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"HEAT RESISTANT WIRE & CABLE AND HEAT SHRINKABLE TUBES"

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ABSTRACT

Radiation processes have been used in industrial fields (e.g. wire & cable, heat shrinkable tubes) for about 30 years. In Japan, 60 electron beam accelerators were used in R & D, 54 in wire and cable, 24 in Tire Rubber, 16 in Paint Curing, 14 in PE Foam and 9 accelerators were used in Heat shrinkable Tubes in 1993.

Many properties(e.g. solder resistance, thermal deformation, and solven tresistance) of wire and cable are improved by using radiation processes, and many kinds of radiation crosslinked wire and cable are used in the consumer market(TV sets, VTR's, audio disc players,etc.), auto- mobiles (automobile wire harnesses, fusible link wires, sensor cables, etc.),and the industrial market(computer cables, cables for keyboards, coaxial cables,etc.).

Another important industrial application of EB radiation process is heat shrinkable tubes. Heat shrinkable tubes, heated by a hot gun, shrink $1/2 \sim 1/3$ of their inner diameters. Heat shrinkable tubes are used for covers of distributing lines terminals, joint covers of tele- communication lines, protection of fuel pipe lines and so on.

In this seminar, actual applications and characteristic properties of radiation crosslinked materials are presented.

INTRODUCTION

Radiation processes have been used in industrial fields (e.g. wire & cable, heat shrinkable tubes) for about 30 years. In Japan, 60 electron beam accelerators were used in R & D, 54 in wire and cable, 24 in Tire Rubber, 16 in Paint Curing, 14 in PE Foam and 9 accelerators were used in Heat shrinkable Tubes in 1993. (Fig. 1)

In this paper, actual applications and characteristic properties of radiation crosslinked materials are described.

RADIATION CROSSLINKED WIRE & CABLE

Many properties (e.g. solder resistance, thermal deformation, and solven tresistance) of wire and cable are improved by using radiation processes, and many kinds of radiation crosslinked wire and cable are used in the consumer market (TV sets, VTR's, audio disc players, etc.), automobiles (automobile wire harnesses, fusible link wires, sensor cables, etc.), and the industrial market (computer cables, cables for keyboards, coaxial cables, etc.).

Recently, automobiles are being controlled by CPU, and many electronic instruments are also used in automobiles. So, wire and cable are used in very severe conditions (high temperature, in oil, high frequency vibration, etc.).

To meet these requirements, we developed wires of radiation cross-linked fluoro-elastomer and radiation crosslinked polyurethane. The radiation crosslinked fluoro-elastomer wire can be used in engine oil at 200 °C. The radiation crosslinked polyurethane wire is used for sensor cables of an Anti-Lock Brake System (ABS), because of its high flexibility, high abrasion-resistance, hot-water resistance, oil resistance and so on.

HEAT- AND OIL-RESISTANT INSULATED WIRE RATED AT 200°C

Heat- and oil-resistant wires are required for engine harness in automobiles because a temperature of engine room is rised by exhausted gass controlling and using high power engines. The developed radiation crosslinked fluoro-elastomer insulated wire is flexible and superior oil resistant. This wire is used for engine harness, automatic transmission of automobiles, and electrical heating aparatuses (e.g. electric oven, electronics jug, etc.).

Life of this wire is decided by aging period to 50% of elongation or 50% retention of tensile strength. From this results, the life is estimated 40,000 hrs at 200°C. (Fig. 2)

For oil resistance, physical properties of the wire are tested after immersing in engine oil at 200°C and gasoline mixtures individually. As results, the physical properties did not change after 168hrs scarcely. (Fig. 3)

After a flexibility test, the radiation crosslinked fluoro-elastomer insulated wire is more flexible than silicone rubber reinforced by glass fibers.

