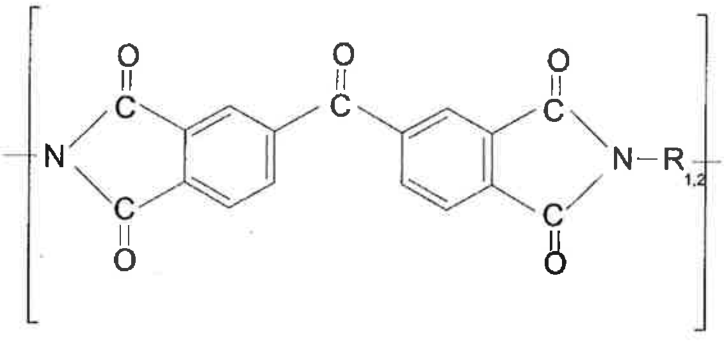
P84® Polyimide

Polyimide –Polymer Blends and Alloys



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Preliminary Information
P84 POLYIMIDE/Polymer - Blends

To reduce the main weakness of thermoplastic polymers in tribological applications it is common to use PTFE and/or graphite.
Now it is possible to reinforce these properties with the use of P84-Polyimide-Powder.
The addition of P84 increase the tribological properties as well as the thermal resistance in some cases.
Blending work has been done with **PES**, **PPS**, **EPOXY**, **PUR** and **PAEK**.

The documentation of obtained properties in the following pages is taken from studies and patents which show the advantage of this possibility.

The major argument for P84 is the availability of the resin and simple processing in combination with other polymers.
The reinforcement levels require only a very small ammount of P84 to obtain the improved properties.
In some cases sufficient results were reached under the use of only 2 to 5% Polyimide in the base resin.

In has been found that in combination with other polymers, the mechanical properties also will be increased. One example is PPS.

The reduction of softening at temperatures near the Tg of such High-Performance-Polymers helps in a lot of applications.
Some examples are:

> Sliding parts in mechanical equipment, compressor seals, piston rings and valve plates.
> Lubricant free bearings and dynamic seals on differnet applications.

Used Literature:

US Pat. 4,017,555	Alvarez	Polyalloy of PPS and PI
	Pacrim Intl.	Miscibility Studies in Blends of PES and P84
US Pat. 4,965,310	Amoco Corp.	Wear Resistant PAEK/PI Blends

Internal tests on blends PES/P84 and PPS/P84 concerning thermal, mechanical and tribological properties.

PPS/P84

The blending of PPS with P84 Powder has been done on a twin screw extruder under PPS moulding conditions.

Barrel-temperatures: 315 to 330°C (600 to 625°F)

The obtained granulate has to be predried at 150°C (300°F) for 6 hours before moulding.

The injection moulding requires following parameters:

Barrel-temperature:	315 to 330°C (600 to 625°F)
Injection-pressure:	750 to 1000 bar (10600 - 14000 psi)
Post-pressure:	350 to 750 bar (5000 - 10600 psi)
Injection-time:	1 to 6 sec.
Post-pressure-time:	10 to 15 sec.
Injection-speed:	slow to medium
Screw-speed (rpm):	medium
Mould-temperature:	130 to 140°C (270 to 280°F)
Cylinder-cleaning:	after every use of PPS cleaning with HDPE.
Release Agent:	Use Silicone Release Agent for the first shots.

Production Stop:

If there is any longer cycle-stop necessary (more than 20 min) reduce barreltemperature to 260 - 290°C (520 - 550°F).

