

SYNTHESIS REPORT

For Publication

Contract N°: BRE2-CT92-0 144

Project No: BE -5093

Title: FLUORINATED THERMOPLASTIC
ELASTOMERS

project Coordinator: AUSIMONT S.p.A.

Partners: AEROSPATIALE
MERCEDES-BENZ AG
PARKER PRÄDIFA GmbH

Reference Period from: 01-02-1993 **to** 31-12-1996

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PROGRAMME

Date: May 1997

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2. SUMMARY

2.1 KEYWORDS

- THERMOPLASTIC
- FLUOROELASTOMER
- ELASTOMER
- FLUORINATED
- TPE

2.2 ABSTRACT OF THE RESULTS AND BENEFITS OF THE PROJECT

Main advantages of thermoplastic elastomers against **thermoset** ones are the easier processing and easier recycling due to the absence of chemical **crosslinking**.

The main disadvantage of nowadays thermoplastic elastomers is the loss of properties at high temperature.

The objective of the present project, was the development of a new family of fluorinated thermoplastic elastomers (**FTPE**) for applications in hostile conditions, in terms of very low and high temperature service and in contact with aggressive chemicals.

A-B-A block copolymers were synthesized using an original **Microemulsion** Polymerization technology, called “Branching & **Pseudoliving**”, able to prepare FTPEs having a network structure “containing both physical and chemical links:

Physical link: obtained by the segregation and crystallization of the hard **polymer** blocks. This is the characteristic link that leads to the network structure of tradition, block copolymer thermoplastic elastomers (**TPE**).

Chemical link: obtained by the “Branching and **Pseudoliving**” technology. This is similar to the characteristic link that constitutes the network structure of traditional thermoset elastomers. However, in this last case, chemical links are **formed** through a chemical **crosslinking** reaction, with all the problems associated with the rubber processing, such as no scrap recycling, compounding and toxic volatile emissions.

The presence of both links confers, to the FTPEs developed by the present research project, an outstanding high temperature resistance in comparison to known commercial **FTPEs**.

The high temperature stability of the network is higher and closer **to** thermoset elastomers, while maintaining the reversible nature, characteristic of melt **processable** polymers.

Important additional tools were developed by the Consortium research activity, such **as** the annealing and radiation curing process, which improves the network stability and increases its high temperature resistance. In particular, it was found that the application of radiation **crosslinking** gives a surprisingly **further** contribution to the high temperature stability of the network, allowing applications in high demanding fields.

FTPEs with tailored molecular weight distribution, showing excellent flowing and processing behaviors, were prepared by a special “**multicomponent** addition technique”.

Industrial hoses and seals, prepared with the new **FTPE** developed by the Consortium showed outstanding performances in terms of both chemical resistance and high temperature mechanical **and sealing** properties in comparison to traditional **FTPEs**.

3. THE CONSORTIUM

3.1 PARTNER ORGANISATION:

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3.2 CONSORTIUM DESCRIPTION

A Consortium Agreement was defined and signed by all the Partners in 1993 with the following main objectives and **rules**:

- Coordination of the tasks of the Partners in order to carry **out the** Project “Fluorinated Thermoplastic Elastomers” with final results as good as possible for the applications indicated in the Technical Annex of EC Contract.
- Each Partner shall perform his **tasks** in accordance with the provisions of the EC Contract under his own responsibility. In carrying out the Project, the Partners shall only cooperate with third parties **after** having obtained the prior approval of the other Partners. The Partners’ are, however, entitled to award subcontracts in accordance with the provisions of this Contract and EC Contract.
- The scope of the tasks to be accomplished by each Partner is evident from the EC Contract.
- The Partners have appointed Ausimont as Coordinator **for** this Project. Without prior written approval of the other Partners, the Coordinator shall not be entitled to make legally binding agreements that **affect** the other Partner/s. According to EC Contract; the Coordinator shall be authorised to receive payments from the Commission on the behalf of the other Partners. The Coordinator shall promptly provide such received payment to such’ other Partners according to the EC Contract. If needed, the Partners will ask the EC to appoint a new Coordinator among them.
- The Partners nominate the following contacts:
 1. Mercedes Benz nominates as contact for technical questions Mr. Dr. **Schuh** , ZWT/WN Dept. and as contact for administrative questions Mr. **Frank**, FTK/S Dept.
 2. Ausimont nominates as contact Mr. V. **Arcella** for the technical operations, and as , contact for administrative questions Mr. A. **Ducato**
 3. Parker **Prädifa GmbH** nominates as contact Mr. P. Krumeich (changed during the work with Mr. G. Streit)
 4. **Aérospatiale** nominates as contact Mr. **Dublineau** (changed during the work with. G. Dallemagne)
- Mutual agreement shall be reached on the contents of the reports to be submitted, according to the EC Contract, on the interim results of the work and the final results of the Project. These reports will be submitted **to the Commission** by the Coordinator. For this purpose, the part of the reports to be turned to the Partners shall be submitted to the Coordinator in time so that the deadlines according to the EC Contract can be met. The Partners shall exchange these reports amongst each other.

The exchange of experience will follow in addition to the reports required by the **Commission**. The Partners shall report on the status of the work and the technical experience gained in the course of the work in meeting to be held in the second and fourth quarter of every year. With a view to tasks affecting’ several Partners, the Partners **shall** inform each other, and agree upon the technical solution envisaged **by them**, the time schedule and the scope **of such** work etc. well in advance. The Commission shall be entitled to attend such consultation meetings.

