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PAPER 3

FLUORINATED COPOLYMERS, THEIR PROPERTIES AND APPLICATIONS IN RELATION TO PTFE

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ABSTRACT

Following the discovery of PTFE in 1938, and its commercialisation in 1946, the chemical industry has sought products combining the very desirable thermal, chemical and dielectric properties of PTFE together with the ability to be melt processed.

A range of fluorinated copolymers based on TFE have been commercialised, starting with FEP in 1960 and followed by PFA and modified ETFE in 1972. Of these products FEP and PFA match the chemical and dielectric properties of PTFE (PFA possibly giving a higher performance in some high temperature areas) - whilst modified ETFE provides desirable mechanical toughness not available from the completely fluorinated products.

FEP, PFA and modified ETFE can be processed by conventional thermoplastic processes, with the resulting cost savings (compared to the special techniques used for PTFE) opening some new markets. Whilst there is interaction between the fluorinated copolymers and PTFE it seems likely that components of simple shape will continue to be made from PTFE, with new application development taking advantage of the melt processability of FEP, PFA and modified ETFE in the design stage (eg. long lengths of wire and cable, injection moulded parts of more complex section).

DEVELOPMENT

Fluorinated plastics have outstanding chemical thermal and dielectric properties owing to the great stability of the fluorine-carbon bond. The best known and most widely used of this family of plastics is PTFE, (polytetrafluorethylene) discovered in 1938 and commercialised in 1946. PTFE requires special processing techniques and ever since its own synthesis, chemists have looked for ways to produce a melt processable fluoroplastic that would give the same outstanding properties. One possible candidate, PCTFE (polychlorotri-fluoroethylene), was in fact synthesised in 1934, 4 years before the discovery of PTFE, but though still in production today has never achieved really wide usage.

As early as 1941, chemists had produced fluorinated copolymers based on TFE (tetrafluoroethylene), but the first such product to give properties similar to PTFE was FEP (fluorinated ethylene propylene), a copolymer of TFE and HFP (hexafluoropropylene). This product, first sold commercially in 1960, differed in only one essential property from PTFE, that of long term service temperature. FEP has a continuous rating of 205°C vs PTFE at 260°C, but as a true thermoplastic can be processed by virtually all conventional plastics converting techniques, though a very high viscosity puts a limit on the speed of processing.

Further research led to the introduction in 1972 of PFA (perfluoroalkoxy) resin, a copolymer of TFE and a fluorinated vinyl ether. The introduction of this product was most significant as PFA matches the performance of PTFE in virtually every facet, its service temperature rating being identical to PTFE at 260°C. With a better retention of mechanical properties at high temperatures, PFA could conceivably outperform PTFE in some areas.

Whilst FEP and PFA are the only fluoroplastics that can be directly compared to PTFE, it has long been evident that the use of fluorocarbon plastics could be extended were a mechanically tougher version available. Early work to this end was done on Ethylene-TFE copolymers and some *patents filed in 1941. However then, as more recently, manufacturers discovered that the properties of straight (unmodified) ethylene-TFE copolymers were not satisfactory, the lack of stress crack resistance being the greatest single drawback.*

In 1972 a modified copolymer of ethylene and tetrafluoroethylene, showing vastly improved stress crack resistance was introduced commercially. It is meeting industry needs where dielectric properties close to those of PTFE together with excellent chemical resistance and rated service temperature of up to 155°C are required (see notes on ageing). Another fluorinated polymer, a homopolymer based on VF_2 (vinylidene fluoride) offers a good degree of mechanical toughness together with good chemical resistance, although not offering the solvent resistance of modified ETFE.

The importance of this group of mechanically rugged fluoroplastics is underlined by the substantial investments being made by the chemical industry in the production of products for a wide variety of applications. The commitment of resources to the production of copolymers based on TFE exceeds that being devoted to the "parent" PTFE.

For the purposes of comparison, a property chart (1a and 1b) is attached listing the chief characteristics of PTFE, FEP, PFA and modified ETFE.