RADIATION CROSSLINKED POLYURETHANE JACKET WIRE

After 1980's, electrification of automobile is advancing and a high performance sensor cable for anti-lock brake systems (ABS) is also required. (Fig. 4) A polyurethane elastomer is one of most flexible and high mechanical strengthened materials as a jacket of sensor cable. On the other hand, a polyurethane is lacking in oil- and water-resistivity. We developed a heat-, oil- and water-resistant ABS sensor cable by using radiation crosslinking process.

Water-resistivity of radiation crosslinked polyurethane is compared with a conventional polyurethane after immersing in hot water at 100°C. A conventional polyurethane was destroyed after 7 days. And especially, a conventional flame-retardant type was destroyed only 3 days. On the other hand, radiation crosslinked polyurethanes (non flame-retardant and flame-retardant) kept their strength after 30 days. (Fig. 5)

For oil-resistivity, a conventional polyurethane is swelled by brake oil, but a radiation crosslinked polyurethane does not change its shape. (Table 3, 4)

HEAT SHRINKABLE TUBES

Another important industrial application of EB radiation process is heat shrinkable tubes. Heat shrinkable tubes, heated by a hot gun, shrink 1/2 ~ 1/3 of their inner diameters. Heat shrinkable tubes are used for covers of distributing lines terminals, joint covers of telecommunication lines, protection of fuel pipe lines and so on.

The mechanism of heat shrinkable tube is as follows: (Fig. 6)

- ① Crystalline polymer like a polyethylene crosslinked by EB
- ② Expanded the crosslinked polymer at over the melting temperature
(Crystal in the polymer is melt)
- ③ Cooling down the temperature of polymer keep its shape
(Recrystallization is occurred in the polymer)
- ④ If the polymer heated up over its melting temperature, the polymer shrinks until its original shape
(Crystal in the polymer is melt again)

This phenomenon is called "memory effect" in generally.

The radiation effects on material properties of heat shrinkable tubes are an improvement of tensile strength and keeping of tubing shapes at high temperatures. For the relationship between tensile strength, elongation and gell fraction (gell: a insoluble part of irradiated polymer in a good solvent), a tensile strength is increasing and a elongation is decreasing with increasing gell fractions which combine with radiation dose. It is very important to product heat shrinkable tubes to select the most suitable radiation dose which must be considered to take well-balance between tensile strength, elongation and keeping the shape at a expanding temperature. (Fig 7, 8)

Expanding methods of heat shrinkable tubes used in industry are a differential pressure method, a parasol(umbrella) method, a rotational roller method, a tape rapping method and so on. (Fig. 9)

Wire & cable and heat shrinkable tubes for electronics field will be required more light weight, higher miniaturization and higher durability in the future. So, materials improved by using radiation processing can be applied more and more in this field.