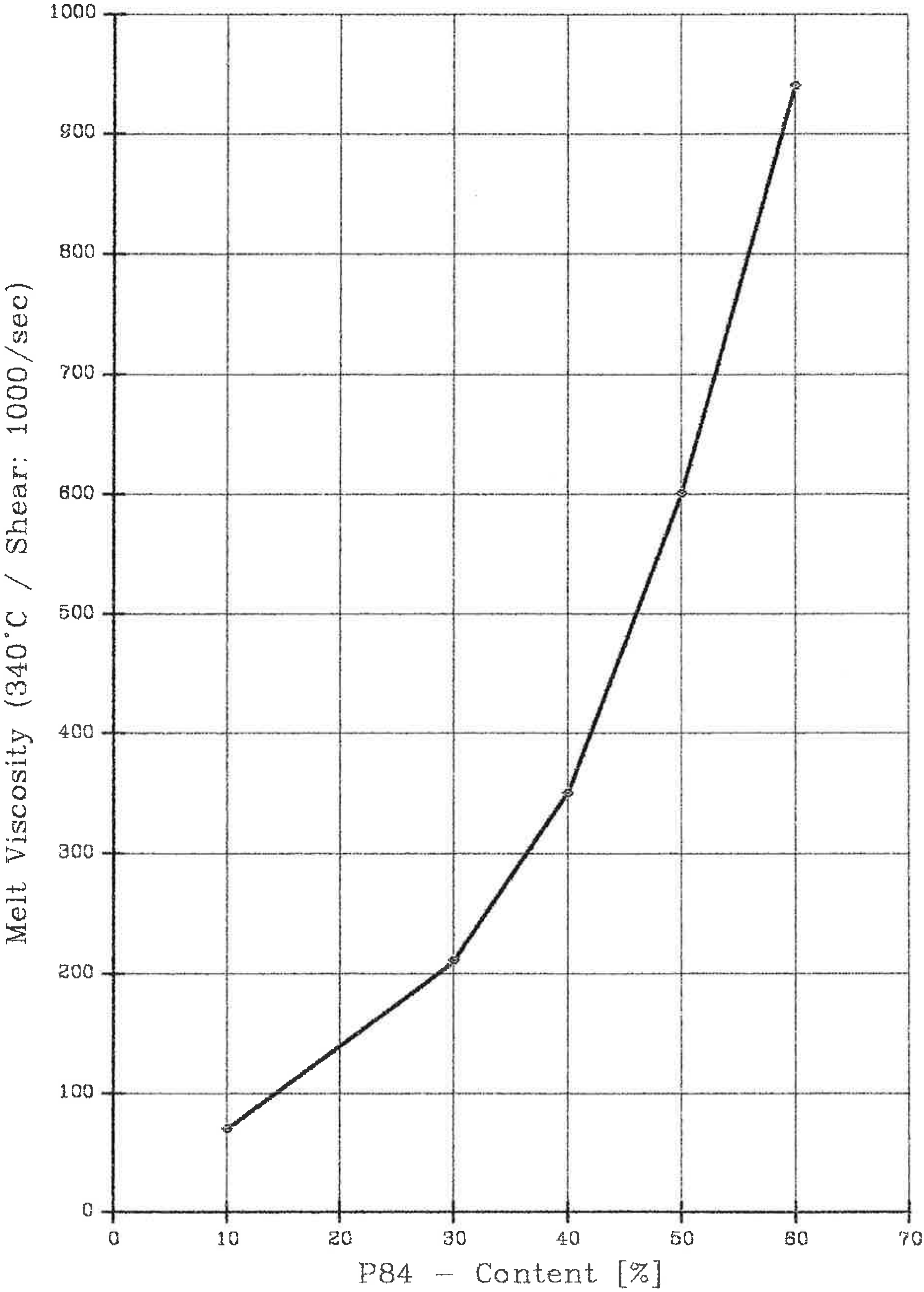
Post-Curing:

Cure the moulded articles after moulding 2 to 6 hours at 220 to 240°C (430 to 460°F).

