,600	11,100	12,800	15,200	11,100
Impact strength at 77°F (25°C) - Notched Izod ft x lb/in.	0.25	0.4	0.8-1.0	0.25	0.25

TABLE IV (continued)  
SELF-LUBRICATING KINEL PROPERTIES

	KINEL 5505	KINEL 5508	KINEL 5511	KINEL 5517	KINEL 5518
<u>THERMAL PROPERTIES</u>					
Heat Distortion Temperature, °F	> 550	> 550	> 550	> 550	> 550
Coefficient of linear expansion	fm 50 to 200°C, in/in/°C	18x10 <sup>-6</sup>	15x10 <sup>-6</sup>	10x10 <sup>-6</sup>	19x10 <sup>-6</sup>
	fm 122 " 392°F, in/in/°F	10x10 <sup>-6</sup>	8.3x10 <sup>-6</sup>	5.6x10 <sup>-6</sup>	10.5x10 <sup>-6</sup>
Thermal conductivity, Btu. in/ft <sup>2</sup> .hr.°F	6.1	10.1	5.4	11.3	1.5
<u>PHYSICAL PROPERTIES</u>					
Specific gravity, g/cc lb/cu.ft	1.5 94	1.55 97	1.65-1.70 87	1.45 91	1.42 89

effective of all graphite KINELs since it may be free-sintered. Typical processing conditions are: cold press 15-30 sec. at 15,000 psi and free-sinter from 360-480°F in a programmed oven. Automatic cold pressing of parts can also be used.

KINEL 5518 is PTFE filled and exhibits the best self-lubrication properties of all KINELs. Coefficients of friction and wear rates are comparable to the best obtained with any filled PTFE compound. Additionally, PTFE compounds are formulated to afford excellent values for one or the other of these properties; KINEL 5518 affords outstanding values for both. High-speed, high-load bearings are the principal outlet for KINEL 5518; such bearings: operate at surface velocities up to 1000 fpm and PV's of 10-20,000, are not temperature restricted as are PTFE bearings, and do not cold flow. Finally, 5518 parts exhibit outstanding electrical properties (see Table IV).

4.2 Initial Properties. Representative mechanical, thermal, and physical properties of self-lubricating PABMs are shown in Table IV. Particularly noteworthy are the high mechanical properties, unattainable with typical thermoplastic bearing compounds. Tensile strengths run 10,000 psi and up, compressive strengths are typically in excess of 15,000 psi.

4.3 Friction and Wear. Graphite, molybdenum disulfide, and PTFE filled PABMs exhibit particularly low wear rates in dry friction vs metal at high PV's and, in particular, at high pressures applied at low velocities.

Figure 10 shows the variations of KINEL 5505 and 5508 coefficients of friction vs pressure at a given velocity.

Conversely to what is observed with other competitive self-lubricating materials, KINELs 5505 and 5508 frictional properties are retained and even improved at elevated temperatures as shown in Figure 11.

Additional coefficient of friction and wear rate data for self-lubricating PABMs are shown in Tables VI and VII, respectively. Both sets were obtained on  $\frac{1}{2}$ " diameter journal bearings operating on hardened steel shafts. Note that dynamic dry coefficients of friction are less than 0.1.

4.4 Properties at Elevated Temperatures. In addition to their very low wear rates, self-lubricating PABMs retain their elevated temperature properties to an exceptional extent.

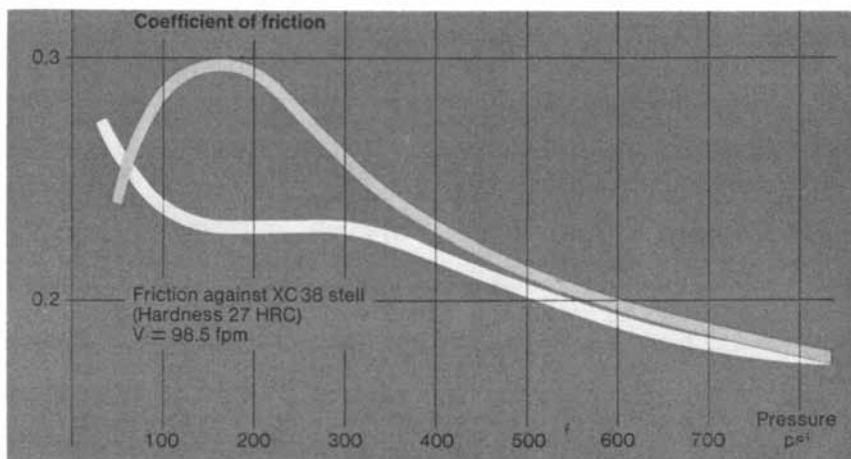


Figure 10. Kinel 5505 and 5508 coefficient of friction vs. pressure

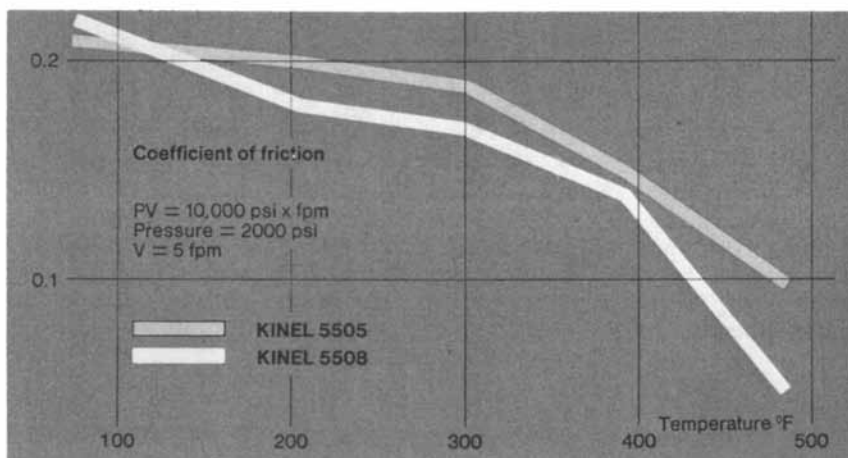


Figure 11. Kinel 5505 and 5508 coefficient of friction vs. temperature

Figures 12 and 13 show the percent retention of flexural strengths and moduli for KINELs 5505, 5508, and 5517 (compression molded and free-sintered).

4.5 Effect of Water on KINELs. Water and moisture are conditions frequently encountered in self-lubricating applications. Part weight change after twenty-four hour immersion is misleading for two reasons—weight change is an inaccurate reflection of dimensional and mechanical changes and few parts are designed to operate for only twenty-four hours. To obtain a more valid assessment of PABM water resistance, molded rings were immersed in 175°F (80°C) water until no further dimensional or weight change was noted. Part stabilization was observed in all cases between 1000 and 1200 hours. Initial ring dimensions were: O.D.-1.2"; I.D.-0.6"; thickness-0.8". Dimensional changes of I.D. and O.D. and weight increases are given below for all self-lubricating KINELs.

KINEL	% O.D. INCREASE	% I.D. INCREASE	% WEIGHT GAIN
5505	0.45	0.55	3.5
5508	0.45	0.45	2.95
5511	0.35	0.35	3.1
5517	0.60	0.65	3.55
5518	0.85	0.95	3.65

Except for KINEL 5518, where the PTFE filler plays a determining role, no dimensional change is greater than 0.65%. Further, water absorption is on KINEL surface only, rather than into core of part. PABMs are thus ideally suited for operation in hot-water and high-humidity environments and in situations where rapid thermal cycling, from moisture saturated atmospheres, occurs.

## 5. Summary

KINEL molding powders and KERIMID 601 laminating resins are based on a thermosetting polyimide, which cures without evolution of volatiles. KINEL compounds are transformed by compression, transfer, or extrusion molding into void-free parts, whose thermomechanical properties exceed those attainable from conventional thermoplastics or thermosets.