The different Partner profile as R&D and. business is the following:

- **Ausimont S.p.A.**, is an international Group that operates in the field of fluorinated materials and specialties and hydrogen peroxide. The main Research facility is located at **Bollate (Milano)**, Italy, where a team of 300 peoples are involved in the **R&D** projects. **Ausimont** concentrates its Business in **fluorinated** elastomers and elastomers, fluorinated and **perfluorinated** fluids, fluorinated coating, hydrogen peroxide and its derivatives for dye production. In this project the main task of **Ausimont** was to study a new way of obtaining fluorinated thermoplastic elastomers having outstanding properties.
- Parker **Prädifa GmbH**, is an international Group that operates in the field of fluorinated materials as a transformer. The main Research facility is located in Germany and in the U.K.. Parker **Prädifa** concentrate its Business production of hoses, O-rings, tubes for the different industrial applications. In this project the main task of Parker **Prädifa** was to define the processing of the new fluorinated thermoplastic elastomers at the industrial **scale**, and to test the obtained products for industrial applications
- Mercedes Benz AG, is a large international Group that operates in the automotive industry with an extremely wide spread of **Bussiness**. The main Research facilities are located in Germany. In this project the main task of Mercedes Benz was to verify as an end user the different hoses and O-rings obtained from Parker **Prädifa** in the automotive market segment.
- **Aerospatiale** is a leading European Comp-any in the aerospace and **aircraft** helicopter market segment where its Businesses are located. The main Research facility is in France. In this project the main task of **Aerospatiale** was to **verify** as an end user the different hoses and **O-rings** obtained from Parker **Prädifa** for the aerospace market segment.

4. TECHNICAL ACHIEVEMENTS

4.1 PROJECT OBJECTIVES

The objective of the present Project was the development of a new family of Fluorinated Thermoplastic Elastomers (FTPE) for applications in a broad temperature range and in hostile environments. Class 1, Class 2 and Class 3 prototypes with specified targets were defined at the starting time of the project, covering a temperature range from -50 to 200°C and compatible with a broad variety of chemicals.

In order to solve processing problems, the research effort was focused on Class 2, which was redefined to include applications previously covered by Class 1 and Class 3:

Redefined Class 2

Temperature use range:	from -40 to 120°C
Compatibility with:	Initially greased lubricated air for pneumatic circuits, mineral oils, natural (rape seed) and hydrocarbon synthetic esters, central hydraulics, helicopter aircraft hydraulic fluids, aircraft fuels , refrigerant HFA 134a and lubricants (air-conditioning), automotive fuels , ATF-gear
Friction:	Better than existing fluoroelastomers especially in pneumatic applications
Coverage:	Industrial fluidpower systems, automotive, aircraft , oil and gasfield exploration (partly), food and drug machinery hydraulic systems

4.2 RESEARCH APPROACH

Thermoplastic elastomers are products that behave like chemically cross-linked "thermoset" rubbers, but are processed like melt processable polymers(1)

There are different ways to produce thermoplastic elastomers, such as block co-polymerization(2) and elastomer and thermoplastic polymer reactive blends by dynamic vulcanization(3).

The most common thermoplastic elastomers are block copolymers of soft (B) and hard (A) segments. The simplest structure is the A-B-A one. The "A" segments generate a crystalline phase that constitutes the cross-linking network among "B" soft segments, as schematized in fig. 1. To process thermoplastic elastomers it is sufficient to overcome the melting temperature of the "hard (A) segments during the molding step. The subsequent cooling step produces their segregation and crystallization which collect the soft (B) macromolecules together, giving rise to the cross-linking structure.

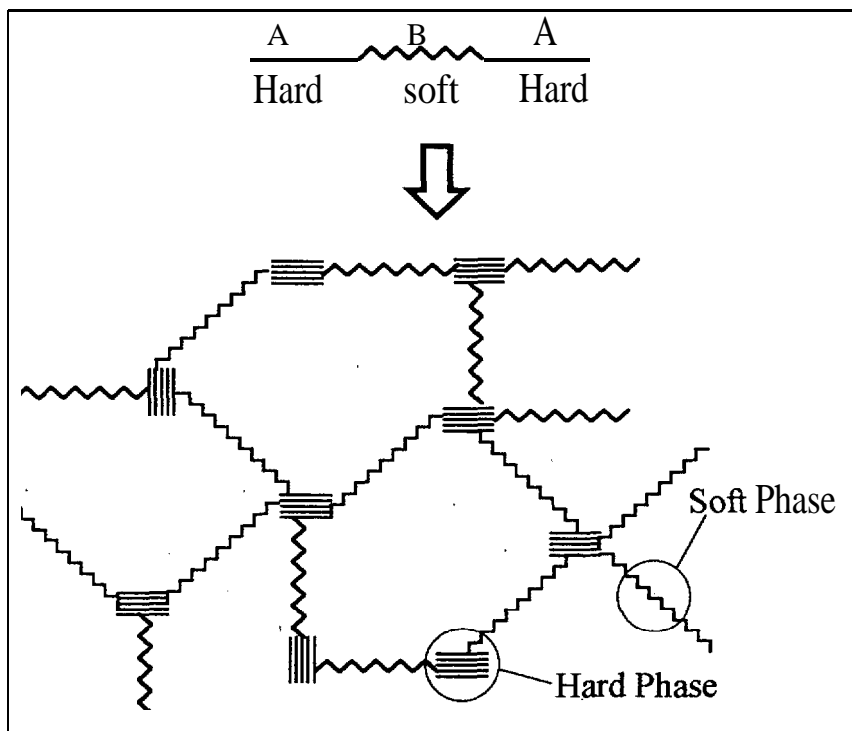


Fig. I. Cross-linking structure of thermoplastic elastomer

4.2.1 *Pseudoliving emulsion polymerization*

A-B-A block co-polymers were prepared by free radical emulsion polymerization, according to the patent literature(4,5).

The A-B-A block structure was obtained polymerizing the B “soft” segment having Iodine atoms as chain ends. Subsequently the polymerization was continued substituting the Iodine atoms with the A “hard” polymer segments.

According to this reaction scheme, the free radical polymerization in presence of Iodine terminated chains, behaves as a “pseudoLiving” reaction taking advantage from the particular weakness of the carbon-iodine bond.

As a matter of fact, the reactivity of the iodine chain-end leads to a continuous chain extension through an activation-deactivation mechanism of the polymer chain.

The polymerization **described** is not **fully** living because irreversible termination events, such as chain transfer to monomer and bimolecular **termination**, can not be completely avoided. However, the Molecular Weight Distribution (**MWD**) of the polymer produced with this technology is **very** narrow, and the **polydispersity** index is lower than 2, thus confirming the pseudoliving evolution of the polymerization.