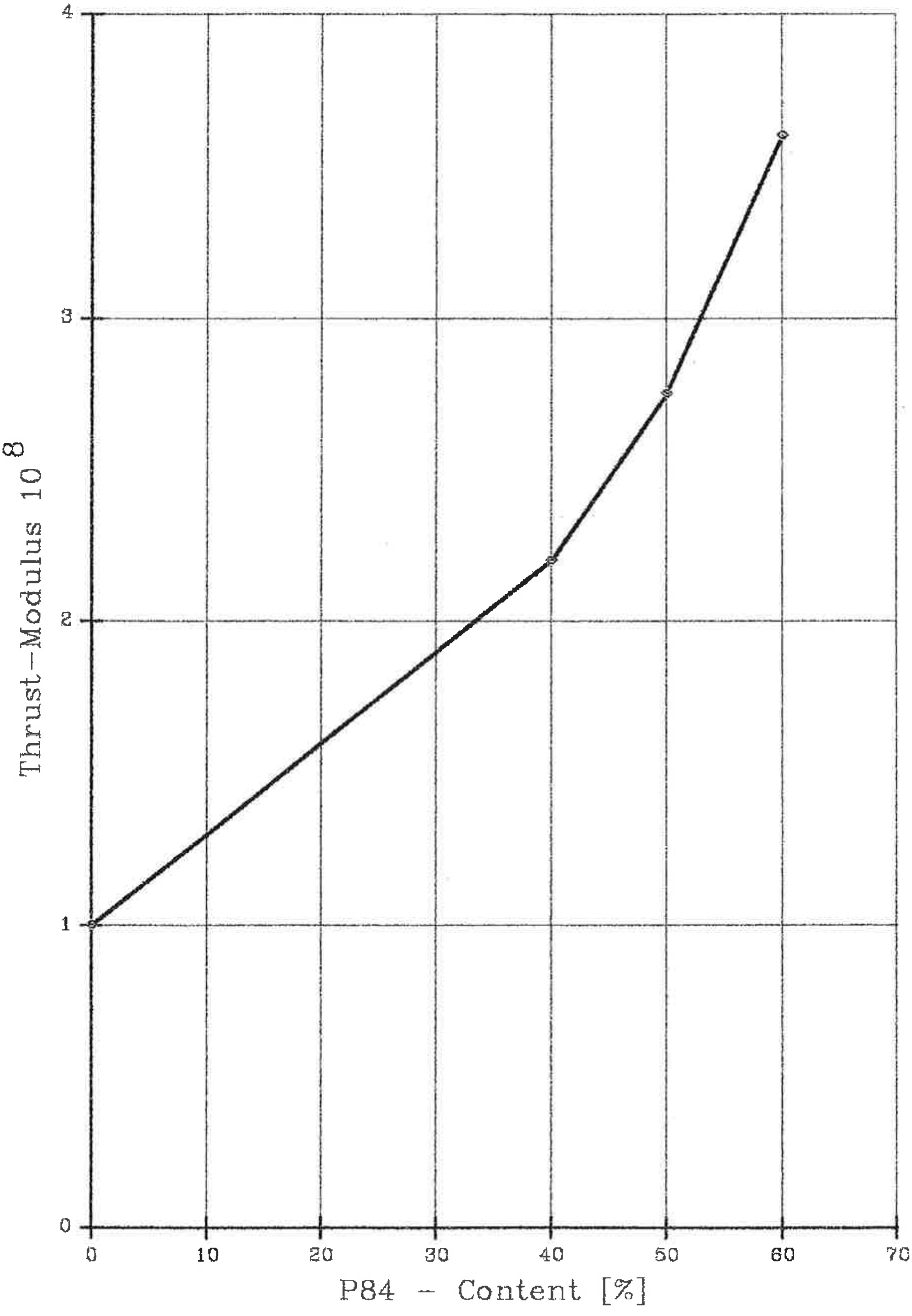
<u>**Properties of PPS/P84**</u>

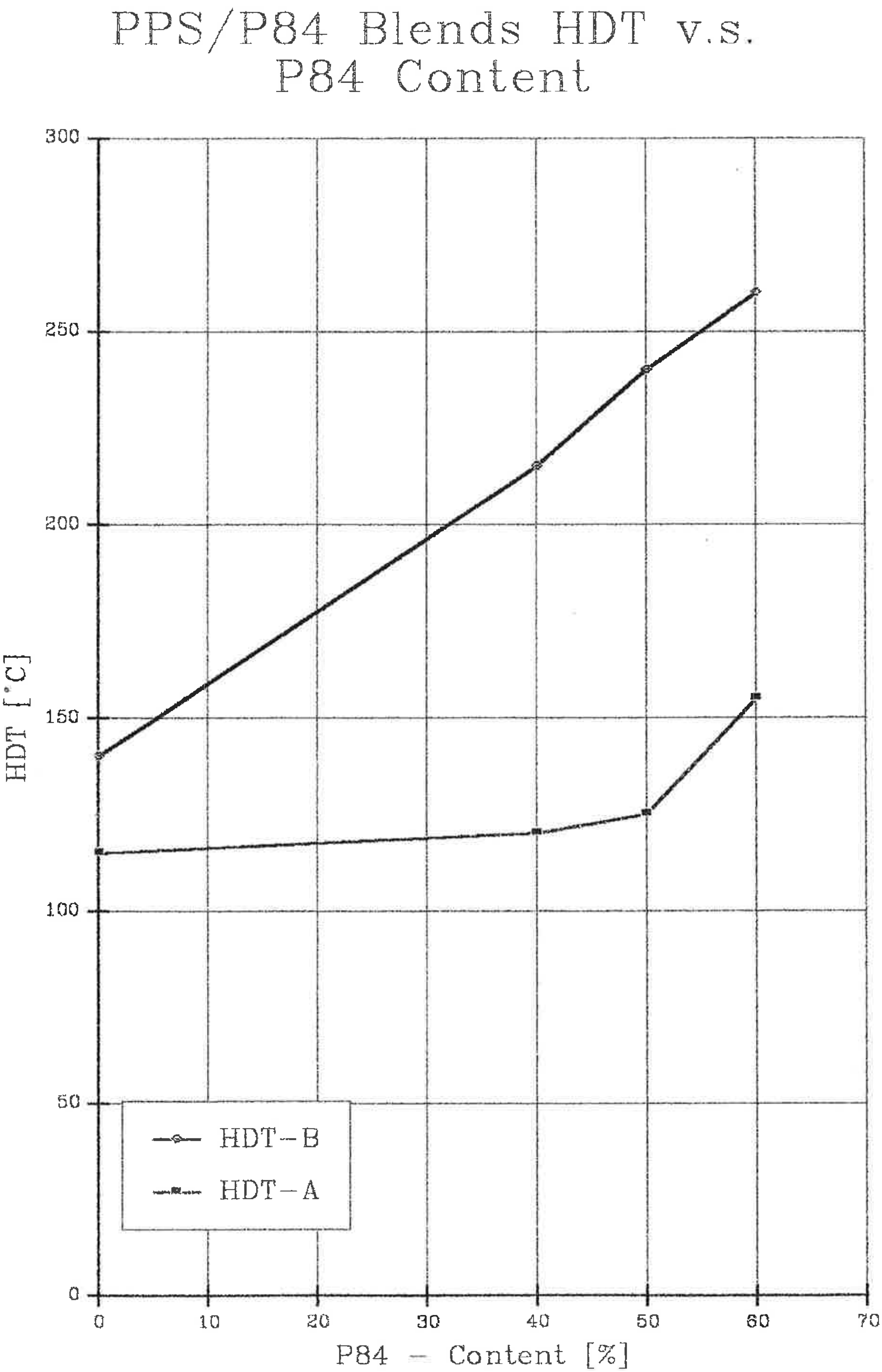
PPS/P84		98/2	95/5	90/10	80/20
Tensile Modulus					
GPa			3.6	3.7	4.0
Psi			51228	52651	56920
Tensile Strength					
uncured	MPa	60	54	53	54
	Psi	854	768	754	768
cured	MPa	67			
	Psi	953			
Elongation					
uncured	%	1.6	1.6	1.5	1.4
cured	%	1.8			
Flexural Strength					
uncured	MPa		144	137	134
	Psi		2049	1950	1907
HDT Temperature					
uncured	°C		107	109	119
	°F		224.6	228.2	246.2
cured	°C				225
	°F				437
MFI					
315°C (600°F)					
216 kg (477 lb)					
	g/10 min		114	99	80