STRUCTURE AND PROPERTIES

The molecular structure of the four above mentioned products is shown in chart (2). The very high molecular weight of PTFE, and the long straight chain structure results in a melt viscosity so high that PTFE is not processable as "normal" thermoplastics. In the case of FEP and PFA the addition of side chains to the molecules can be seen, the lower melt viscosity rendering these products melt processable. For both products, the complete "fluorination" means that the molecular structure is as well protected as PTFE and the resulting properties very similar. In the case of FEP the melting point is down to 270^{o}C (from a "gel" point of 327^{o}C for PTFE) and service temperature to 205^{o}C. However for PFA, the existence of the oxygen atom, spacing the side chain away from the main backbone , relieves a great deal of stress in the molecule and the polymer does not reach its melting point until 305^{o}C.(Chemical molecules "vibrate" as their temperature is increased. In the tightly packed FEP molecule this vibration results in a high stress level in the links between the side chain and backbone, and in simple terms, to the dropping of the melting point).

The oxygen atom remains protected by the sheath of fluorine atoms,and the thermal stability of the carbon-oxygen bonds is at least equivalent to a carbon-carbon bond. Thus PFA, whilst being melt processable, has thermal stability at least equivalent to PTFE. The results of ageing tests on PFA, run for 20000 hours and more at 285^{o}C, show the mechanical properties and stress crack resistance to have improved with time, a remarkable performance.

Modified ETFE gains its melt processability from the ethylene components in its structure. This product is available in grades of various viscosity, in some cases allowing processing at rates closer to polyamides than to the fluorocarbon family.

PTFE, FEP, PFA are quite exceptional among plastics in ageing properties. When a service temperature of 260°C is stated for PFA, it means that it can be exposed at that temperature for an unlimited time without loss of properties. For a plastic that ages any service temperature rating should be accompanied by a definition of what percentage of original properties can be expected after a given period of time. Thus modified ETFE has a service temperature of 155°C based on retention of 50% of its original elongation after 20000 hours exposure at that temperature. PVDF, ECTFE and other polymers require similar definition.

PROCESSING

The ease of processing is the key to the development of the copolymers discussed. FEP, PFA and modified ETFE can be processed by most standard thermoplastic techniques. Commercial processes in Europe include :

- *Melt extrusion*
  - *Tubing*
  - *Wire coating*
  - *Monofilaments*
  - *Rods and sheets*
- *Injection moulding*
- *Transfer moulding*
- *Compression moulding*
- *Powder coating*

There are substantial differences in the processing of the above products, and these differences are related to melt viscosity. The chart 3 shows the relative viscosity ranges available and it will be understood that whilst the lowest viscosity versions of modified ETFE are nearly as easy to process as polyamide, the high viscosity versions of FEP and PFA have to be transformed more slowly. Be that as it may, the fact is that FEP, PFA and modified ETFE are all melt processable; PTFE is not. The advantages over PTFE in cost of transformation and flexibility of design are enormous and it seems inevitable that a larger and larger proportion of new applications for fluoroplastics will be met by the melt processable products.

APPLICATIONS

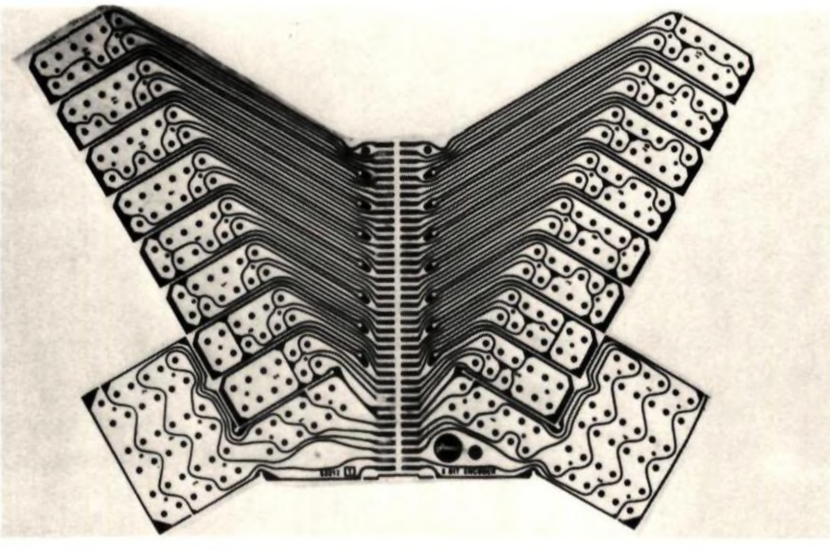
There is, of course, considerable overlap in applications between PTFE and the fluorinated copolymers, and where both products meet the functional needs of the application then cost of the finished part will dictate the choice of raw material. It is the writer's opinion that in the foreseeable future PTFE will continue to be the preferred material for most simple shapes, owing to its basic cost advantage. Rods, tubes (apart from long lengths), sheets and all but the largest quantities of components of simple shape will be made from PTFE.