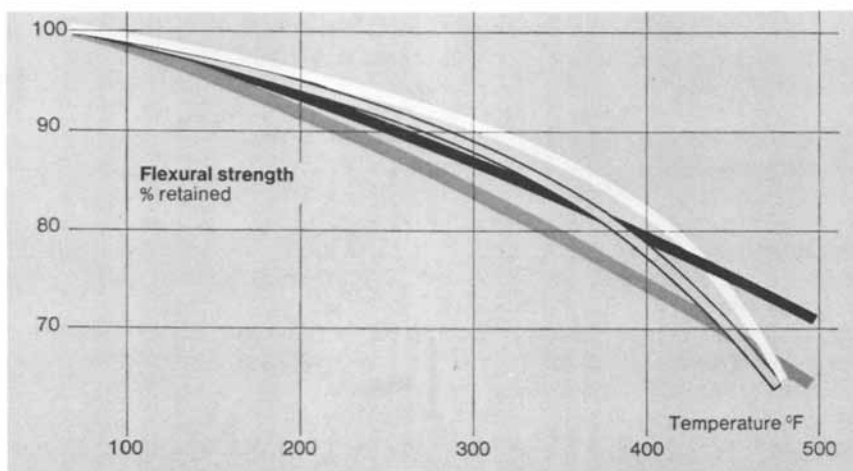


Figure 12. Kinel 5505, 5508, and 5517 flexural strength vs. temperature (% retention)

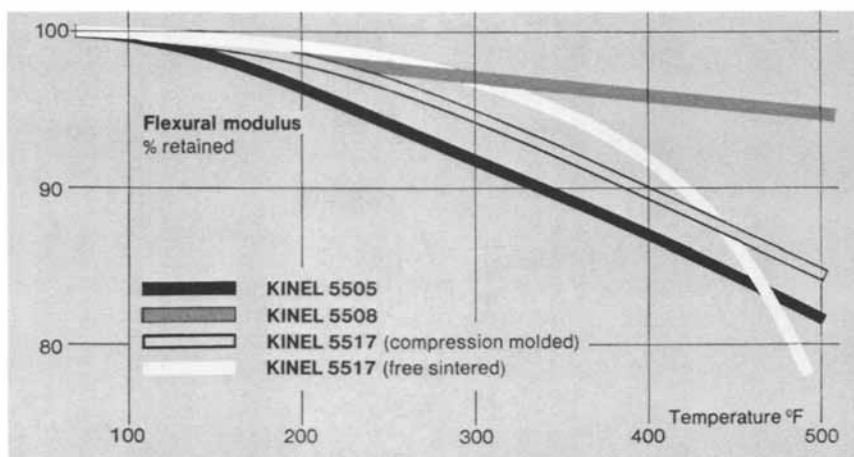


Figure 13. Kinel 5505, 5508, and 5517 flexural modulus vs. temperature (% retention)

KINEL structural and self-lubricating compounds and KERIMID 601 laminates exhibit:

- high tensile flexural, and impact strengths;
- low wear rates and coefficients of friction;
- excellent retention of mechanical properties at 480°F (250°C);
- several thousand hours of thermal stability at 390-480°F (200-250°C);
- easy moldability and machinability;
- outstanding dimensional stability;
- exceptional creep resistance; and
- insensitivity to fire, chemical reagents, solvents, oils, cryogenic temperatures, radiations, and moisture.

These properties, combined with excellent long-term economics, insure that numerous large-volume applications will be found for PABMs.

## 6. Acknowledgments

Data presented in this paper were developed by Rhone-Poulenc in France.



# Catalytic Trimerization of Aromatic Nitriles for Synthesis of Polyimide Matrix Resins

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## Synopsis

Aromatic nitriles may be trimerized at moderate temperature and pressure with *p*-toluenesulfonic acid as catalyst. Studies were conducted to establish the effect of the reaction temperature, pressure, time, and catalyst concentration on yield of the trimerized product. Trimerization studies were also conducted to establish the effect of substituting electron donating or withdrawing groups on benzonitrile. Preliminary results of using the catalytic trimerization approach to prepare *s*-triazine cross-linked polyimide/graphite fiber composites are presented.

## Introduction

High temperature resin/fiber composites have the potential of meeting the performance requirements for many advanced aerospace structures. The composites need to exhibit retention of mechanical properties during continuous use at 316°C (600°F) or above (1). Among the high temperature resins, polyimides occupy a preeminent position. Aromatic polyimides (PI's) exhibit thermal stability in excess of 500°C (932°F) as determined by thermal gravimetric analysis (2). However, processing difficulties have limited their use as matrices in resin/fiber composites. Various approaches have been used to solve the processability problem of polyimides. Lubowitz (3) and Burns et. al. (4) developed a new system of processable addition-type (A-type) PI's by end-capping imide oligomers with norbornenyl groups. After removal of the solvent, the norbornene-terminated imide oligomers are polymerized through the double bonds without evolution of byproducts. Serafini et. al (5) and Delvigs et. al. (6) developed an improved processing technique for A-type PI's called the in situ polymerization of monomeric reactants (PMR).

Although the in situ PMR approach does provide void free A-type PI composites with good property retention at 316°C (600°F), the alicyclic ring structure derived from the norbornene groups does appear to limit the thermo-oxidative stability (TOS) of A-type PI's (7). To achieve A-type PI's with improved TOS at 316°C (600°F) or above, our approach was to replace the norbornenyl groups with aromatic nitriles. Trimerization of aromatic nitrile-terminated imide oligomers should lead to new polyimides containing triaryl-s-triazine rings. Triaryl-s-triazine ring is known to exhibit good thermal stability (8).

The purpose of the present investigation was to study the trimerization of aromatic nitriles under the conventional resin/fiber composite fabrication conditions using p-toluenesulfonic acid as a catalyst. Trimerization parameters investigated included reaction temperature, pressure, time, and concentration of catalyst. The influence of the nature of aromatic nitriles on trimerization was also studied. Also presented are preliminary results on the use of the catalytic trimerization of the nitrile-terminated imide oligomers to fabricate graphite fiber reinforced composites.

### Experimental Procedure

**Materials.** All of the aromatic nitriles except p-cyanophthalanil used in this study were purchased from commercial sources and used as received. The p-cyanophthalanil was synthesized by a method similar to that used for synthesizing N-phthalyl-L- $\beta$ -phenylalanine (9) except that p-aminobenzonitrile was used instead of L-phenylalanine.

**Catalytic Trimerization.** About 0.01 mole of the aromatic nitrile together with 0.5 to 5.0 mole percent of the p-toluenesulfonic acid (PTSA) catalyst was introduced into a 45-milliliter stainless steel pressure vessel. The vessel was flushed with nitrogen gas and the initial pressure in the vessel was varied from 0 to 2.76 MN/m<sup>2</sup> (0 to 400 psi). The vessel was then heated to temperatures in the range of 100 to 316°C. The selected temperature was maintained for 24 to 90 hours. The PTSA catalyst and unreacted nitrile were then removed from the product by washing with water followed by distillation under reduced pressure. The product was then recrystallized from xylene or glacial acetic acid. Melting point and infrared spectrum were determined for identification purposes.

### Results and Discussion

**Trimerization Study.** Bengelsdorf (10) reported that

aromatic nitriles could be trimerized in the absence of catalysts at temperatures in the range of 350<sup>o</sup> to 500<sup>o</sup>C and at pressures which ranged from 3.55 x 10<sup>5</sup> to 5.06 x 10<sup>5</sup> MN/m<sup>2</sup> (35,000 to 50,000 atmospheres). Cairns et.al. (11) used various alcohols as catalysts and were able to effect trimerization of aromatic nitriles at 60<sup>o</sup> to 150<sup>o</sup>C and 0.3 x 10<sup>5</sup> MN/m<sup>2</sup> (above 3000 atmospheres). Kunz et.al. (12) employed chlorosulfonic acid to trimerize aromatic nitriles at temperatures in the range of -10<sup>o</sup> to 30<sup>o</sup>C and at atmospheric pressure. These latter workers used an excess of chlorosulfonic acid which apparently served as both the solvent and catalyst. Because of the high pressures or the nature and quantity of catalyst employed none of the methods described above are suitable for the synthesis of high temperature resistant s-triazine cross-linked polyimide matrix resins for fiber reinforced composites.