A comparison between the MWD obtained using a classical chain transfer agent, such as **ethylacetate**, and **diiodoperfluorohexane** as **I-Rf-I**, is reported in **fig.2**. It should be noted that the polydispersity index of “living polymer” is $1.7 < 2$. This experimental evidence of polydispersity lower than 2 can be explained only assuming a living behavior of the polymerization process.

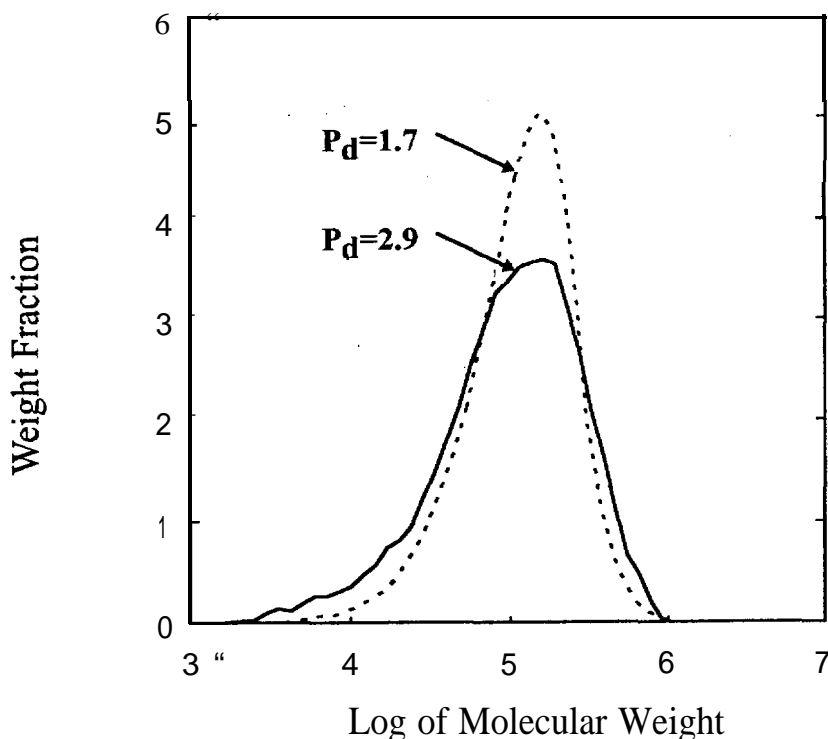


Fig. 2. Emulsion copolymerization of VF2/HFP. Solid line: reaction performed with ethylacetate as CTA. Dotted line: reaction performed with perfluoroalkyl iodide as CTA.

The lability of the Iodine-Carbon bond can be used to produce block copolymers. For this purpose, the reaction is carried out sequentially, producing in a first step the elastomeric segment B and in the second step the crystalline segments to obtain the A-B-A FTPE structure.

It is worth noting that a number of Iodine chain ends per macromolecule at the end of the first step should be equal or preferably greater than two in order to obtain the A-B-A block FTPE copolymer. However this technology leads to Iodine functionality always lower than two because there are chain ends from the initiator and from inevitable termination mechanisms, such as transfer to monomer and bimolecular terminations. As a consequence, only a fraction of the polymer has the A-B-A structure while other molecules have the A-B or even the B morphology.

First A-B-A block copolymers were prepared using vinylidene fluoride (VF2), Hexafluoropropylene (HFP) and Tetrafluoroethylene (TFE), at approximately 50/25/25 molar concentration, to obtain an elastomeric amorphous terpolymer as the B soft segment.

VF2 was used to obtain a semi-crystalline polyvinylidene fluoride homopolymer (PVDF), as the A hard segment.

Ammonium persulphate (APS) was used to initiate the free radical emulsion polymerization.

Just a very low amount of APS was used to reduce as much as possible chain end initiator residuals, in order to obtain the maximum possible Iodine chain functionality.

Preliminary soft segments resulted in a maximum Iodine chain functionality of about 1.4 Iodine/chain. The resulted thermoplastic elastomer (80/20 soft/hard weight ratio) gave a compression set value (measurement of sealing capability) of 90% at 100°C, indicating

unsatisfactory high temperature properties of no practical interest. It has to be noted that the higher is the compression set the worse are the sealing properties. A compression set value of 100% means that the product has no elastic recovery and no sealing capability.

Unsatisfactory high temperature results were assumed to be related, at least in part, to a low linking between hard and soft segments, as a consequence of a too low Iodine chain **functionality**, obtainable with the current technology.

In addition the polymerization trials suffered **from** a very low reaction kinetics, due to the low amount of initiator used, to obtain a Iodine chain functionality as high as possible.

This problem obviously means that it is difficult to obtain products having acceptable costs using the current technology, since very expensive large high pressure polymerization reactors should be used.

4.2.2 *Microemulsion polymerization process*

To **overcame** these problems and to increase both Iodine chain **functionality** and reaction kinetics a special process, based on a "**microemulsion**" polymerization technology, patented by Ausimont for the production of high. **performance fluoropolymers** (6), was applied to the **FTPE** polymerization.

This special polymerization process consists of carrying out the polymerization in the presence of a **microemulsion**, previously prepared by mixing in water a perfluoropolyether oil and a **perfluoropolyether** emulsifier.

The peculiarity of a **microemulsion** is the ultra low dimension of the dispersed phase, which acts as the nucleating phase for the polymerization reaction.

The **microemulsion** polymerization rate is much higher than that obtained **with** the standard emulsion polymerization process, since in **microemulsion** polymerization the number of polymerization loci is much higher than that generally present in a standard emulsion polymerization.

The polymerization rate can be given by the following expression:

$$R_p = \frac{K_p M_p N_p \bar{n}}{N_a}$$

R_p :	reaction rate
K_p :	propagation rate constant
N_a :	Avogadro's number
M_p :	monomer concentration in the polymer particles
N_p :	Number of polymer particles
\bar{n} :	Average number of active chains per particle

In standard emulsion polymerization N_p is about 10^{16} particles per dm^3 , while in the case of **microemulsion** polymerization N_p is about 1018, i.e. two order of magnitude higher.

The application of **microemulsion** polymerization to the synthesis of **FTPEs** has to be considered "original".

Higher functionality and higher reaction rates were obtained using the **microemulsion** polymerization to synthesize both the soft and the hard blocks. Correspondingly improved high temperature sealing properties were obtained.