Melt – Viscosity v.s. P84 Content of PPS/P84 Blends



PPS P84 Blend
Thrust Modulus at 210°C



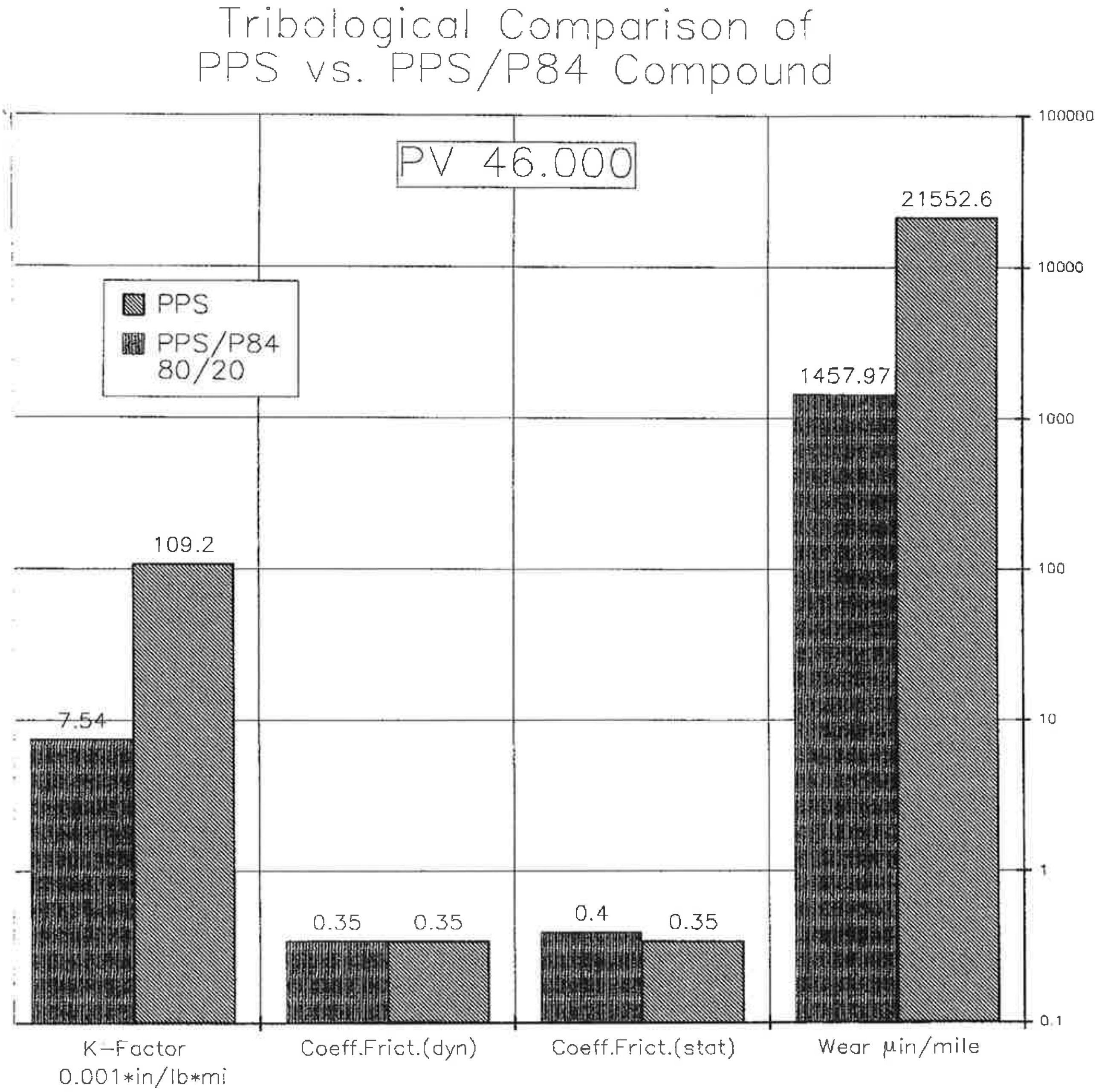

PPS/P84 Blends HDT v.s.
P84 Content
300
250
200
150
100
50
0
HDT [°C]
0
10
20
30
40
50
60
70
P84 - Content [%]
HDT-B
HDT-A

Test Results PPS/P84 Blends

PPS: TEDUR (Bayer)	%	60	50	40	PPS
Polyimide P84 -325 mesh	%	40	50	60	
<u>Viskosity</u>					
Eta 1000; 340°C	Pa.s	349	602	930	
<u>Flexural Test</u>					
Flex-Strength	N/mm^2	126	124	125	123
Elongation	%	3.7	3.6	3.6	5.2
Flexural-Modulus	N/mm^2	3500	3500	3600	3050
IZOD - unnotched	kJ/m^2	18	16	15	14
HDT-B	°C	221	240	257	140
HDT-A	°C	121	132	155	112
<u>Coefficient of lin. thermal expansion</u>					
MD/CD RT - 100°C	10^{-8} K^{-1}	50/48	48/49	47/47	53/52
100 - 200°C	10^{-8} K^{-1}	92/72	83/77	78/73	121/116

Lenzing P84

HIGH PERFORMANCE PRODUCTS



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Toughening of thermosets with P84

1. Epoxies

Epoxy resins, used for structural applications, are commonly found as composite matrix resins in glass- and carbonfiber fabrics. These find widespread use in the aerospace field as laminates in different parts of both civil and military aircrafts especially where highly damage tolerant composites are critically needed. Nevertheless these materials suffer from weaknesses which are mainly due to brittleness and lack of toughness of the resins. Throughout this brief account the term "toughness" refers to the capability of a resin to absorb impact energy [1].