The aromatic nitrile and catalyst selected for this study were benzonitrile and PTSA, respectively. Studies were conducted to establish the effect of reaction conditions on yield of trimerized product. Figure 1 shows the effect of varying the reaction temperature on yield between 100<sup>o</sup> and 290<sup>o</sup>C at a constant PTSA catalyst concentration of 5 mole percent, pressure in the range of 4.14 to 5.17 MN/m<sup>2</sup> (600 to 700 psi), and for a constant reaction time of 66 hours. It can be seen from the figure that there was no yield at 100<sup>o</sup>C and the yield nearly doubled on going from 232<sup>o</sup> to 290<sup>o</sup>C. Because of practical processing considerations for the fabrication of fiber reinforced composites, higher temperatures were not investigated. The effect of reaction pressures in the range of 0.2 to 5.17 MN/m<sup>2</sup> (30 to 750 psi) on yield are shown in figure 2. The data shown in this figure were obtained for reactions conducted with a PTSA concentration of 5 mole percent at 232<sup>o</sup>C for 66 hours. The figure shows that the use of higher pressures resulted in higher yields. Hereto, practical processing consideration limited the highest pressure studied to 5.17 MN/m<sup>2</sup> (750 psi). Figure 3 shows the effect of reaction time on yield for reactions conducted with 5 mole percent PTSA at 232<sup>o</sup>C (450<sup>o</sup>F) and 5.17 MN/m<sup>2</sup> (750 psi). It can be seen in the figure that the yield upon increasing reaction time from 24 to 66 hours underwent slightly more than a two fold increase. Figure 4 which shows effect of catalyst concentration on yield shows that at 232<sup>o</sup>C (450<sup>o</sup>F) and 5.17 MN/m<sup>2</sup> (750 psi) and 66 hours the yield increased from 5% to 17% for a ten fold increase in catalyst concentration.

The results of these trimerization parameter studies indicated that useful levels of trimerized product (cross-links) could be anticipated from the use of this catalytic trimerization approach in fabricating resin/fiber composites. Two additional points need to be made with respect to the

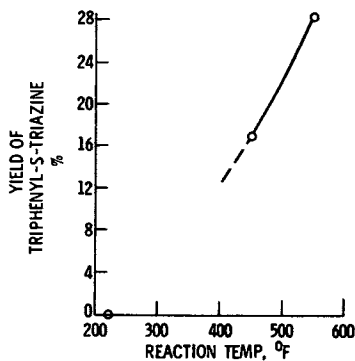
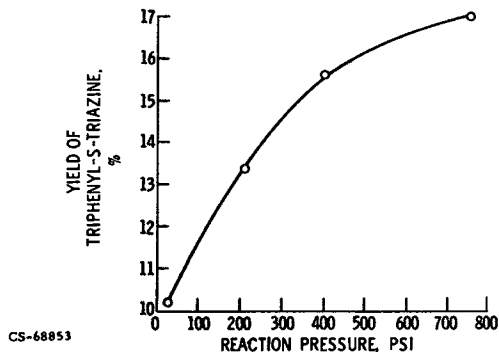


Figure 1. Effect of reaction temperature on trimerization of benzonitrile (PTSA 5 moles %, 600–750 psi, 66 hr)



CS-68853

Figure 2. Effect of reaction pressure on trimerization of benzonitrile (PTSA 5 mole %, 450°F, 66 hr)

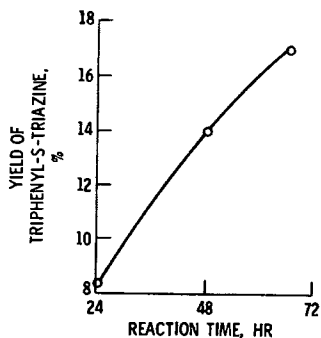
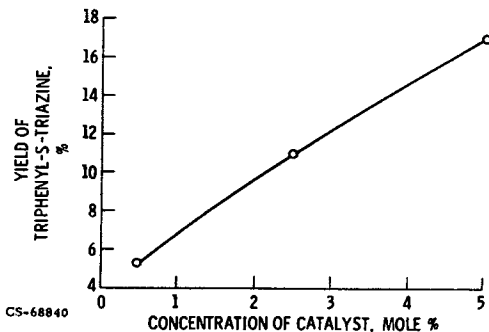


Figure 3. Effect of reaction time on trimerization of benzonitrile (PTSA 5 mole %, 450°F, 750 psi)



CS-68840

Figure 4. Effect of catalyst concentration on trimerization of benzonitrile (PTSA, 450°F, 750 psi, 66 hr)

yield of trimerized product. First, the yield of trimerized product (cross-links) in an actual resin/fiber composite might be increased by post-curing at elevated temperatures. And secondly, extensive cross-linking may not be necessary for improved composite properties and indeed may be deleterious to certain composite mechanical properties.

Nature of Aromatic Nitriles. The experimental results on the influence of ring substituents on the ease of trimerizing benzonitriles are summarized in Table I. It can be seen that the benzonitriles bearing electron withdrawing ring substituents such as carboxyl and nitro groups are more susceptible to trimerization than those bearing electron donating substituents such as methyl and methoxy groups. The lower yield of trimerized product from the *o*-nitrobenzonitrile compared to *p*-nitrobenzonitrile can be accounted for by steric effects. The very high yield of trimerized product from the *p*-cyanobenzoic acid might have resulted from a reaction in which the *p*-cyanobenzoic acid itself served as a co-catalyst.

For the synthesis of processable polyimides, our results suggested the use of 4-cyanophthalic anhydride as the end-capping reagent. The 4-cyanophthalic anhydride or its esters might be preferable because the electron withdrawing carbonyl groups would be directly attached to the aromatic ring containing the nitrile to be trimerized. However, because of the commercial availability of *p*-aminobenzonitrile, it was selected as the end-capping reagent for preliminary studies.

Trimerization of *p*-Cyanophthalanil. *p*-Cyanophthalanil was synthesized as the model compound to study the effectiveness of PTSA in promoting trimerization of a chemical structure which would be found in the polyimide precursors.

*p*-Cyanophthalanil was prepared from commercially available *p*-aminobenzonitrile and phthalic anhydride. The white crystalline powder has a melting point of 189°C (lit. 187°C, ref. 16). Its infrared spectrum showed a nitrile band at 2240 cm<sup>-1</sup>, imide bands at 1795, 1755, 1735, and 1380 cm<sup>-1</sup>, and phenyl ring bands at 1610 and 1520 cm<sup>-1</sup> respectively (fig. 5(a)).

Catalytic trimerization of *p*-cyanophthalanil with 5 mole percent *p*-toluenesulfonic acid at 250-300°C and 4.97 to 5.52 MN/m<sup>2</sup> (720-800 psi) for 90 hours gave a 97% yield product, with a m.p. > 340°C. The infrared spectrum showed the disappearance of the nitrile band at 2240 cm<sup>-1</sup> and the broadening of the *s*-triazine bands at 1520 and 1380 cm<sup>-1</sup> (fig. 5(b)). Further identification of the formation of the *s*-triazine was done by refluxing the trimerized product with a 10% NaOH solution for 4 hours. The infrared spectrum of

TABLE I. - CATALYTIC TRIMERIZATION\* OF  
SUBSTITUTED BENZONITRILES

Aromatic Nitrile	M. P. °C	Trimerized Product	Percent yield	M. P. °C (Value in Lit.)
p-Tolunitrile	26-28		5.0	> 340 (278-9 <sup>13</sup> )
Anisonitrile	55-56		6.0	> 340 (217 and 224 <sup>13</sup> )
Benzonitrile	-14		14.0	232-235 (232 <sup>13</sup> )
o-Nitrobenzonitrile	102-106		37.8	> 340 <sup>14</sup>
p-Nitrobenzonitrile	146-149		52.3	> 340 (> 360 <sup>13</sup> )
p-Cyanobenzoic acid	220-222		75.0	> 340 (374-5 <sup>15</sup> )

\* Reaction conducted at 232° C, and 600 to 750 psi., with 5 mole percent of PTSA catalyst for 48 hours.

the insoluble hydrolysis product showed that those imide bands at 1795, 1755, 1735, and 1380  $\text{cm}^{-1}$  had nearly disappeared (or greatly weakened). The characteristic s-triazine band at 1520  $\text{cm}^{-1}$  was not affected (fig. 5(c)).