Tab. 1 reports Iodine functionality and high temperature compression set of the 17317/11 FTPE sample obtained by the "**microemulsion**" polymerization process, in comparison with an FTPE obtained by the **current** emulsion polymerization process.

	Sample from standard emulsion	Sample from Microemulsion (17317/11)
Reaction time (hr)	20	3
Iodine functionality (I/chain)	1.4	1.7
Compression set at 100°C (%)	90	70

Tab. 1. Comparison between emulsion and **microemulsion** technologies'

Fig.3 shows the much higher polymerization kinetics, described as monomer conversion vs.. polymerization time, obtained by the new process compared to the standard one.

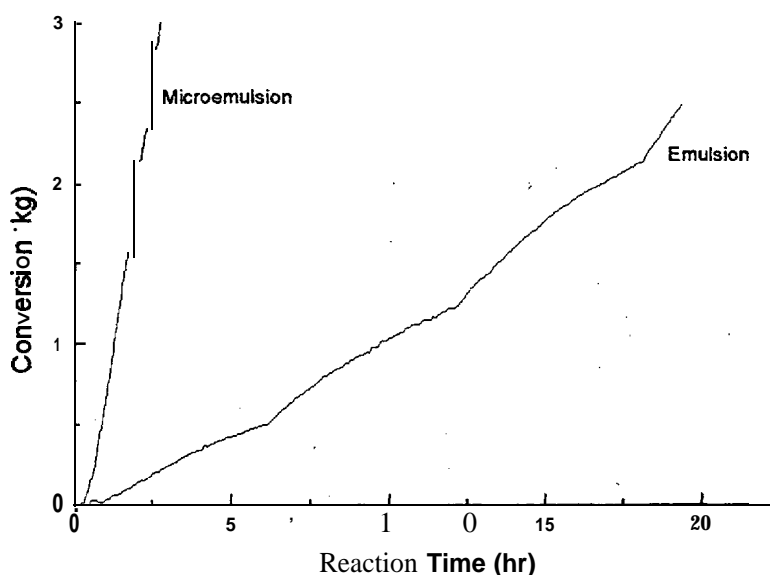


Fig. 3. Comparison between emulsion and **microemulsion** technologies

4.2.3 Branching & *pseudoliving* technology

In order to obtain a substantial improvement of the high temperature FTPE properties, the "Branching & Pseudoliving Technology" patented by Ausimont was used (7). This is a special technology to produce high performance fluoroelastomers and allows to synthesize controlled branched fluoroelastomer chains.

Since chemical links at branching points can be regarded as chemical “**pre-crosslinks**” in a subsequent cross-linked structure, this concept was applied to prepare A-B-A block FTPE’s, where the soft block is a controlled branched polymer.

“**Branching & Pseudoliving Technology**” is a new approach for the synthesis of thermoplastic elastomers and in the framework of this project is used for the first time to prepare FTPEs.

A patent which covers the process and the relating obtained products was applied (8).

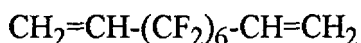
In order to understand the basic idea of preparing “**pre-crosslinked**” FTPE’s it is necessary to consider standard known thermoplastic elastomers obtained by block structures. In this case the cross-linking is obtained by the crystallization and subsequent segregation of the hard segments, that constitutes **the** linking among different hard block polymer chains by collecting more segments together. So the **crosslink** is obtained through the crystallization of the hard segments and thus, it is a “physical” link.

During the polymer processing, when the temperature reaches the melting temperature of the crystalline hard segments, polymer molecules are no longer linked together, and are able to flow in the mold cavities, giving the desired item shape **after** cooling.

After these considerations it is clear that the stability of the thermoplastic elastomer item at high temperature may be affected by the creep tendency of the molecules of the hard segments, which are the cross-link. This phenomenon will depend on the nature of the hard phase, i.e. creep will be higher if the polymer constituting the hard phase has lower, mechanical properties at high temperature and **viceversa**. Creep will be higher as **far** as the temperature approaches the melting point of the hard phase.

“Branching and the Pseudoliving Technology” can be used to design the polymer chain morphology that matches the desired applicative properties.

The introduction of a small amount of a special fluorinated **diene** in the **free radical** polymerization medium was used to increase both the Molecular Weight and the number of long chain branching. In particular the fluorinated **diene**, **1,6-divinylperfluoroexane, (di-olefine)** turned’ out to be a very efficient **crosslinker** for fluorinated polymerization. The chemical structure is the following:



It appears that, while the high molecular weight region is deeply modified by the diene, the low molecular weight region is mainly determined by the **pseudoliving** mechanism.

In conclusion, the experimental results show that it is possible a close control of **the shape** of the **MWD** of the polymer produced. Actually, the iodo-substituted fluorocarbon reduces the **polydispersity** index and the polymer **molecular weight (pseudoliving)**, while the presence of the **di-olefine** increases the polymer molecular weight, the **polydispersity** index and the number of Iodine-chain-ends per macromolecule (branching).

An important consequence of the use of the fluorinated diene is that the number of **Iodine-chain-ends** per macromolecule increases **with** the diene content.

Using a suitable amount of the fluorinated **di-olefine**, the Iodine **functionality** of the elastomeric B soft segment can be increased till two or more than two. In this way, in the second step of the FTPE synthesis, a real A-B-A block copolymer is obtained.

It is worth pointing **out** that with the Branching & Pseudoliving technology, the structure of the FTPE block copolymer can be modified in detail so as to produce a tailor-made polymer that matches the required end-use properties. Fig. 4. shows the modified FTPE network with both chemical and physical **crosslinks**.

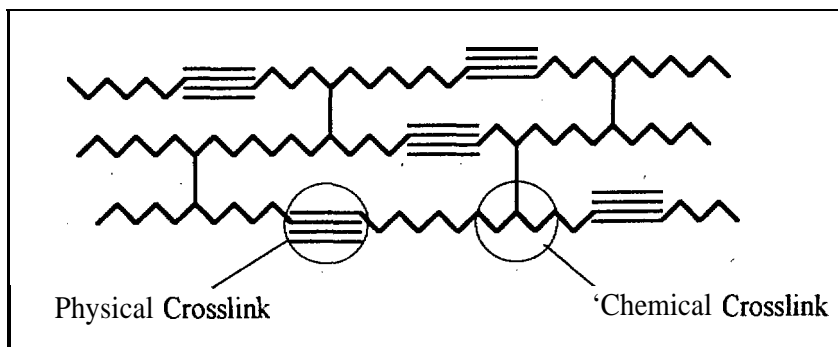


Figure 4. Schematic representation of the **crosslinked** structure obtained after curing of a block fluorinated **copolymer** obtained using the “**Branching & Pseudo living**” technology.