Fig 1 Total Number of EB System

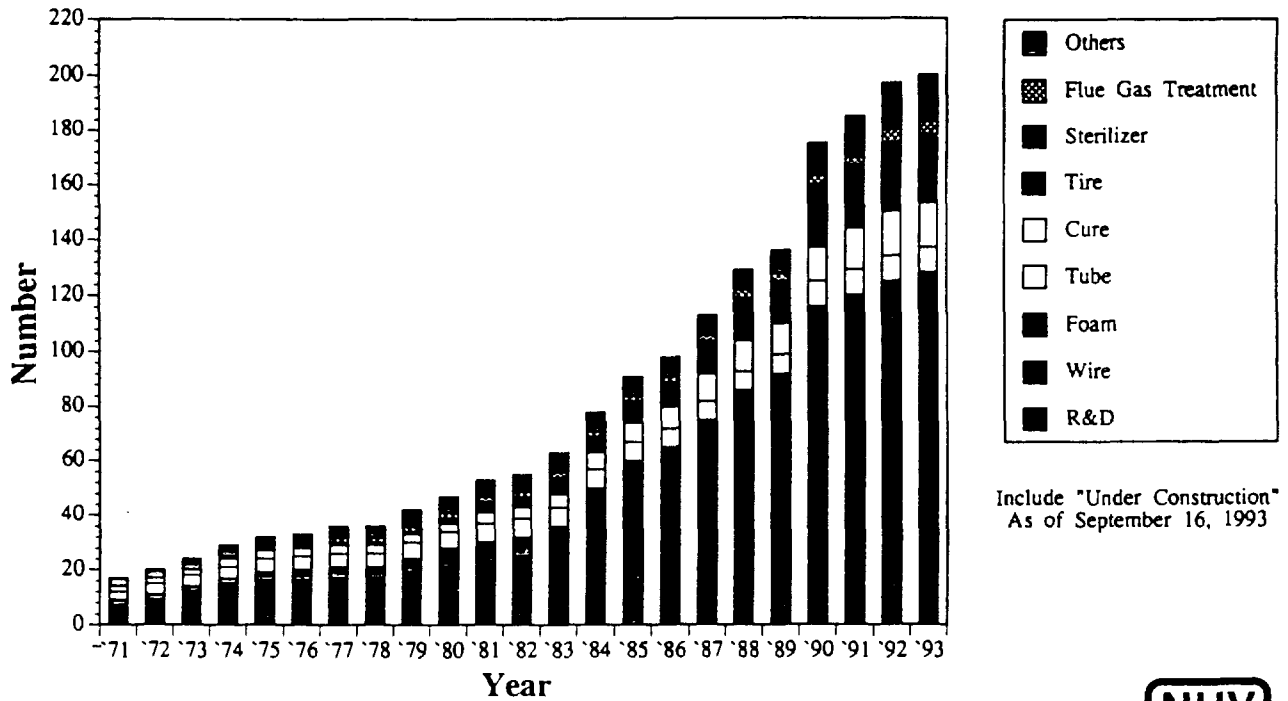


Table 1 Construction of test specimen wire

Item	Unit	Description
Conductor	Section area	mm ² 0.5
	Material	- Tinned annealed copper
	Composition	strands/mm 20/0.18
	Outer diameter	mm 1.0
Insulation	Material	- Irradiated crosslinked Highly flexible Fluoropolymer (RX ₃)
	Thickness	mm 0.35
	Outer diameter	mm 1.70

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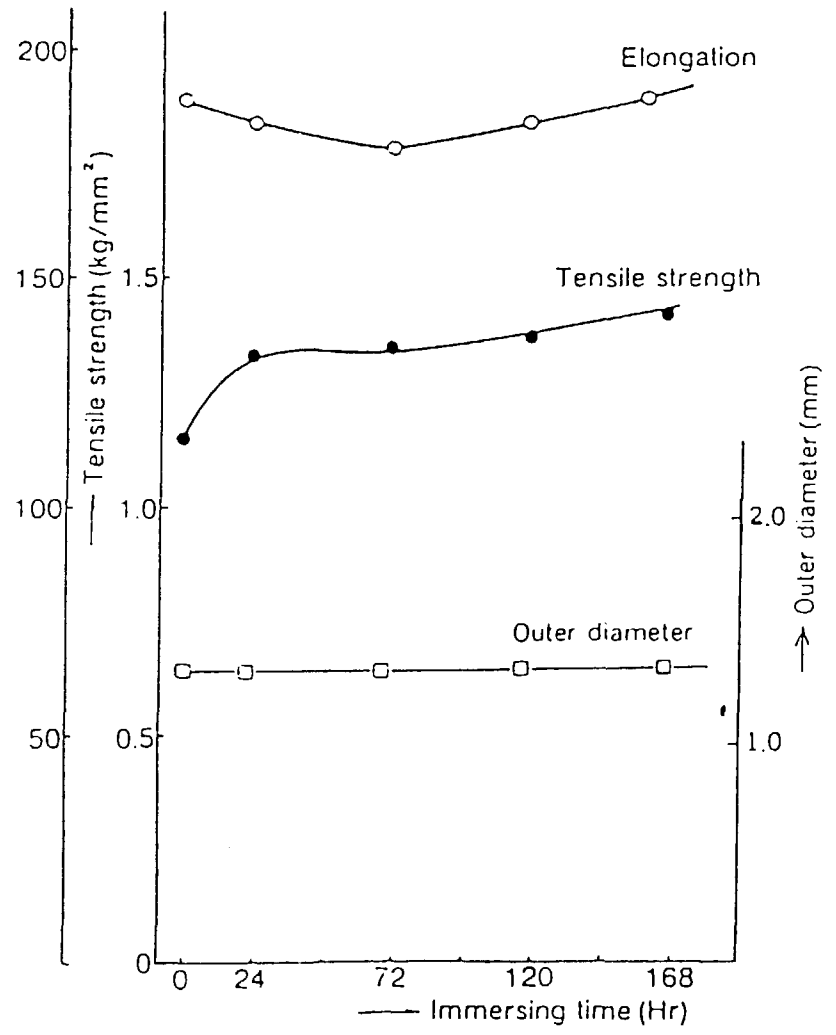