However melt processing has clear advantages in the production of long lengths of extruded shapes (eg. wire and cable, some hose), the production of complicated shapes such as linings of valves and fittings for corrosion resistance purposes, and the injection moulding of parts that would require considerable machining from stock shapes of PTFE. In addition FEP, PFA and modified ETFE can be melt bonded to themselves permitting the assembly of structures in much the same way as is done with, for example, polypropylene. Modified ETFE has a degree of mechanical ruggedness not enjoyed by PTFE, FEP or PFA and as a result can be used in areas where fluorocarbons have previously been considered desirable but not strong enough. Typical applications include industrial wire and cable and solid (as opposed to lined) components for the chemical industry.

The following examples give some idea of where fluorinated copolymers have been used to fulfil functions not readily met by PTFE.

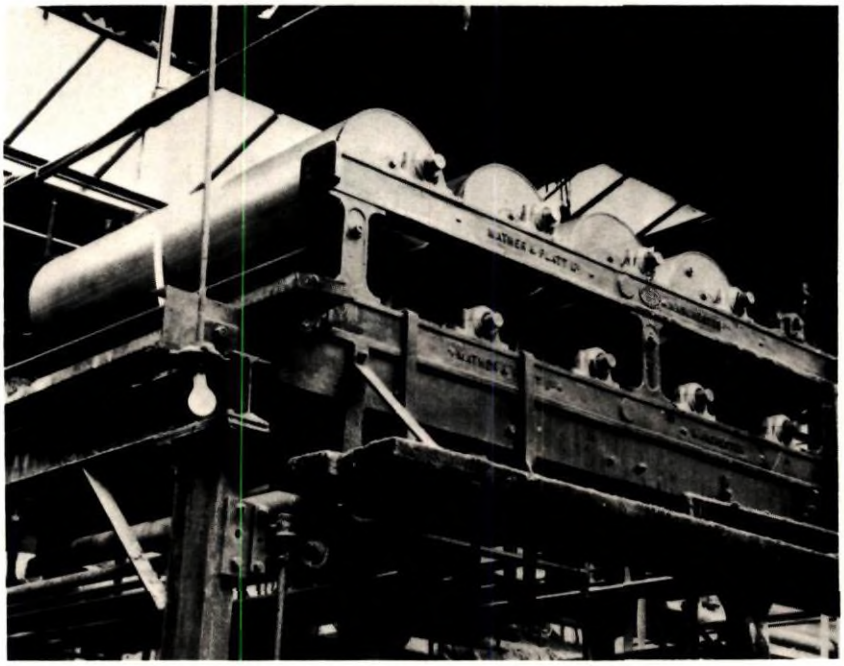
1) Cable Spacers

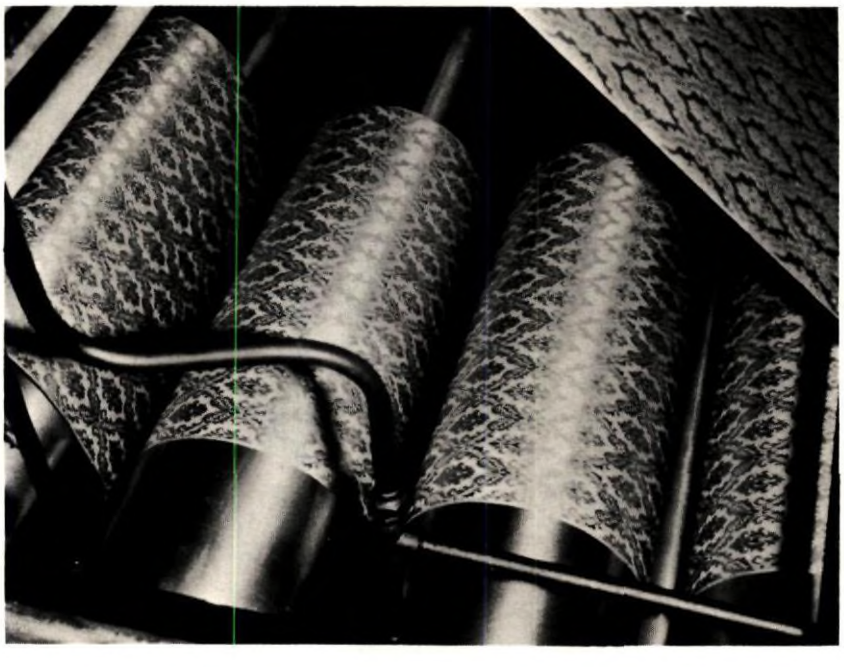