The introduction of **pre-crosslinks** resulted in a substantial improvement of polymer properties. The presence of **pre-crosslinks** based on covalent bonds improves the stability of the thermoplastic elastomer at high temperature. This behavior is the result of the low tendency of the total network to give creep due to the presence of **pre-crosslinks**, based on covalent bonds. The special “micro-emulsion” polymerization technique described before was used to incorporate the **di-olefine** at a good yield and reaction rate. The **di-olefine** was introduced in the polymer during the reaction as **function** of conversion. In order to achieve the required low temperature **performance** of class 2, the **perfluoromethylvinylether (MVE)** was used to realize the **soft** polymer segment.

4.2.4 Application of radiation crosslinking

FTPE prototypes gave very good compression set value, if compared with that shown by commercially available FTPE grades. However mechanical and sealing **performances** were not judged sufficient to meet practical industrial requirements. Especially in the Automotive segment, compression set measured according to the severe VDA method, was not sufficient. In order to improve high temperature sealing properties, the radiation **crosslinking** of end items was developed. Although not foreseen by the original work **program**, surprisingly improved mechanical and sealing **performances** were obtained. As a matter of fact, modulus and tensile were increased from three to five times the original values, **while** compression set was reduced from **20** to **30** percent of the starting values. Since radiation curing is done only on end shaped items, it does not **affect** the processing, and thus, the recycling of scraps during the manufacturing of the items can still be done.

4.2.5 Multicomponent Addition Technique

First FTPE prototypes, processed in field by Parker, showed a very bad **processability** both in extrusion and in injection molding. A research program was immediately set up to solve the **p r o b l e m** :

A new "Multicomponent Addition Technique" was developed able to prepare bimodal molecular weight distribution (MWD) FTPEs by multicomponent systems, containing FTPEs with different molecular weight (MW) and different ratio hard/soft. A typical bimodal MWD is reported in fig. 5.

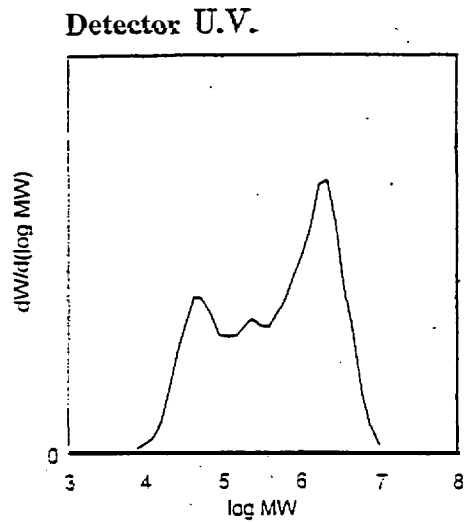


Figure 5. MWD of bimodal FTPE.

4.2.5.1 *Hoses*

Industrial hoses production trials were done with success. The following hose was prepared from X3 bicomponent FTPE :

- . inner diameter = 7.5 mm
- wall thickness = 1 mm

X3 bicomponent is a blend 64/34wt% of the component 1 and component 2, respectively whose properties are reported in table 2.

	Component 1	Component 2
MW soft phase	high	low
di-olefine in soft phase	yes	no
Hard/soft phase ratio	high	low

Table 2. Characteristics of X3 bimodal FTPE components.

Processing was very good and much better than previous FTPE prototypes.
The permeation rate of the hose resulted as low as 0.48 g/m d.
Permeation tests were performed, according to DIN5 1604, in FAM B: 84.5% FAM A, 15% methanol, 0.5 % H2O (FAM A: solution of 50% toluene, 30% isoctane, 15% di-isobuthylene, 5% methanol).
At present, standard FPM/CSM-hose lines (inner diameter= 7.5 mm, with FPM imer veneer of about 0.7 mm thickness) have permeation rates of about P = 2-3 g/m d.

Bursting pressure tests **already** gave good results, However, **further** fictional tests using a **reinforcement** with technical woven are required.'

Mechanical and sealing properties of X3 bicomponent FTPE before and **after** radiation curing **are** shown in the table 3.

From table 3 it appears that tensile tests at low and high temperature was good even with low radiation curing dosage, for **example** the tensile strength was 18.0 Mpa at 23 °C and 4.5 Mpa at 100 °C with 21.5 kGy.

Bursting pressure test, tear resistance, and tension set up **to** 150 °C, appeared quite good.

tensile test 23°C	σ max [MPa]			ϵ at σ max [%]	σ at $\epsilon=50\%$ [MPa]	σ at $\epsilon=100\%$ [MPa]
original	5,0	5,1	5,2	198	1,5	2,6
27,5 kGy	13,7	18,0	19,1	217	1,5	5,7
43 kGy	13,5	19,7	20,1	217	3,0	7,5
64,5 kGy	13,5	19,7	20,1	217	3,3	8,4
86 kGy	15,5	17,5	17,9	152	3,4	8,9

X3 hoses, annealed for 3 h at 150 °C, tensile test at 23 °C (Median, rein- and max-value), (ISO37)

tensile test 100°C	σ max [MPa]			ϵ at σ max	σ at $\epsilon=50\%$ [MPa]	σ at $\epsilon=100\%$ [MPa]
original	1,1	1,3	1,3	79	0,7	3,1
21,5 kGy	3,8	4,5	5,5	112	2,3	4,6
43 kGy	4,2	4,7	5,1	93	2,3	4,6
64,5 kGy	3,9	4,5	5,6	73	2,6	-
86 kGy	2,8	4,1	4,8	53	2,5	-

X3 hoses, annealed for 3 h at 150 °C, tensile test at 100 °C (Median, rein- and max-value), (ISO37)

bursting pressure test S4,5 kGy hose	
	[bar]
specimen 1	21,3
2	24,3
3	21,4
x:	22,3

X3 hoses, annealed for 3 h at 150 °C, bursting pressure test (DIN 53758), 40bar/min / 27°C,

tear resistance vtest = 100 mm/min	23°C [MPa]	100°C [MPa]
43 kGy hose		
specimen 1	3,1	0,5
2	2,9	0,4
3	3,2	0,3
4	3,3	0,4
5	2,9	
x:	3,1	0,4

X3 hoses, annealed for 3 h at 150 °C, tear resistance test, incision in the direction of extrusion (DIN 53507-1)

tension set	100°C [%]	125°C [%]	150°C [%]
43 kGy	29	43	46

X3 hoses, annealed for 3 h at 150 °C, tension set (25% const. elongation/24h)

Table 3. Mechanical and sealing properties of X3 bicomponent hoses.