Trimerization of Terephthalonitrile. Since terephthalonitrile has two nitrile groups and the nitrile group itself is also electron withdrawing, catalytic trimerization of terephthalonitrile should proceed readily and result in a polymeric product expected to exhibit good thermal stability. The experimental results confirmed this prediction: Catalytic trimerization of terephthalonitrile with 5 mole percent of PTSA catalyst at 232°C and 5.17 MN/m<sup>2</sup> (750 psi) for 48 hours gave a product (99.5% yield) with a melting point > 340°C (644°F). The infrared spectrum of terephthalonitrile showed a very strong nitrile band at 2230  $\text{cm}^{-1}$  and a sharp aromatic ring band at 1500  $\text{cm}^{-1}$  (fig. 6(a)). The infrared spectrum of the trimerized product showed strong and broad characteristic s-triazine ring bands at 1525 and 1370  $\text{cm}^{-1}$  with a residual nitrile band of medium strength at 2230  $\text{cm}^{-1}$  (fig. 6(b)). Thermal gravimetric analysis (fig. 7) showed that the weight losses of terephthalonitrile polymer were about 7% after heating to 316°C (600°F) and 18% after heating to 538°C (1000°F) respectively. Anderson and Holovka (17) reported weight losses of about 25% after heating to 316°C (600°F) and 75% after heating to 538°C (1000°F) respectively from the terephthalonitrile polymer which they obtained by treating terephthalonitrile with chlorosulfonic acid at 0°C. This greater thermal oxidative stability of the trimerized product using PTSA as the catalyst may be due to having achieved a higher cross-link density during reaction at 232°C (450°F) and 5.17 MN/m<sup>2</sup> (750 psi).

Polyimide/Graphite Fiber Reinforced Composite. Since aromatic nitrile-terminated imide oligomers are similar in nature as p-cyanophthalanil and possess the same functionality as terephthalonitrile, they should be able to trimerize and form the s-triazine ring containing polymers under the similar reaction conditions.

Preliminary work for the synthesis of nitrile terminated polyimides was carried out by using p-aminobenzonitrile, 4,4'-methylenedianiline, 3,3',4,4'-benzophenonetetracarboxylic dianhydride and methanol with 2.5 mole percent of PTSA catalyst. The stoichiometry of the monomeric reactants was adjusted to yield an in situ prepolymer having an average formulated molecular weight of 1500. Composite fabrication and testing were performed essentially according to the method used in reference 5. The results from some preliminary composite fabrication and characterization studies

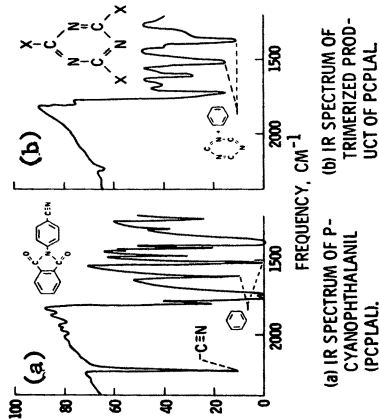


Figure 5. (a) IR spectrum of p-cyanophthalanil (PCPLAL); (b) IR spectrum of trimerized product of PCPLAL; (c) IR spectrum of PCPLAL trimerized product after refluxing with 10% NaOH for 4 hr.

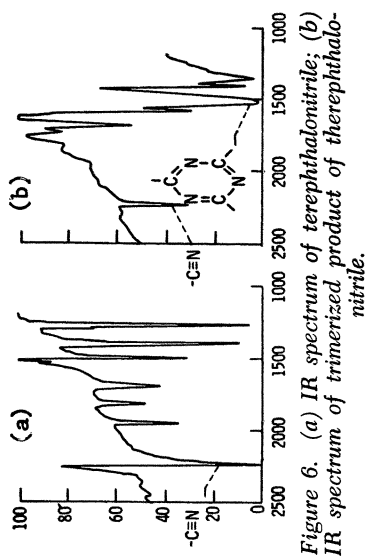


Figure 6. (a) IR spectrum of terephthalonitrile; (b) IR spectrum of trimerized product of terephthalonitrile.

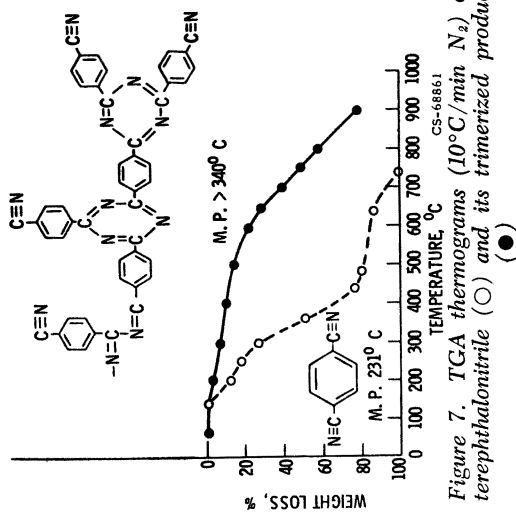




TABLE II. - MECHANICAL PROPERTIES OF TRIARYL-S-TRIAZINE  
CROSS-LINKED PI/HMS FIBER COMPOSITES<sup>a</sup>

Specimen	Interlaminar shear strength, psi			Flexural strength, psi		
	Room temperature	600° F		Room temperature	600° F	
		No post cure	Post cure (16 hr 600° F)		No post cure	Post cure (16 hr 600° F)
1	8 370	4620	7500	155 000	148 200	167 500
2	10 130	4520	6800	130 200	145 700	157 500

<sup>a</sup>Resin/fiber ~40/60 by weight.

indicate that the trimerization technique by employing PTSA catalyst provides high performance composites.

Table II shows the interlaminar shear strength and flexural strength of the triaryl-s-triazine cross-linked PI/HMS graphite composites at room temperature and 316°C with and without post curing. The data clearly indicate that the HMS graphite fiber reinforced composite prepared from a nitrile terminated PI exhibited very good retention of flexural strength during short time exposure in air at 316°C. More important, the data also indicate that both the interlaminar shear strength and flexural strength of the composites improved after a 16 hour post cure at 316°C. Apparently this resulted from an increase in triaryl-s-triazine rings during post cure at 316°C.

### Conclusions

The results of this investigation lead to the following conclusions:

1. Aromatic nitriles can be trimerized in the temperature range of 200°C to 316°C (392°F to 600°F) and pressure range of 1.38 to 5.52 MN/m<sup>2</sup> (200 to 800 psi) with p-toluenesulfonic acid as catalyst.
2. Benzonitriles bearing electron withdrawing ring substituents were found more susceptible to trimerization than those bearing electron donating ring substituents.
3. Polyimide matrix resins containing s-triazine cross-links can be easily prepared using the aromatic nitrile end-capping approach and trimerization with a p-toluenesulfonic acid catalyst.