FEP was chosen for the injection-moulded cable spacers of one of the world's largest high-frequency coaxial cables because of its melt process-ability, its unvarying dielectric constant, and its low dissipation factor. The heat resistance of FEP (up to 205°C in continuous use) is also required, because the temperature of the inner conductor can reach 140°C.



2) Flexible Printed Circuits

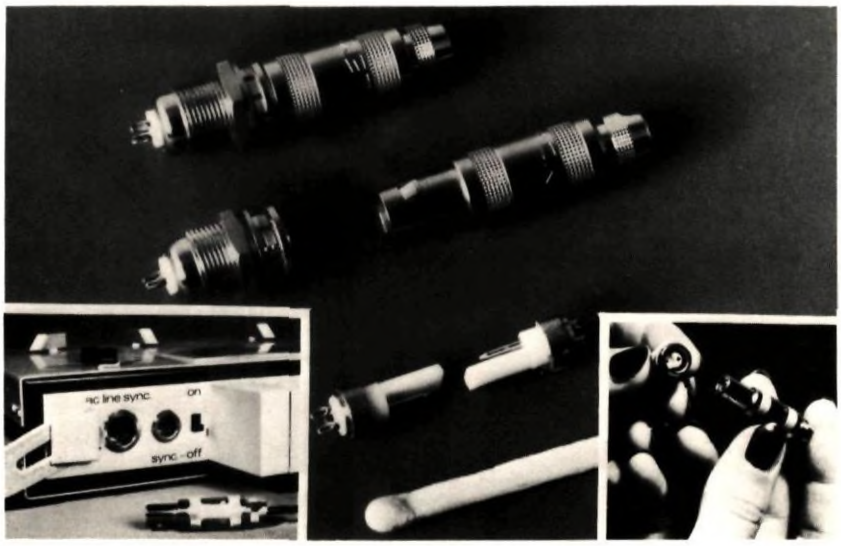
FEP's low dielectric constant is also of value in a British-made flexible printed circuit used in radar equipment, because this reduces crosstalk. The circuits are part of a computer encoder which receives information from computer keyboards and translates it into electrical impulses which are relayed to memory stores.





3) <u>Roll Covers of FEP</u>

FEP roll covers help reduce downtime in textile finishing industry when heat-shrunk over drying cylinders. The roll covers provide an easy-to-clean surface leading in turn to less product waste, improved quality of work, and no mark-off from one batch to the next.