4.2.5.2 O-Rings

Processing in injection molding trials, for the manufacturing of o-rings, resulted also highly improved.

O-Rings were produced using Y3 tricomponent FTPE. Y3 is a blend of component 1 and component 2 of table 2 plus low MW PVDF. The ratio of the three components is 64/26/10 wt%, respectively,

Process conditions related to different O-ring size dimensions (profile) and different cross sections are described in the table 4.

Parameter	FTPE Y3	FTPE Y
CROSS SECTION (MM)	2.11	3.52
Drying condition	-	-
Mold cavity	18	2 in 18
Casing technology	gateless	gateless
Injection condition		
Nozzle °C	238	200
Zone 1 °C	234	195
Zone 2 °C	228	190
Zone 3 °C	225	180
Injection pressure (bar)	60	60
Injection speed (mm/sec)	35 to 92	25 to 40
Injection time (sec.)	1.1	1.1
Holding pressure	-	15
Holding time (sec.)		1
Cooling time (sec.)	30	30
Mold temperature (°C)		
nozzle side	55	30
ejector side	55	30
Total cycle (sec.)	57	57
Post curing	-	
Remarks	FTPE Y	FTPE Y

Table 4. Processing conditions of two O-Rings with different size.

O-rings were characterized in terms of swelling tests and physical properties. All tests were performed on annealed and crosslinked O-rings (66.1 kGy)
 The tab. 5 shows really good chemical resistance for both the O-rings with different size. The swelling is comparable with a high fluorinated thermoset 'elastomer.

O-Ring Size		Volume Change (%) in	
Cross section	Dimension	M e t h a n o l	Toluene
2.14'	16.4 x 2	6.2	6.6
3.62	24.99 x 3.53	2.6	4.4

Table 5. Chemical resistance of two O-Rings with different sizes.

Tab.6 shows mechanical properties of the two different O-rings size. Tensile reaches more than 11 Mpa at an elongation of more than 259 %. Hardness measured in Micro IRHD is in both sizes about 65 IRHD. These are really good data compared with normal elastomers.

Cross section (mm)	Stress at break (Mpa)	Elongation (%)
2.14	11.90	261.00
3.62	14.70	227.00

Tab. 6. Mechanical properties of two O-Rings with different sizes.

Three point bending tests in a dual cantilever device have been performed only on 24.99 x 3.53 O-rings. Fig. 6 describes the onset point of change in modulus at -36 °C. This is acceptable for applications in the automotive industry.

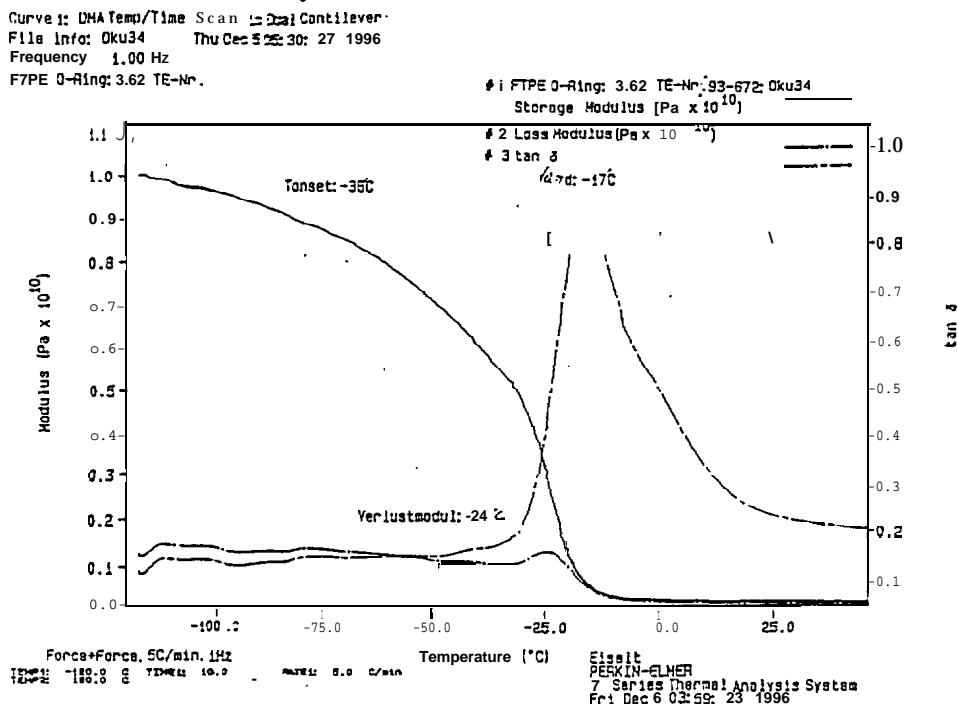


Figure 6. DMA temperature/time scan in dual Cantilever of 3.62 mm size O-Ring.

Also **thermo** mechanical analysis shows an onset in modulus change at about -36 °C. At **higher** temperature the O-ring starts to weaken at 161 °C. Nevertheless the O-ring shape doesn't change (see fig. 7).