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## Poly(p-Oxybenzoyl Systems): Homopolymer for Coatings; Copolymers for Compression and Injection Molding

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Development work has been going on for several years at The Carborundum Company on p-oxybenzoyl polymer systems. The early work mainly focused on the homopolymer (EKONOL)<sup>1,2,3</sup>. This polymer has excellent thermal stability and also very good friction and wear properties and has found use recently as an additive to PTFE for molded shapes and coatings. The homopolymer however is very difficult to fabricate by itself and this has led to the development of copolymer systems which retain the excellent thermal stability of the homopolymer; but have sufficient flow for compression and injection molding.

Para-hydroxybenzoic acid (PHBA) by itself does not have sufficient reactivity to permit the growth of a polymer to any useful molecular weight. This has been overcome by using the phenyl ester of PHBA. With a slow controlled heating to temperatures of 320-340°C, this monomer has sufficient reactivity to build the molecular weight to a useful level. However, the reaction will not go to 100% completion in the melt state. Carrying out the polymerization in a heat transfer medium, such as a mixture of partially hydrogenated terphenyls, produces a polymer with a molecular weight of ~10,000.

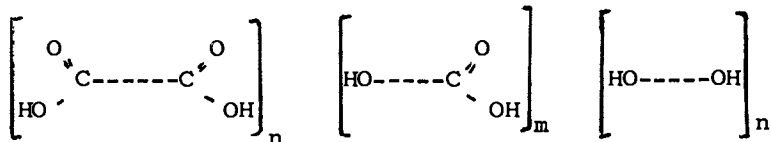
The p-oxybenzoyl polymer when properly made has a melting point above its decomposition temperature (> 1000°F). The highly crystalline nature of the polymer persists up to ~625°F. At that temperature, the polymer undergoes a broad endotherm which most likely corresponds to the loss of order in one dimension. However, even above this transition, the flow is extremely limited and is insufficient to make compression molding a useful tool for fabrication. Only very thin sections can be molded (< 1/4") and the resultant

strengths are quite poor (5500 psi flexural strength). It is felt that this is related to the drastic change in thermal expansion from 625-675°F resulting in micro-cracks.

One method of fabrication that has been used successfully is plasma-spraying for coatings,<sup>1,3</sup> using either 100% of the homopolymer, or blends with various metals. However, noting that the wear resistance of compression molded parts of the polyester is extremely good and also that the polymer can withstand exposure at 700°F made it an excellent additive for PTFE blends (in sintering compounds as well as in a dispersion for spraying). The wear resistance of the blend increases dramatically as the percentage of homopolymer increases, up to ~25% (by weight). Beyond this level the wear resistance<sup>4</sup> of the blend is relatively constant, up to 100% polyester. This seems to indicate that the PTFE is functioning only as a matrix to bind the polyester particles. When sufficient homopolymer is incorporated (25% by weight, 33% by volume) the blend can be used at temperatures up to 600°F.

The need for moldable grades of polyester prompted a major research effort in the area of copolymers (the chemistry of the materials described here was developed by Dr. Steve Cottis).<sup>5</sup> To retain the excellent thermal resistance of the p-oxybenzoyl homopolymer (continuous use temperature of 550-600°F, short exposure temperatures of 750-800°F), only completely aromatic systems were investigated. Para-hydroxybenzoic acid was formulated with several co-monomers.<sup>5</sup> These included the meta and para diacids (isophthalic and terephthalic acid), and various dihydroxy aromatic compounds, such as hydroquinone and resorcinol.

As expected, the melt properties of the polymers changed drastically as the monomers were varied, and also as the ratio of the reactants was changed:



For any particular combination of monomers, varying the ratio of  $\frac{m}{n}$  generally produced a melting point curve that showed a definite minimum. This is illustrated in Figure 1 for two different systems. For polyesters based on isophthalic acid, p-hydroxybenzoic acid and hydroquinone, a melting point curve is obtained with a minimum near 50% (on a mole

basis) of p-oxybenzoyl units. (This corresponds to value of 2 for  $\frac{m}{n}$ ). The melting points range from  $\sim 500^{\circ}\text{F}$  to  $\sim 700^{\circ}\text{F}$ . (These polymers can be made non-melting by oxidatively crosslinking them at temperatures above the melting point). Substituting terephthalic acid for isophthalic acid raises the curve  $\sim 300^{\circ}\text{F}$ . These all para systems however are non-melting, and the data in Figure 1 refers to softening temperature. The minimum softening temperature of  $\sim 800^{\circ}\text{F}$  occurs at 50-70% p-oxybenzoyl units.

For compression molding, the copolymer that was found to have optimum properties contains isophthalic acid, PHBA, and a dihydroxy aromatic (trade name EKKCEL C-1000). The polymerization is run to 100% completion in a heat exchange medium. However the polymer at this stage does not have very good high temperature properties: it has a glass-transition at  $\sim 300^{\circ}\text{F}$ , and a melting point of  $\sim 700^{\circ}\text{F}$ . By introducing a crosslinking step in the production of the copolymer, the glass transition is eliminated and the polymer becomes non-melting. However, it still softens sufficiently at high temperatures to permit compression molding both with and without the addition of fillers (fiber-glass, graphite, PTFE, etc.). Furthermore, good strength is retained at  $500^{\circ}\text{F}$ .

Processing conditions are the same for compression molding or confined sintering. The powder is heated (in the mold) to  $680-700^{\circ}\text{F}$  for one hour per 1/4" effective thickness. A pressure of  $\sim 10,000$  psi is then applied, and the part can be stripped immediately. Some of the significant properties of compression molded samples are listed in Table I.

The crosslinked copolymer behaves as a thermoplastic since no significant advancement occurs during molding. By using a higher pressure, 100% reground material can be molded.

The crosslinked copolymer just described does not have sufficient flow for injection molding. If the crosslinking step is eliminated, the copolymer can be injection molded, but only with considerable difficulty. Also, the parts obtained have poor strength above  $300^{\circ}\text{F}$ . It was felt that an all para system was necessary to overcome the poor hot strength. The combination of monomers that provided optimum properties and processability was found to be terephthalic acid, p-hydroxybenzoic acid, and a dihydroxy aromatic. The synthesis can be carried out in the melt, or in a heat exchange medium. The product has a fairly sharp melting

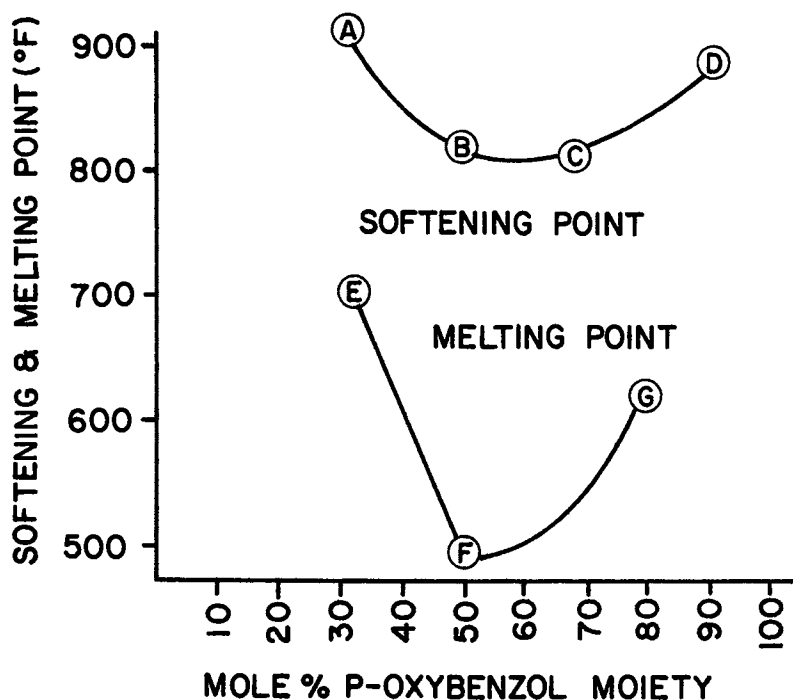


Figure 1. Melting point or softening point vs. mole % p-oxybenzoyl moiety for the following aromatic copolyesters (where I is isophthalic acid, T is terephthalic acid, P is p-hydroxybenzoic acid, and H is hydroquinone):

Polyester	Components	Mole Ratio of Components
A	T:P:H	1:1:1
B	T:P:H	1:2:1
C	T:P:H	1:4:1
D	T:P:H	1:18:1
E	I:P:H	1:1:1
F	I:P:H	1:2:1
G	I:P:H	1:8:1

point at  $\sim 775^{\circ}\text{F}$  but softens slightly at a lower temperature. It can be extruded at  $\sim 725^{\circ}\text{F}$ , and run on a standard injection molding machine with a barrel temperature of  $725\text{--}775^{\circ}\text{F}$  with the mold ranging in temperature from room temperature to  $550^{\circ}\text{F}$  using pressures of  $\sim 10,000$  psi. The physical properties of the parts obtained are relatively constant over a wide range of molding conditions, and are listed in Table II.