There are a number of methods of modifying epoxy resin formulations as a result of the economic importance of the composites and because of the enormous structural variability of the resins. Among them, appropriate thermoplastic High-Tg materials designated as tougheners for epoxy resins play an important role. In these systems the thermoplastic normally represents a separate phase in the crosslinked matrix.

P84 Polyimide has outstanding performance in combination with epoxies. The addition of micropulverized polyimide (PI) to the monomeric epoxy component without the additional need of a solvent yields composites which are characterized by their good processability and their high thermal resistance. It is thought that the source of improved toughness in these cases is the existence of a dispersed high-temperature resistant polymer microphase [1].

However, critical evaluation of the appropriate epoxy resin had to be put into consideration since there is a strong dependence of the chosen epoxy on the observed toughening effects. For example, a resin formulation consisting of a mixture of one part of a DGEBF - epoxy and three parts of an epoxy resin derived from phenolated dicyclopentadiene (DCPD - epoxy), after addition of Lenzing´s P84, poor impact strength values are measured and composites were sometimes even observed to delaminate after impact [3],[4].

To achieve highly toughened composite formulations comprising of P84, epoxies based on bisphenol A and bisphenol F are recommended. In these cases thoughness properties like fracture toughness values and compression after impact (CAI) values are excellent.

Resins can further be modified by employing more than two epoxies in order to reduce the viscosity of the mixture. After adding the PI at slightly elevated temperatures, the amine hardener is added [2].

Prepregs produced therefrom can be cured like standard epoxy types - for example by vacuum bag curing [2].

A typical procedure for preparing a toughened epoxy matrix formulation consists of heating an epoxy blend at 50-60C, followed by slow addition of 20% P84, which has been milled to an average particle size of 10-20u. On the addition of P84 normally neither dissolution of the PI nor swelling is observed. The resulting mixture is stirred at 60C for about 30 min, whereupon the amine hardener, usually 25% DDS , is added [4].

<u>Literature:</u> [1] Mühlhaupt R., Chimia <u>1990</u>, 44, 43-52.
[2] PCT WO 91/02029 to HITCO Co.
[3] EP 377348 to BASF AG
[4] EP 392348 to BASF AG

2. Bismaleimide (BMI) resins

Thermosetting BMI resins find prolific use in many applications, particularly as structural materials, mainly in the aerospace field.

Among the advantages of BMI-based polyimides their comparably easy handleability has to be mentioned. Despite of the good processability of most of the thermosets, manufacturers face severe problems with the materials. Bismaleimide resins (BMI`s) sometimes are subject to microcracking, brittleness and diminished impact tolerance.

Thus toughening of thermoset resins is considered to be increasingly important. Among these, reinforcement by addition of High-Tg thermoplastics exhibits considerable importance [1].

Lenzing´s P84 polyimide, due to its outstanding mechanical and thermal performance is a serious candidate for enhancing thermoset resin properties while good processability is maintained. The thermoplastic and the thermosetting polyimide are thought to form an interpenetrating network (IPN), which is herein defined as a mixture of distinct polymer phases that cannot be separated physically [2].

Literature is sparse in the field of BMI-resin toughening with P84, but positive results already available are stimulating further endeavour in development.

Finely powdered P84 (8-10u) is added up to an extent of 20% to the BMI resin, which has been heated to 80-90C, while thorough mixing at high velocity is maintained. The product is then used to prepare a reinforced prepreg. Carbon fiber prepregs can be manufactured employing standard methods (vacuum bag, autoclave) [3].

Tests of composites using various resin systems [3]:

BMI	**Thermoplastic**	**CAI (MPa)**
Compimide	none	193
Compimide	Matrimide 5218	214
Compimide	LARC TPI	103
Compimide	Polysulfone (ICI)	179
Compimide	P84	262
Compimide	P84 (dual filming)	303

CAI refers to "compressive strength after impact", after impact of 4.45 kJ/m.

Literature: [1] PCT WO 90/09410 to Hexcel Co.
[2] Pater R.H., SAMPE J., 1988, 24, 25-32.
[3] EP 383174 to BASF AG