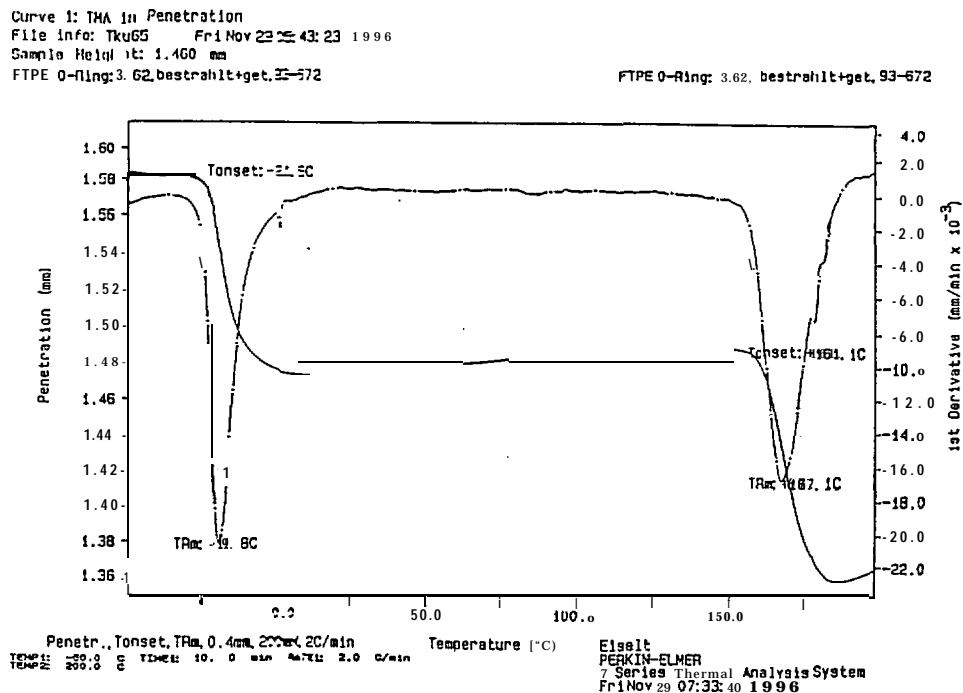


Figure 7. Thermomechanical analysis of 3.62 mm size O-Ring.

From the point of view of processing, a major problem was the dimensional stability of the material **after** the annealing and radiation curing steps.

An appropriate procedure was **defined** for the production of dimensionally stable items, consisting of the following consecutive steps:

- a) processing
- b) radiation crosslinking
- c) annealing at 150 °C

An o-ring prepared by the **above** curing procedure gave a compression set value at 150 °C (according to **VDA**) of 58 %.

This value is not **far from** 50%, acceptable for automotive applications, and today achieved only by **thermoset** fluoroelastomers.

Tensile tests, reported **in** table 7, are good at any shear rate and also the tension test at 125 °C appeared sufficient.

Extrapolated data at 150 °C should give a tension test **still** sufficient (see the case of hoses made with the X3 FTPE compound reported in **tab.3**).

tensile test	σ_{max} [MPa]	ϵ at σ_{max} [%]	σ at $\epsilon=50\%$ [MPa]	σ at $\epsilon=100\%$ [MPa]
„Y“ (3499 mm x 3,53 mm) annealed 4h at 150°C vtest= 200 mm/min 66,1 kGy	14,0 18,0 18,7	140 188 201	3,3 3,6 3,8	8,3 9,1 9,4

O-ring tensile test at room temperature (Median, rein-, max-value), @ased on DIN 5350-21)

tension set	125°C [%]
„Y“ (24,99 mm x 3,53 mm) annealed 4h at 150°C 66,1 kGy	41,3

tension set of Y (25% constant elongation/125°C/24h)

Table 7. Tensile tests and tension test ‘on O-Rings made of Y polymer.

4.3 RESULTS AND CONCLUSIONS

The main **result** of the present research project was the development **of an** original technology to produce a new **family** of fluorinated thermoplastic elastomers for applications in **hostile** conditions, in terms of very **low** and high temperature **service** and in contact with aggressive chemicals.

, This technology called “Branching & **Pseudoliving**” allowed to synthesize new block copolymer **FTPEs**, where the end product **at** the solid state was formed by a network **structure** containing both physical and chemical links.

Important additional tools were developed during the research project **work**, such as the annealing and radiation curing process, which improve the network stability and increase its **high** temperature resistance. In particular, it was found that the application of radiation **crosslinking** gives a substantial **further** contribution to the high temperature stability of the **network**, **allowing** applications in high demanding fields, such as Automotive and Aerospace.

Class 2 objective was achieved, **although** a complete assessment of **properties/application** was not possible for time constraints.

Processing problems of Class 2 products were solved by the development of a **special** multicomponent addition technique, which allowed the preparation of **FTPEs** with tailored

molecular weight distributions. These polymers showed excellent flowing and processing behaviors.

Industrial Class 2 FTPE Hoses were prepared and tested.

4.4 ACKNOWLEDGEMENTS

The satisfactory conclusion of this research appears largely due to the interaction of chemical, physical, processing and engineering aspects, the **work** of the specialists in different areas being synergically eased and sped up by the collaboration.

This kind of highly integrated explorations appears to be possible only in the fertile ground of the **Brite** Eurarn Projects, for which the Consortium wish to acknowledge the European Community and the **DGXII** for the financial support that made possible this Project to be undertaken and brought to a successful conclusion in the **Brite** Euram **programme**. Dr. H. von den **Driesch** is thanked for the stimulating discussions and suggestions along the work evolution.

Parker **Prädifa** U.K. is thanked for the support given to the processing aspects of the Project. V. **Arcella** warmly thanks the Partners for the outstanding **quality** of the work done and the collaboration within the Consortium.

4.5 REFERENCES

1 -C. P. **Rader**; in Handbook of Thermoplastic Elastomers, Van Nostrand Reinold, New York (1988)

2-R. P. Quirk and **J.Kim**; Rubber **Chemistry** and Technology, 64,450 (1991)

3-E. N.**Kresge**; Rubber Chemistry and Technology,64,469 (1991)

4-USP 4158678

5-USP 4472557

6-USP 4864006

7-USP 5 5 8 5 4 4 9

8-USP 5612419

5. EXPLOITATION PLANS AND FOLLOW-UP ACTIONS

In the Cooperation Agreement before mentioned in point 3.2, it is foreseen how to exchange the technical results among the Partners. Each Partner will grant to the other Partners for the Foreground working results, an irrevocable, non-exclusive, non-transferable right of use, according to the EC rules.,

Even if every Partner will keep an individual , strategy of dissemination and commercialization of the products under study, it is foreseen to verify the possibility to increment the new products exploitation with common actions among all the Partners.