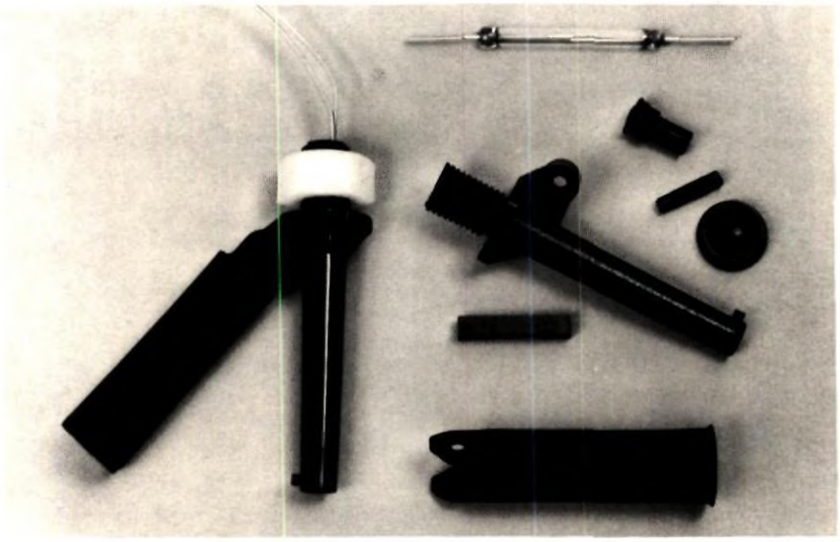


4) <u>Electrical Connector - Insets</u>

Inserts for electrical connectors made by a Swiss manufacturer exemplify at once the easy injection mouldability of PFA, the excellent electrical insulation properties, and the resistance to high temperatures.

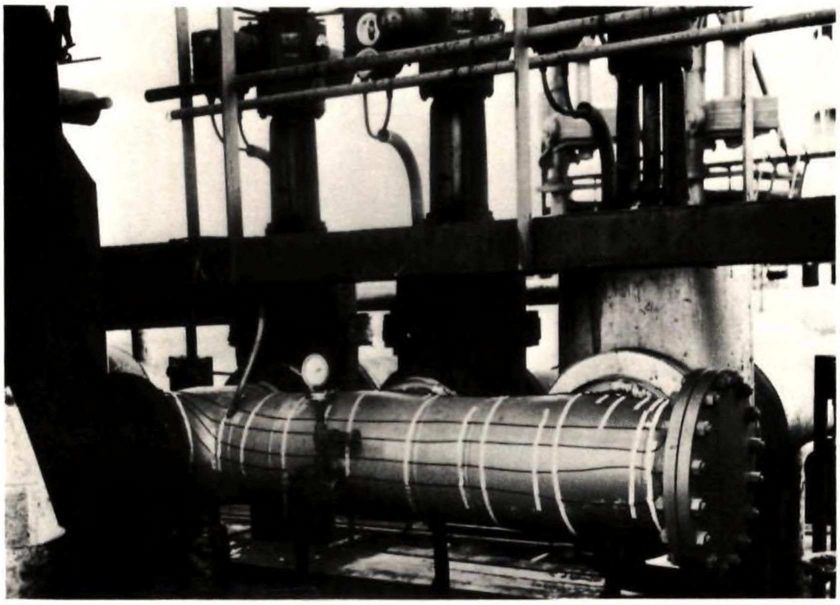
5) <u>Lined Equipment for the Chemical Industry</u>

Easy processing by transfer moulding as well as outstanding resistance to most chemicals, high continuous service temperature, good mechanical and surface properties make lining of chemical equipment such as valves, pumps, pipes and fittings one of the favoured areas of application of PFA.



6) <u>Liquid Level Control</u>

The housing of this English-made float switch is made of modified ETFE. It acts as a level control in a variety of fluids. The fluoropolymer has been chosen for easy injection mouldability into parts which retain good electrical and mechanical properties in most fluids even at temperatures as high as 155°C for continuous service, and up to 200°C for a limited duration.



7. *Wire and Cable Insulated with modified ETFE*

The largest single area of application for modified ETFE is as wire insulation. Typical multiconductor cables are shown in Photo 8. A typical application is for the insulation of heating cables attached outside pipelines leading from piers to oil storage tanks in a Dutch port. The cable outer jacket of ETFE is designed to withstand a cable temperature of 140°C, well below the 155°C maximum continuous service temperature rating. In addition, ETFE does not absorb moisture and resists corrosion due to brackish water and polluted air. Finally, the toughness of the modified ETFE means that the insulation can take a large amount of physical abuse (Photo 9).