Table I

Physical Properties of Compression Molded Parts

<u>Property</u>	<u>A.S.T.M.</u>	<u>Value</u>
Tensile Strength, $73^{\circ}\text{F}$	D638	10,000 psi
Tensile Strength, $500^{\circ}\text{F}$	D638	3,000 psi
Tensile Modulus, $73^{\circ}\text{F}$	D638	190,000 psi
Flexural Strength, $73^{\circ}\text{F}$	D790	15,000 psi
Flexural Strength, $500^{\circ}\text{F}$	D790	5,000 psi
Flexural Modulus, $73^{\circ}\text{F}$	D790	450,000 psi
Flexural Modulus, $500^{\circ}\text{F}$	D790	125,000 psi
Flammability (UL-94)		SEO
Heat Distortion, 264 psi	D648	$572^{\circ}\text{F}$
Heat Distortion, 66 psi	D648	$>600^{\circ}\text{F}$
Water Absorption	D570	0.040%
Hardness (Rockwell "R")	D785	124
Dielectric Constant $10^3$ Hz,	D150	3.68
$73^{\circ}\text{F}$		
Dissipation Factor $10^3$ Hz,	D150	.0085
$73^{\circ}\text{F}$		
Dielectric Strength, 125 mil	D149	450 V/mil

The tensile strength of this copolymer (EKKCEL I-2000) is 14,000 psi at room temperature, and 3,000 psi at  $500^{\circ}\text{F}$ . Its heat deflection temperature is  $560^{\circ}\text{F}$ , and the upper use temperature for the polymer will probably be in the range of  $\sim 575^{\circ}\text{F}$ . The water absorption is extremely low for this material, as it is for all the aromatic polyesters described here.

The aromatic copolyesters described have been shown to have a broad range of flow properties that permit fabrication under a variety of conditions. It is expected that further research will extend their application to other areas such as film and wire coatings while maintaining the high temperature capabilities of the molding grades.



Table II

Physical Properties of Injection Molded Parts

<u>Property</u>	<u>A.S.T.M.</u>	<u>Value</u>
Tensile Strength, 73°F	D638	14,000 psi
Tensile Strength, 500°F	D638	3,000 psi
Tensile Modulus, 73°F	D638	350,000 psi
Elongation, 73°F	D638	8.0%
Flexural Strength, 73°F	D790	17,000 psi
Flexural Strength, 500°F	D790	4,000 psi
Flexural Modulus, 73°F	D790	700,000 psi
Flexural Modulus, 500°F	D790	200,000 psi
Compression Strength, 73°F	D695	18,000 psi
Compression Modulus, 73°F	D695	500,000 psi
Flammability	LOI	37%
	UL-94	VE-0
Impact Strength, Notched	D256	1.0 ft-lb/in
Impact Strength, Unnotched	D256	3.0 ft-lb/in
Deformation Underload	D621	3.5%
Heat Distortion, 264 psi	D648	560°F
Coefficient of Thermal Expansion	D696	$1.6 \times 10^{-5}$ in/in/°F
Mold Shrinkage		.012 in/in
Specific Gravity	D792	1.40 g/cc
Water Absorption	D570	.025%
Hardness (Rockwell "R")	D785	88
Coefficient of Friction, 110 psi, 90 fpm		0.14
Dielectric Constant,	D150	
100 Hz, 73°F		
$10^3$ Hz, 73°F		3.16
$10^6$ Hz, 73°F		2.87
Dissipation Factor,		
100 Hz, 73°F	D150	
$10^3$ Hz, 73°F		.010
$10^6$ Hz, 73°F		.025
Dielectric Strength, 125 mil	D149	350 V/mil
Volume Resistivity, Measured	D257	$10^{15}$ $\Omega$ /cm
Surface Resistivity, Measured	D257	$10^{15}$ $\Omega$ /cm <sup>2</sup>
Arc Resistance	Tungsten Rod Method	100 Sec

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## Round-Table Discussion

### Plastics without Petroleum

Rudolph D. Deanin, Plastics Department, Lowell Technological Institute,  
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Plastics have a great history; and, with our help, they can have an even greater future.

Table 1

U.S. Plastics Sales, 1973, 1000 Metric Tons (1)

Low-Density Polyethylene	2664
Polystyrene & Copolymers	2407
Polyvinyl Chloride & Copolymers	2171
High-Density Polyethylene	1254
Polypropylene	978
Phenolics	654
Polyurethane Foam	593
Polyesters	496
Urea & Melamine Resins	464
Miscellaneous Vinyls	391
Alkyds	342
Acrylics	233
Coumarone-Indene & Petroleum Resins	157
Epoxy Resins	99
Nylon Plastics	80
Cellulosics	77
Others	122
	<u>13,182</u>

In the early days of the plastics industry, industrial organic chemists used a variety of raw materials to make their polymers and additives.

Coal was the most versatile raw material. Coal tar chemistry was to them what petrochemicals are to us today. Simple distillation produced many of the intermediates we still use today: benzene, phenol, cresols, xylenols, toluene, naphthalene, coumarone, indene, and carbazole (2). Coke was also the starting

material for calcium cyanamide and acetylene which, particularly in Germany, were the intermediates for a great variety of polymers and plastics chemicals: melamine, acrylonitrile, methyl methacrylate, acetic acid and anhydride, vinyl acetate, butyraldehyde and polyvinyl butyral, vinyl chloride, and chloroprene (3). Coke also led, through water gas and methanol, to formaldehyde, still a monomer in a number of important plastics (4).

Plastics have also been manufactured from a number of raw materials other than petroleum (Table 2). Rubber from trees has been used in both solid and latex form, and also converted further into isomerized and chlorinated polymers of very different properties and uses. Wood from trees is used directly for plywood, composition board, and wood-flour reinforcement of phenolic resins. The cellulose from wood is purified and used for laminates and for regenerated cellulose products such as cellophane, viscose rayon, and vulcanized fibre. The lignin from wood has been explored for use in plastics, but never carried through to complete commercial success.

Plants grown as crops have provided a variety of raw materials for plastics. The cellulose from cotton has always been the quality raw material for cellulosic plastics. The cellulose from other plants is used in a variety of building materials. The oils from plants provided glycerol, and mono- and di-basic acids, for many plastics and plasticizers. Fermentation was used successfully to produce acetone and a number of alcohols and acids useful in polymers and plasticizers. Even the protein in plants, and in animal by-products, has been used in a number of plastics applications.

In the past 30 years, the ready availability and low cost of petroleum and natural gas, plus the ingenuity of petroleum chemists and engineers, have made this the most convenient and economical raw material for synthesis of plastics, to the point where we have abandoned many of the older processes, or at least allowed them to remain relatively minor in importance (5).