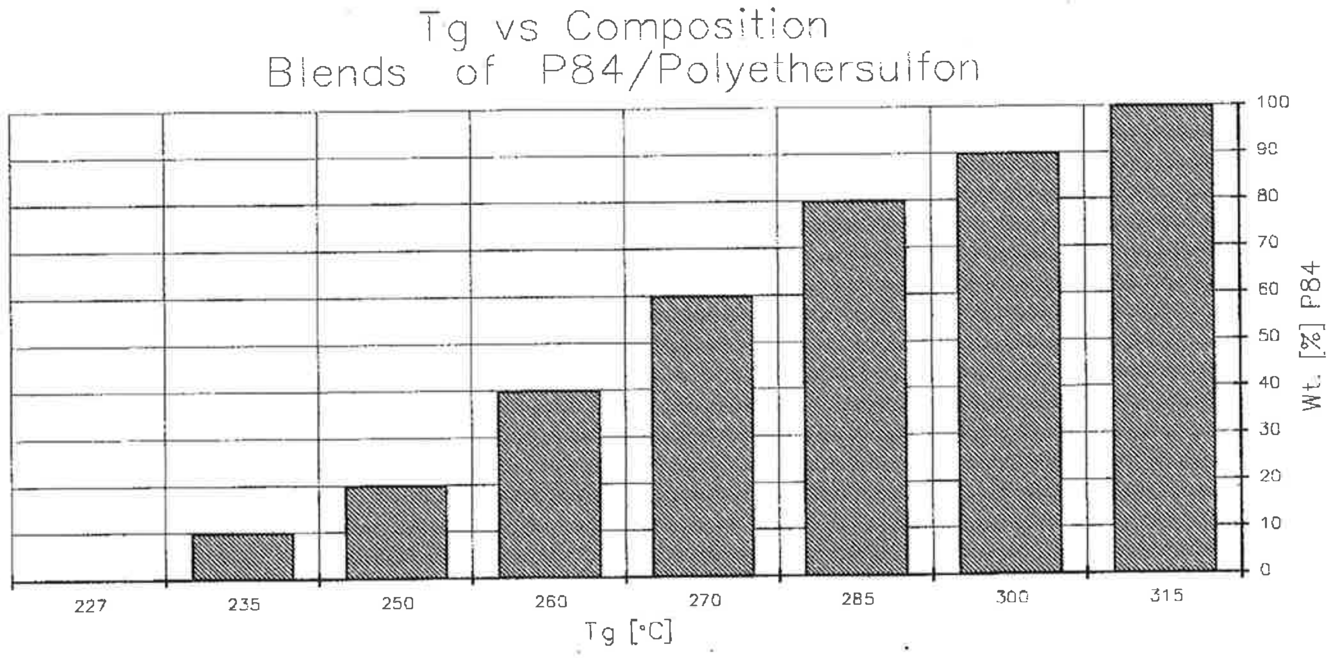
PES/P84

Polyethersulfone/P84 blend can be done on a twin-screw-extruder as well as thru solution blending.

Due to the possibility of diccolving both polymers in NMP or DMF it is possible to make homogenous blends in the solution stage of both plastics.

The thermal properties of such blends are described in the Miscibility Study in Blends of Polyethersulfone and P84 made by PACRIM Intl Inc. Branford, CT - USA.

The results concerning Glass-Transition-Temperature are shown by the following graph.



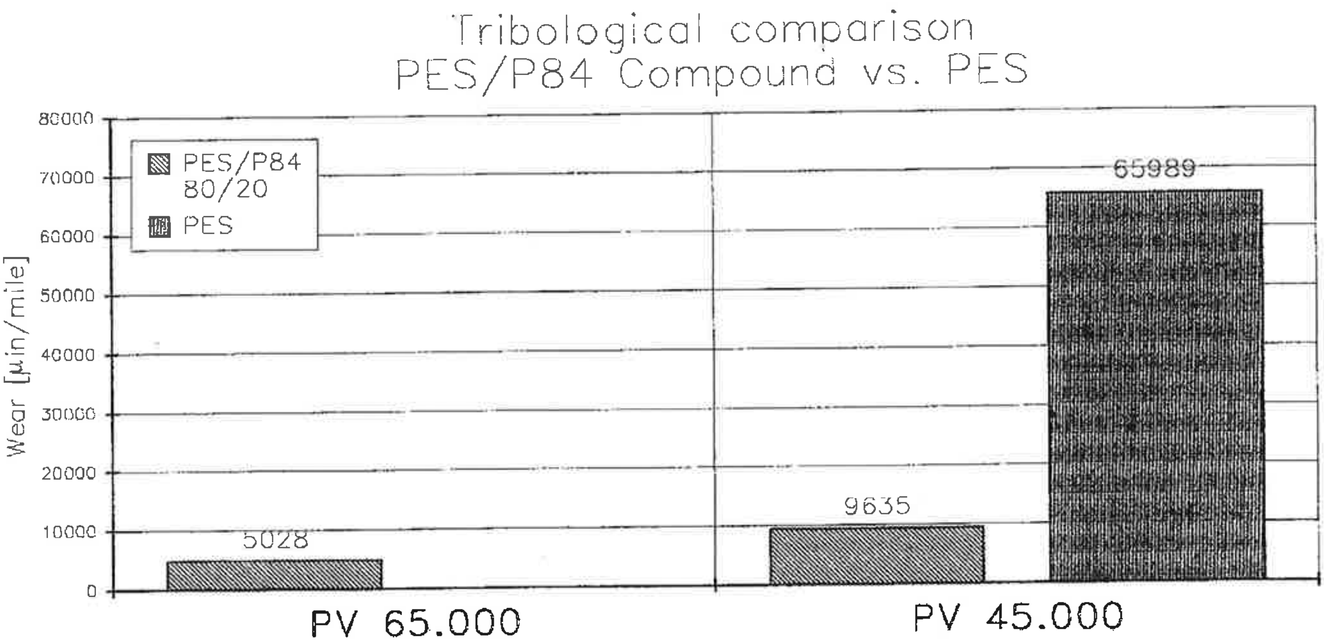
Processing:

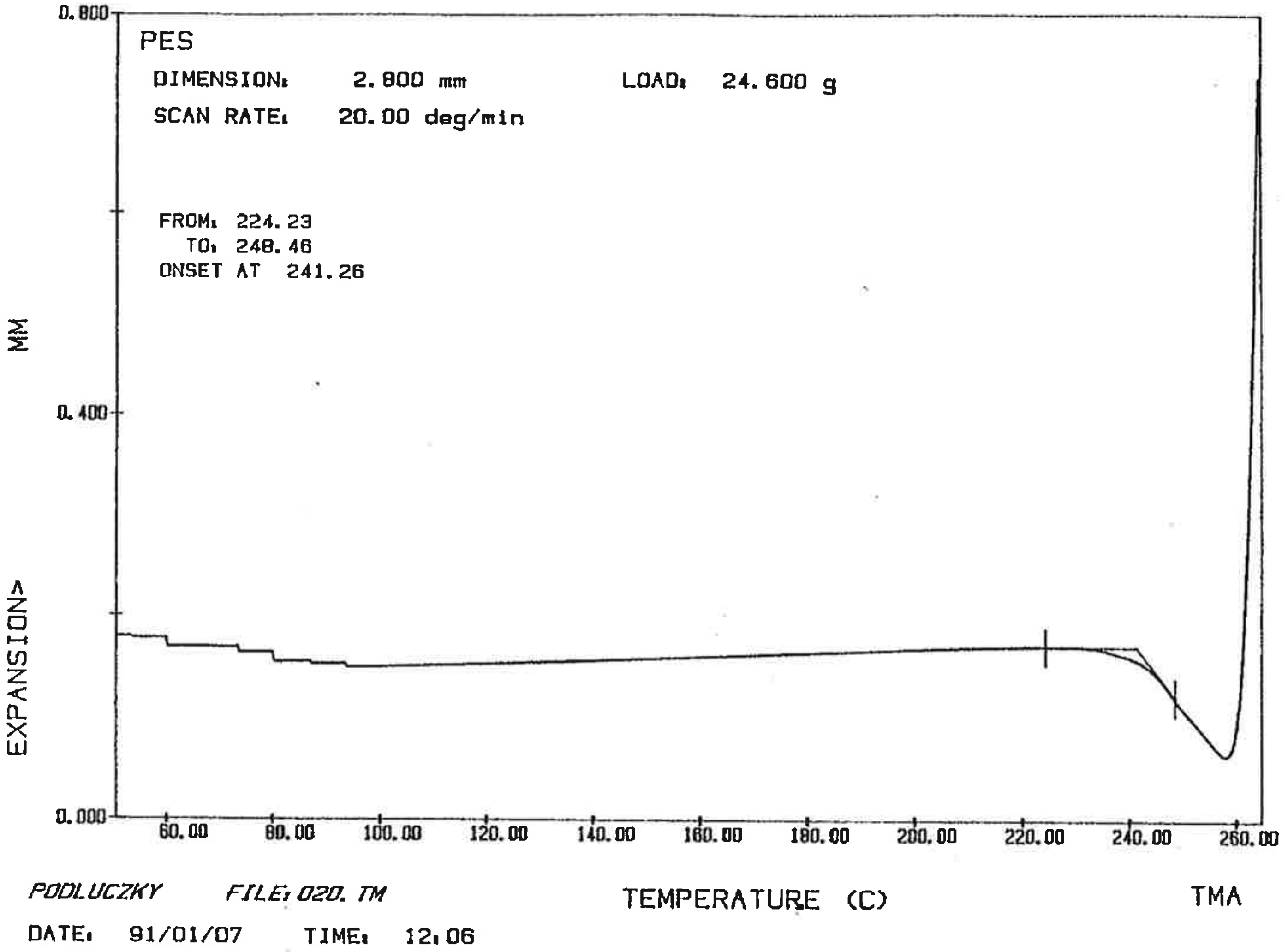
The processing of extrusion-blended PES/P84 is similar to virgin PES. Injection moulded parts show very high homogenity. The color of this blend is red-brown, similar to PEI.