CONCLUSION

The availability of the melt processable fluoroplastics FEP, PFA and modified ETFE complements the wide range of PTFE types produced. When choosing the type of fluoroplastic for the manufacture of a given part, the design engineer must decide which resin combines the characteristics in processing and use best suited to the mechanical, thermal, chemical and electrical requirements of the particular application he has in mind, including such factors as form dimension, number of parts, dimensional tolerance and price.

ICE:jg

Chart 1a

General properties of PTFE and TFE Copolymers PTFE, Modified ETFE

PROPERTY		PTFE	FEP	PFA	Modified ETFE
Chemical Resistance: hydrocarbons, ethylene glycol, battery acid, brake fluids, other chemicals		NO EFFECT	NO EFFECT	NO EFFECT	NO EFFECT
Resistance to weathering		NO EFFECT	NO EFFECT	NO EFFECT	NO EFFECT
Water absorption (ASTM D570)		>0.1%	>0.1%	>0.1%	>0.1%
Flammability (UL 83, Vertical Wire Flame Test)**		NO AFTER BURN	NO AFTER BURN	NO AFTER BURN	NO AFTER BURN
Melting Point ° F		621	530	590	520
Melting Point ° C		327	275	300	270
Upper Service Temperature ° F	1500-2000 hrs. estimated	550	450	550	400
	20,000 hrs.	500	400	500	300
Cold bend @ −65° C, 2.5 KV for 5 min.		PASS	PASS	PASS	PASS
Specific gravity		2.15	2.15	2.15	1.70

Chart 1b

Mechanical and Electrical properties of PTFE and TFE Copolymers PTFE, Modified ETFE

PROPERTY		PTFE	FEP	PFA	Modified ETFE
Tensile strength, psi (73° F) ASTM D638		3,500	3,000	4,000	6,500
Elongation,s% (73° F) ASTM D638		350	300	300	200
Flexural modulus, psi (73° F) ASTM D790		95,000	95,000	95,000	200,000
Flex life, MIT (7-9 mils) 180° Flexes		750,000	100,000	200,000	30,000
Impact strength, ft.-lb./in.: ASTM D256	Room temperature	NO BREAK	NO BREAK	NO BREAK	NO BREAK
	−65° F	30	10	10	>20
Coefficient of friction, >10 fpm, 100 psi		0.1	0.3	0.2	0.4
Dynamic cut-through (lbs) Instron 1/16" radius blade moving at 0.2"/min.	23° C	56^1 129^2	49^3 118^4		354^5
	75° C	43^1 82^2	25^3 73^4		132^5
Dielectric constant, ASTM D50		2.1	2.1	2.1	2.6
Volume resistivity, ohm-cm ASTM D257		$>10^{18}$	$>10^{18}$	$>10^{18}$	$>10^{16}$
Dissipation Factor, ASTM D150, 10^2-10^6 Hz		0.0002	0.001	0.0004	0.005

1–0.016" insulation thickness
2–0.033" insulation thickness
3–0.017" insulation thickness
4–0.031" insulation thickness
5–0.020" insulation thickness