Now that the supply of petroleum and natural gas is decreasing, the cost becoming greater, and the political uncertainty of foreign supply becoming a serious problem, we can best insure the healthy future growth of the polymer industries by turning our research and development efforts to the variety of raw materials available to us, particularly those which can be grown as commercial crops and are therefore replenishable, and also more likely to produce waste

Table 2  
 RAW MATERIALS OTHER THAN PETROLEUM FROM WHICH PLASTICS HAVE BEEN MANUFACTURED

Commercial Plastics	Coal		Trees			Plants		
	Coke	Distill	Rubber	Wood	Cellulose	Oil	Ferment	Protein
Low-D Polyethylene								X
PS & Copolymers	X	X	X					
PVC & Copolymers	X							
High-D Polyethylene								
Polypropylene					X			X
Phenolics	X	X	X					
Urethane Foam	X	X				X		
Polyesters	X	X				X		
Urea & Melamine	X		X		X			
Miscellaneous Vinyls	X							
Alkyds						X		X
Acrylics	X							
Coumarone-Indene		X						
Epoxy Resins	X	X				X		X
Nylon Plastics	X	X				X		X
Cellulosics	X							
Others	X			X	X			X
Plasticizers	X					X		X

products which can be returned into the ecocycle efficiently.

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### Plastics without Petroleum

Richard G. Sinclair, Thomas R. Steadman, Melville E. D. Hillman, and E. S. Lipinsky, Polymer Chemistry and Chemical Economics Sections, Battelle-Columbus Laboratories, 505 King Ave., Columbus Ohio 43201

A major objective of polymer technology for many years has been the development of a complete line of plastics from petrochemicals. Professor Deanin has already pointed out that this effort has been quite successful. However, in less than one year the situation has changed remarkably as the once abundant supply of petrochemicals has become scarce. How serious is this shortage and how prolonged will it be? It is estimated that our petroleum imports were reduced by about 15 percent by the Arab oil embargo. Since approximately 5 percent of the petroleum finds its way into the plastics industry as monomers, solvents, etc., it comes as no surprise that there is a shortage of monomer and polymer supplies. It is estimated that these shortages will remain to some extent for many years.

One alternative for supply of plastics is the use of agricultural products as raw materials. These are renewable resources. Although incapable of supplying all the needs of the plastics industry, agricultural-derived products could, it is estimated in principle from the available growing acreage, supply approximately 10 percent of the industry's need. This might be just enough to offset the projected shortages. A second alternative is the use of coal as raw material.

It is suggested that some realignment be employed of our basic thumb rules for use of plastics. For example, polystyrene has been extensively employed in

many uses because it was cheap and readily available. As it becomes more expensive, perhaps polystyrene will be replaced in some uses by other plastics, such as acrylics or ABS, which previously could not compete price-wise but which have generally superior properties. Along this line, elegant materials such as thermo-plastic elastomers may become in great demand. Traditionally, cheaper materials have been grafted, filled, blended, and copolymerized with a variety of other materials to obtain desirable properties. Table 1 shows that some petrochemical raw materials have increased in price by as much as 165 percent during the past year.

Table 1

Price Increases of Some Petrochemical  
Raw Materials for Plastics

	<u>Dollars/Pound</u>		<u>Increase, Percent</u>
	<u>4/15/74(1)</u>	<u>4/16/73(2)</u>	
Ethylene (Contract)	0.06-0.07	0.035-0.0375	71-87
Propylene/gal	0.20-0.25	0.145	38-72
Benzene/gal	0.759	0.286	165
Styrene	0.15-0.25	0.0725-0.09	107-178

The use of coal as an alternative raw material for some plastics materials is easier to see than that of agricultural (renewable) resources. Thus, polymers and copolymers of formaldehyde are well established commercial products. The primary raw material for these polymers, methanol, can be made from coal just as readily as from natural gas or oil. Certainly, in the case of a new plant for making methanol, the cost and availability of natural gas or petroleum relative to coal must be weighed carefully. Even an operating plant might be converted from natural gas to coal as raw material much more easily than perhaps any other petrochemical operation.

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## Coal—"New" Source for Plastics

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Coal can liberate the U. S. from the plastics shortage as well as the energy crisis. It is abundant, and we have the technology to convert it to precursors for plastics at costs that are suddenly cheap compared to the price tags on chemicals from imported petroleum. Ethylene, propylene, benzene, toluene, xylene, phenol and other raw materials for polymers and plastics can become plentiful again; but we must speed up R&D as well as plant construction.

The U. S. has more than half the world's known coal reserves, over 3 trillion tons. Only 5% of this is feasible to mine with present technology, but even this is a 300 year supply at our present rate of use of 500 million tons per year. Evolving techniques will make much larger quantities available, however.

Coal is significantly higher in carbon content and lower in hydrogen than petroleum, and is in this respect a better source for production of aromatics. Other products available from coal conversion include phenol and other tar acids, ammonia, sulfur and hydrogen, as well as ring nitrogen compounds.

Polymers and plastics are the major outlets for most of these chemicals, as shown in the following table.

Table 1

### Polymeric End Uses for Coal Chemicals (1,2,3)

<u>Chemicals</u>	<u>Percent Going to Polymers/ Plastics</u>	<u>Some End Products</u>
Ethylene	65	PE, PS, ABS, SAN, SBR, PVC, Unsat'd. & sat'd. polyesters.
Propylene	64	PP, EPR, Acrylic fibers, SAN, Urethane, Polyester, Phenolic.
Benzene	90	PS, SAN, ABS, SBR, Polyester, Phenolic, Epoxy, Nylons 6&66.
Toluene	70	Coatings, Urethanes, Arom's.
Xylenes & Ethyl Benzene	85	Polyesters, Plasticizers, Styrene derivatives.
Naphthalene	60	Plasticizers, Alkyds.



The naphthenes, obtainable in high concentration in syncrudes from coal, are converted predominantly to aromatics by reforming processes.

Table 2

Major Aromatic Products Obtained by Reforming  
Of Naphthenes from Coal (1,2,3)

<u>Naphthene</u>	<u>Aromatics</u>
Methyl cyclopentane, Cyclohexane	Benzene
Methyl Cyclohexane	Toluene
Dimethyl Cyclohexane	o-, m-, p-xylene, Ethyl benzene
Trimethyl Cyclohexane	Trimethylbenzenes
Cis- & Trans-Decahydro- naphthalene	Naphthalene

In addition to these more obvious derivatives, many specialty aromatics are available in such high proportion as to change the economics of the polymers based on them. A notable example is durene (1,2,4,5-tetramethylbenzene), a starting material for pyromellitic dianhydride, which is reacted with diamines to give the high-temperature-resistant polyimides. Gasoline from coal contains about 2% of durene, some 10 times the volume found in typical petroleum gasolines. Conceivably the price could be cut to a fraction of its present value, with resultant reductions in the cost of polyimides, polyamide-imides and polyester-imides. A great increase in the use of these materials is thus a possibility.

Among the exotic condensed ring derivatives are carbazole, from which can be made N-vinyl carbazole for polymers to be used as dielectrics and in photo-sensitive systems; and pyrene, from which BBB pyrrone fibers can be derived.

The most advanced technique for making gasoline from coal is the COED process, developed by FMC. Crushed and dried coal is heated successively in four fluidized bed reactors at selected temperature, e.g. 600, 850, 1000 and 1500°F, the temperatures just below the level at which each type of coal would agglomerate. In each bed, some volatiles are released. Later, the oil obtained by pyrolysis is partially hydrogenated(4).

Another technique for producing syncrude is the H-Coal process developed by Hydrocarbon Research Inc., of Trenton, N. J. Here powdered coal is hydrogenated

in an ebullating bed. Pittsburgh and Midway Coal Mining Co., Kansas City, Mo., has a solvent-refined coal process, using lignite or bituminous feedstocks.

The U. S. Office of Coal Research has sponsored most of the experimental work on making syncrude and syngas from coal; but EXXON and other energy companies are developing proprietary processes.

Clearly, coal is the fossil of the future!