Ausimont S.p.A. intends firstly to market their FTPE to the Partners at favorable conditions and then also to the open European and world market. For this purpose, **Ausimont** will develop at the industrial scale the new product, test and deliver samples to the Partners.

Parker Prädifa intends to use the new FTPE in order to produce hoses and seals to be tested into the market.

Mercedes-Benz and **Aerospatiale** will receive the new samples after testing done by **Ausimont**, and evaluate them from a technical and commercial point of view, to verify the market segments where they can be used.

Ausimont and **Parker Prädifa** will also jointly publish technical papers dealing on the applicative results and evaluation of the new FTPE in the different market segments.

6. REFERENCES

1. “Fluorinated Thermoplastic Elastomers having Superior Mechanical and Elastic Properties”, V. Arcella, G. Brinati, M. Albano, V. Tortelli, USP5612419.
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3. “Fluorinated Thermoplastic Elastomers”, 5th Conference on Industrial Technologies, Brussels, December 6-8 1994.
4. “New High Performance Fluoroelastomers”, la Chimica e l’Industria, 79, p.345, 1997.

7. COLLABORATION SOUGHT

As per Consortium Agreement signed by all the Partners, the exploitation will be done firstly among the Partners, and then the new elastomers will be spread by Ausimont in the European and world market.

New channels of dissemination and exploitation are of interest by Ausimont. It is also advisable to verify the possibility to participate to the Imovation program of the EC in order to speed up the introduction of the new materials into the market, In particular Ausimont is interested in further product development and in increasing the collaboration and sampling to new partners, especially SME.

SUMMARY REPORT

For Publication

Contract No: BRE2-CT92-O 144

Project No: BE -5093

Title: FLUORINATED THERMOPLASTIC
ELASTOMERS

project Coordinator: AUSIMONT S.p.A.

Partners: AEROSPATIALE
MERCEDES-BENZ AG
PARKER PRÄDIFA GmbH

Reference Period from: 01-02-1993 **to** 31-12-1996

Starting date: 01-02-1993 **Duration:** 47 Months



PROJECT FUNDED BY THE EUROPEAN
COMMUNITY UNDER THE BRITE/ EURAM
PROGRAMME

Date: May 1997

PARTNERSHIP

Ausimont S.p.A., Centro Ricerche e Sviluppo, Via San Pietro 50/a - 20021 Bollate (Milano) Italy, leader in fluorine chemistry, and Project Coordinator, has provided new thermoplastic elastomers for their processing and end user testing.

Parker Prädifa GmbH, Postfach 1641, Arnold-Jäger Straße- D-74306 Bietigheim-Bissigen Germany, operates in the field of polymer processing. Tasks of Parker-Praedifa were the definition of processing conditions of the new fluorinated thermoplastic elastomers at industrial scale, and the testing of the obtained items for fluidpower applications,

Mercedes-Benz AG -H120 ABT ZWT/KE. Mercedesstraße 136, D-70322 Stuttgart Germany, is a large international Group that operates in automotive. The task of Mercedes Benz was to verify as an end user in the automotive market segment, the different hoses and O-rings obtained from Parker Prädifa.

Aerospatiale -Societe Nationale Industrielle SA 12 Rue Pasteur 92152 Suresnes Cedex France, is a leading european Company in the aerospace and aircraft helicopter. The task of Aerospatiale was to verify as an end user in the aerospace market segment, the different hoses and ()-rings obtained from Parker Prädifa.

TECHNICAL DESCRIPTION

After a first period of research, it was verified that class 1 and class **3** presented high technical problems for the development, and therefore during the mid-term meeting it was decided to stop these activities and concentrate all the efforts in the definition of class 2.

Good results were obtained for class 2, although problems arose in the processing stage that required further work to be solved. A redefinition of class 2 was done in order to cover also some market segments previously visualized for class 1 and 3. The redefined class 2 was the following:

redefined Class 2

- temperature use range: from -40 to 120°C
- Compatibility with: initially greased lubricated air for pneumatic circuits, mineral oils, natural (rape seed) and hydraulic synthetic esters, central hydraulics, helicopter aircraft hydraulic fluids, aircraft fuels, refrigerant 134a and lubricants (air conditioning) automotive fuels, ATF-gear.
- Friction: better than existing fluoroelastomers especially in pneumatic applications
- Coverage: industrial fluidpower systems, automotive, aircraft, oil and gasfield exploration (partly), food and drug machinery, hydraulic systems

At the end of the project the redefined Class 2 was achieved and processing problems solved at pilot stage.

RESULTS AND CONCLUSIONS

A-B-A block fluorinated thermoplastic elastomers were synthesized using an original microemulsion polymerization technology called “Branching & Pseudoliving”, able to prepare FTPEs with high temperature stability network structures.

Using particular monomer compositions for the soft and the hard block, the product profile for class 2 objective was achieved.

Additional tools, such as annealing and radiation cross-linking, giving surprisingly improved mechanical and sealing properties, were developed.

A special "multicomponent addition technique, able to impart excellent processing behaviors was also developed.

At the end of the project Fluorinated thermoplastic elastomers of class 2, showing outstanding performances, were obtained.

Hoses and o-rings were produced and tested.

The satisfactory conclusion of this research appears largely due to the interaction of chemical, physical, processing and engineering aspects, the work of the specialists in different areas being synergically eased and sped up by the collaboration.

This kind of highly integrated explorations appears to be possible only in the fertile ground of the Brite Euram Projects, for which the Consortium wish to acknowledge the European Community and the DGXII for the financial support that made possible this Project to be undertaken and brought to a successful conclusion in the Brite Euram programme. Dr. H. von den Driesch is thanked for the stimulating discussions and suggestions along the work evolution.

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KEYWORDS

- THERMOPLASTIC
- FLUOROELASTOMER
- ELASTOMER
- FLUORINATED
- TPE