CHART 2

Molecular Structure of PTFE and TFE Copolymers

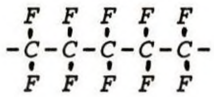
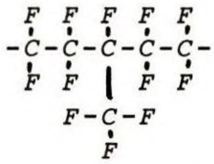
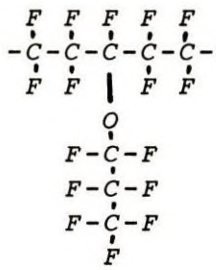
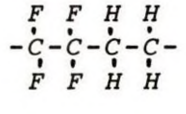
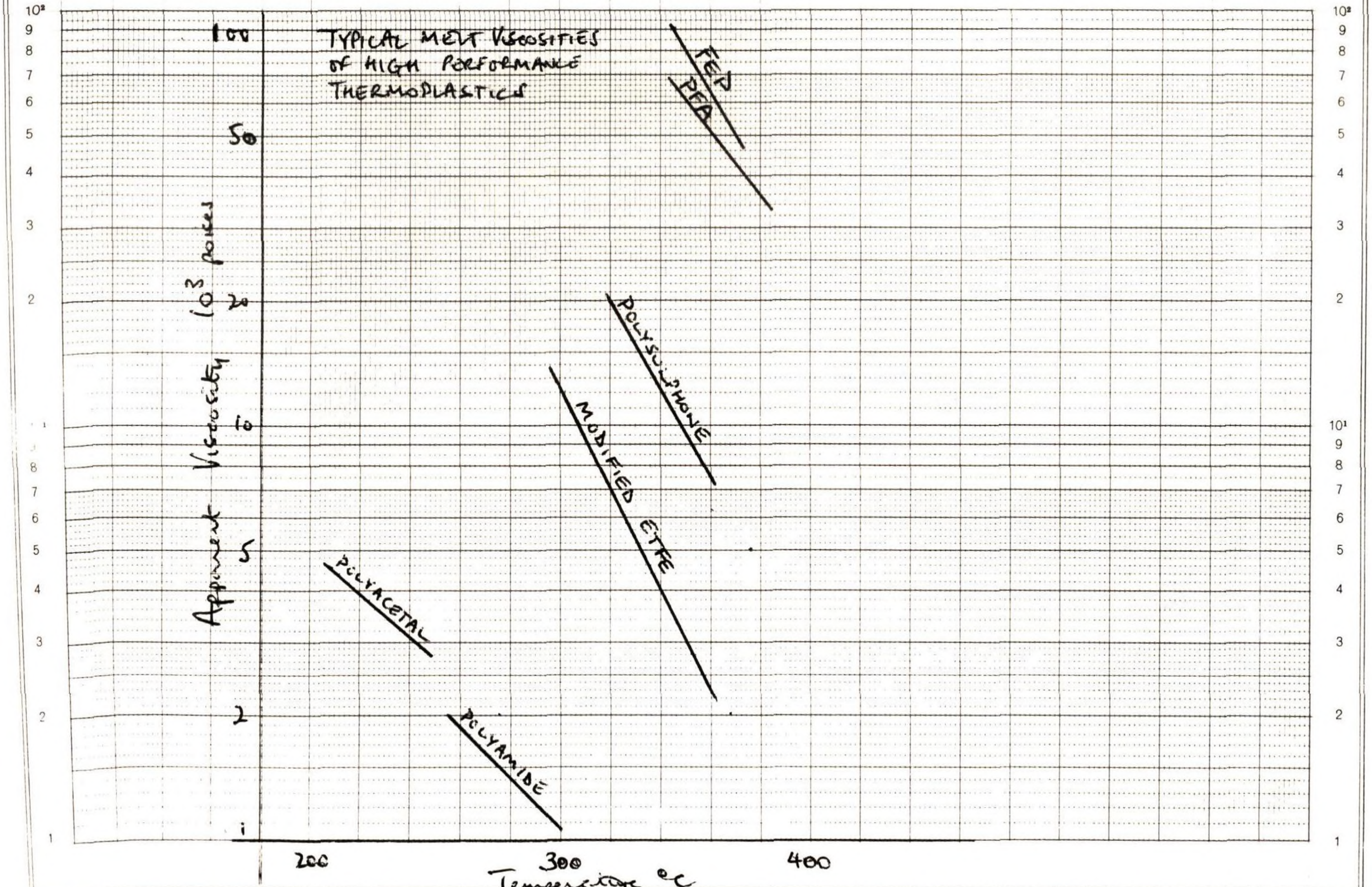
PTFE	$-\left[CF_2 - CF_2\right]_n-$	
FEP	$-\left[CF_2 - CF_2\right]_m-\left[CF(CF_3) - CF_2\right]_n-$	
PFA	$-\left[CF_2 - CF_2\right]_m-\left[CF(OC_3F_7) - CF_2\right]_n-$	
ETFE Modified	$-\left[CF_2 - CF_2 - CH_2 - CH_2\right]_n-$	

CHART 3



TYPICAL MELT VISCOSITIES OF HIGH PERFORMANCE THERMOPLASTICS
FEP
PFA
POLYSULPHONE
MODIFIED ETFE
POLYACETAL
POLYAMIDE
Apparent Viscosity 10^3 poises
100
50
20
10
5
2
1
200
300
400
Temperature °C