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### Renewable Resources and Solar Energy Conversion Systems

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Renewable resources, such as wood and the by-products from the pulp and paper and the agricultural industries, are becoming increasingly attractive as raw material sources in light of the present shortages in the petrochemical business. The longer term development is, however, going to be governed by the economic balances involved, primarily related to the cost of energy. This development is also most likely going to be in favor of renewable resources. Ecological and public concern will also affect the trends. Carbohydrates and lignin can probably be used to a much greater extent with or without extensive modification, or they can be used as the feed stock for chemicals such as alcohols, ethylene, butadiene, phenols, proteins, etc. Improvement in the processes

for these conversions can most likely be made, but it must be realized that these developments are more or less totally governed by the economic incentives. Projections about the cross-over points in the cost-time curves and the future slopes for petroleum vs. renewable resources cannot be done just based on past experiences or assumptions about surprise-free futures.

It appears highly justified just now that the research on renewable resources is dramatically increased, and that this is done within the scope of these raw materials being a part of solar energy conversion systems. Land use policies and improvements in the efficiency of the use of solar energy and nutrients for the production of organic materials also have to be brought into the picture. As a wood chemist I find it tragic that the ACS division that used to have "Wood" in its name now has dropped it in favor of the textile application.

I would like to put your attention to a conference on "Wood Chemicals - A Future Challenge," to be held in Syracuse, New York, May 20-24, 1975. The conference is sponsored by the Technical Association of the Pulp and Paper Industry and the State University of New York. Those of you who might be interested in participating can contact Dr. T. E. Timell at the Cellulose Research Institute in Syracuse. As program co-chairman I am also anxious to get proposals for relevant papers discussing the future trends or technologies in the use of renewable resources as a raw material base for the chemical industry.

### **Furfural and Furfuryl Alcohol**

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I would like to remind the group of the utility of furfural and furfuryl alcohol in the making of many plastic materials. The furfural industry is based on converting the pentosan fraction of plant materials to furfural. The products available are well known because the technology for doing this chemistry was pioneered by the Quaker Oats Company over 50 years ago. For a more detailed picture of the products, the interested reader should be referred to Volume 7 of the Encyclopedia of Polymer Science & Technology.

## Development of Pullulan: Its Characteristics and Applications

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Pullulan was reported by R. Bauer in 1938 as a product obtained on cultivation of a yeast, Pullularia pullulans. Its elaboration conditions, structure and derivatives were studied and gradually revealed by many investigators who were stimulated by the report; however, no substantial approaches were attempted on its characteristics.

With a specific objective, the research group of Hayashibara Biochemical has commenced and gradually increased their production of pullulan. Eventually they drew their attention towards its characteristics and succeeded in the economical commercial production of pullulan. Particularly, improvement of the yeast species and the selection of a suitable medium led to favorable yield and to the development of a commercially feasible purification procedure, which made production more advantageous.

Pullulan is a linear polymer consisting of maltotriose units, non-reducing and reducing terminal groups of which are linked repeatedly in a  $\alpha$ -1,6-fashion, possessing a few percentages of maltotetrose but no branches, and a molecular weight which ranges from thousands to millions. Hayashibara Biochemical has discovered that pullulan with the desired molecular weight is obtainable ad libitum by using a yeast mutant and varying the cultivation conditions. The institute is producing pullulan of various molecular weights - 30,000, 50,000, 70,000, 100,000, 150,000, 200,000, and 400,000 - and also down to 5000 to 10,000 and even up to 4,000,000 to meet specific demands, as well as being engaged in research and development of suitable applications utilizing the characteristics resulting by varying the molecular weight.

The main characteristics of pullulan and its derivatives can be enumerated as follows. Pullulan and its derivatives:

- 1) are obtainable as bland, odorless white powder,
- 2) are insoluble in organic solvents in general,
- 3) are easily and highly water-soluble, although non-hygroscopic in powder form,
- 4) in aqueous solution, have a high viscosity which varies with molecular weight,

- 5) in aqueous solution, increase their viscosity with rise in molecular weight; however, the increase is not as sharp as noted with other polymeric substances,
- 6) dissolve in water about three to four times faster than PVA,
- 7) are decomposable by pullulanase, forming over 90% of maltotriose, a few percentages of maltotetraose, and traces of glucose and maltose,
- 8) are difficultly decomposable by amylases in general,
- 9) are absolutely non-crystallizable, and
- 10) can be etherified or esterified to retard proportionally the swelling and water-solubility with increasing degree of substitution. The products are difficultly water-soluble, but still decomposable by soil microorganisms.

Based on the above findings and characteristics, Hayashibara has developed the following applications and is currently extending their research to exploit more useful potential applications.

### 1. Films

Pullulan in aqueous or moistened powder form can be converted into odorless, transparent and tenacious films by any usual method. In comparison with other films, these films have remarkably low oxygen permeability and surpass others as oxidation-preventive barriers. Moreover, the films can be prepared with water as the sole plasticizer. A slight addition of polyhydric alcohol will lead to the production of more flexible films, if desirable. Pullulan with a molecular weight exceeding 150,000 is preferable for film formation.

### 2. Plastics

Colorless and transparent shaped or molded articles are easily produced by subjecting pullulan, to which a few to ten percent of water has been added, to compression molding at 100-200°C or to extrusion. Mixtures of different molecular-weight pullulans yield favorable results, as in the case of petrochemical polymers. Needless to say, foamed products are also easily preparable with pullulan, its derivatives or combinations thereof.

### 3. Fibers

The wet or dry spinning method is employable for preparing fibers from pullulan. However, the method depends on the desired property in the final product: easily, difficultly, or non-water-soluble. As in the case of petrochemical polymer fibers in general, favorable results are not attainable if the molecular weight of pullulan is excessively low or high.

### 4. Adhesives

Highly concentrated aqueous solutions of pullulan have high adhesive strength, because pullulan has a linear structure as well as being non-crystallizable. The adhesive may be applied on paper or other material and dried, to be used subsequently and conveniently by remoistening. However, in some cases the adhesives can be prepared with special care so that they will become water-insoluble after adhesion. A characteristic that distinguishes these adhesives from others is their firm adhesion to glass surfaces. Use of pullulan thus avoids harmful toxic gases when used as adhesives for interior construction or as surface paints.

### 5. Pharmaceuticals and Medical Supplies

A number of applications in the medical field have been proposed, suggested and developed for pullulan of various molecular weights, pullulan derivatives and combinations thereof. Details will be reported upon completion of current long-term tests.

### 6. Foods

Although pullulan is a natural gum obtained by cultivation of yeast, it is superior to conventional natural gums or synthetic gums because it is acid- and salt-resistant, viscous, and moreover because it is suitable for retaining the texture of foods and improving their quality. The retention of desired properties and the ease of production using pullulan in foods are additional advantages. Due to the absence of pullulan-decomposing enzymes in mammal and human digestive tracts, pullulan can be utilized as an effective ingredient for low-calorie food preparation by replacing a major portion of cereals with this non-digestive carbohydrate. Whereas non-digestive food ingredients generally induce loose passage and

diarrhoea, such symptoms are not noted with pullulan. Short and long term toxicity tests on pullulan and the yeast have thus far shown no unfavorable results.

Conventionally, plasticization of starches, modified starches and amylose have often been attempted often without satisfactory results. The development of these applications was accomplished by the discovery of a process to decompose carbohydrates into glucose units and rearrange these into pullulan. Pullulan is advantageous in view of environmental pollution prevention, because the process is biochemically based and neither requires an enormous energy consumption nor releases or generates excess heat or harmful gas.

Pullulan relies on starch as a starting material, a limitless source as far as solar energy and water are available, while petroleum is a maldistributed underground resource.

It may be emphasized that the pullulan industry can be characterized as being based on the cycle of Nature, i.e. life cycle, from the production of its starting material to its ultimate disposal and disappearance.

This paper was contributed through the courtesy of Dr. Yasumasa Takeuchi, Japan Synthetic Rubber Co., Ltd., No. 1, 1-Chome, Kyobashi, Chuo-Ku, Tokyo, Japan.

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