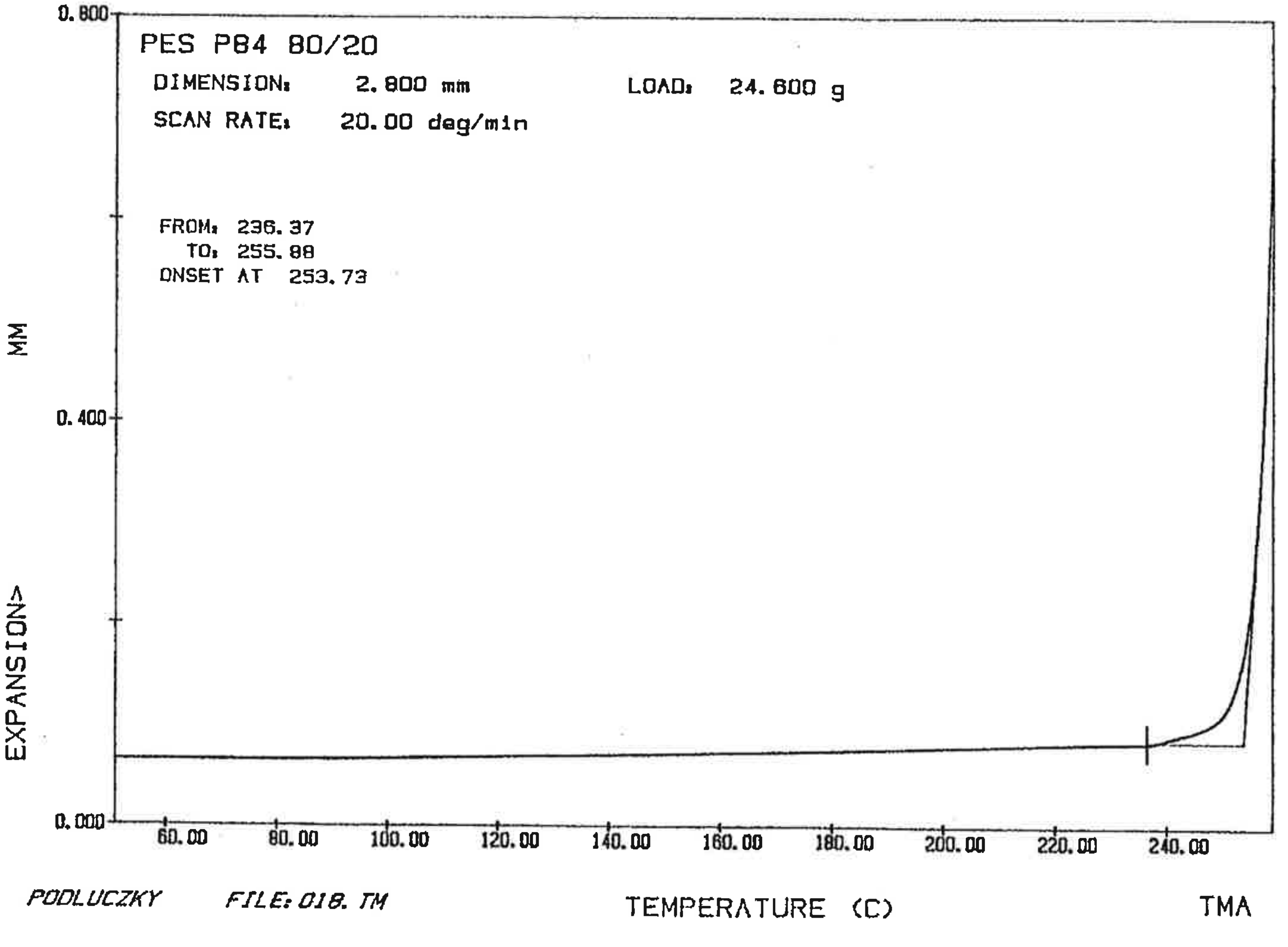
Tribological Properties:

Tests were done on a PES/P84 80/20 blend made via blending on a twin-screw extruder. The final compound was injection moulded and the test specimen machined. The comparison is done with virgin PES.

Test number	Material	P/Load psi/lb	F 1 hr	F 16 hr	Wear 1 - 16 hrs = 15 hrs	µin/mi	Speed ft/min
1	80/20	1625 17	0.5	9 hrs 0.45	1-9=8 hrs 0.0018 in	8 hrs 5028	40
2	VIRGIN PES	1625 17	0.6	N/A	1 hr > 0.04 in		40
3	80/20	1625 17	0.55	6 hrs 0.40	1-6=5 hrs 0.028 in		40
4	VIRGIN PES	1160 12.5	1 hr 0.63	N/A	1 hr 0.029 in	65989	40
5	80/20	1160 12.5	0.60	0.52	1-7=6 hrs 0.026 in	9635	40




PES
DIMENSION: 2.800 mm
LOAD: 24.600 g
SCAN RATE: 20.00 deg/min
FROM: 224.23
TO: 248.46
ONSET AT 241.26
0.800
0.400
0.000
EXPANSION> MM
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
260.00
PODLUCZKY
FILE: 020.TM
TEMPERATURE (C)
TMA
DATE: 91/01/07
TIME: 12:06


PES P84 80/20
DIMENSION: 2.800 mm
LOAD: 24.600 g
SCAN RATE: 20.00 deg/min
FROM: 236.37
TO: 255.88
ONSET AT 253.73
0.800
0.400
0.000
EXPANSION> MM
60.00
80.00
100.00
120.00
140.00
160.00
180.00
200.00
220.00
240.00
PODLUCZKY
FILE: 018.TM
TEMPERATURE (C)
TMA

PAEK/P84

The first trials in blending PAEK with P84 were done by AMOCO Corp. They blended PEEK (ICI) and P84 to form a 75/25 PEEK/P84 Compound. Tests were done to determine tribological properties. The end-use of such alloys would be in the field on compressor parts like piston rings and other friction and wear applications.

The main reason to develop PAEK/P84 blends was the weakness of PAEK in friction and wear properties at temperatures above 150°C (300°F). Due to softening of the matrix material, the wear-factor for most applications is too high.
The addition of carbonfibers and PTFE and/or graphite does not reduce the softening sufficiently. To overcome the demanding friction and wear requirements in many applications.

Tribological Properties of PEEK vs. PEEK/P84 Compound:

Source: US Pat. 4,965,310 AMOCO Corp.