Fig. 3 Oil resistance of RX3 at 200°C

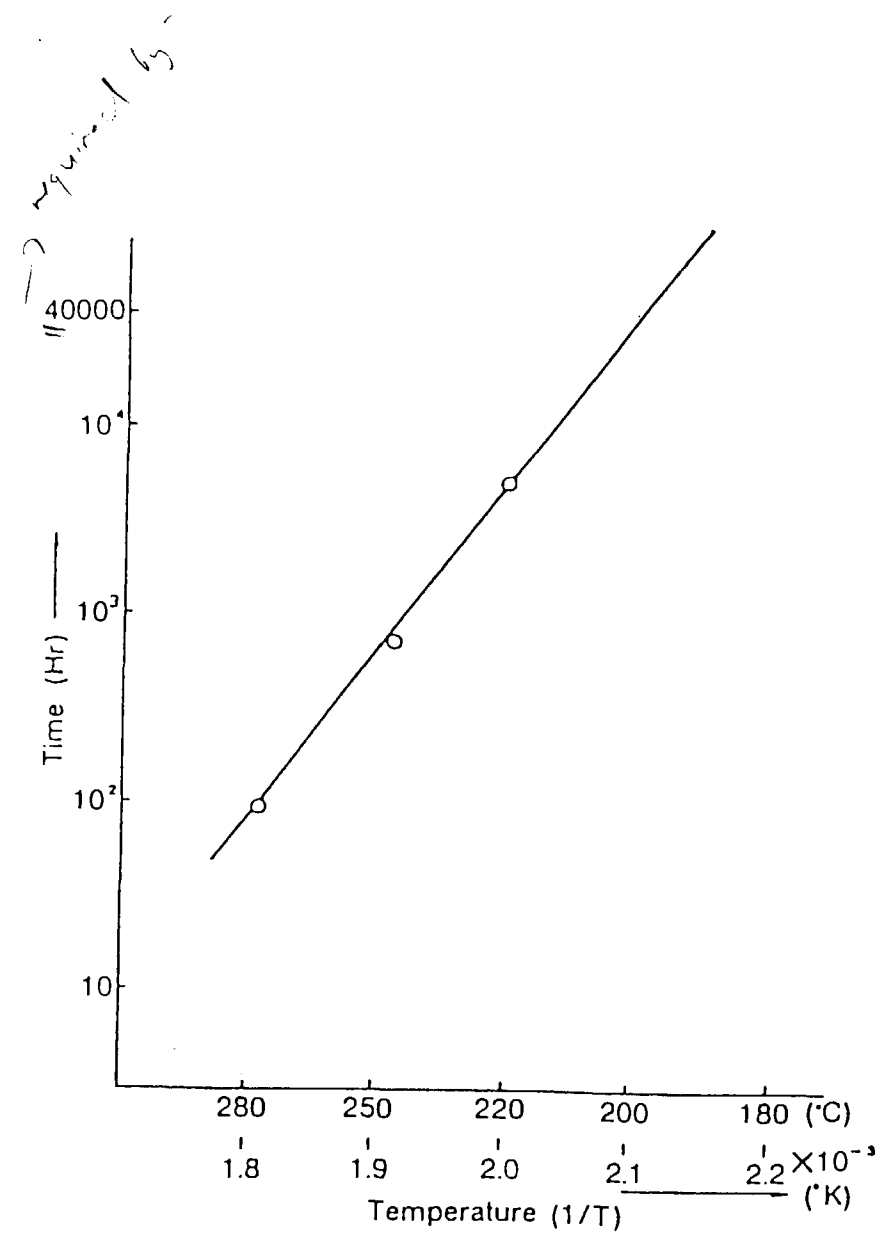


Fig. 2 Life curve of RX3

The Percentage of Passenger Cars Fitted ABS

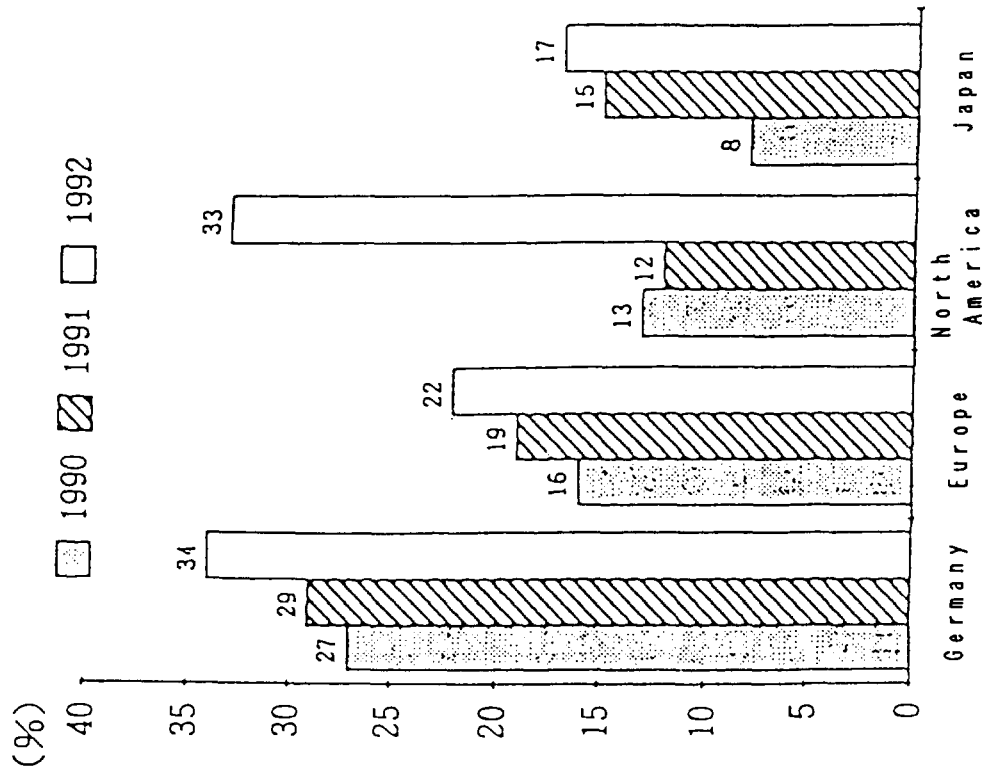


Fig. 4 (資料: Bosch Annual Report 1992)

Table 2 Dimensions of the sensor cables

Items		Unit	Test results	
Type		-	BXRA	FRBXRA
Conductor	Material	-	Copper alloy	
	Nominal section area	mm ²	0.5	
	Stranding	No/No/mm	7/38/0.051 ~ 0.053	7/38/0.051 ~ 0.054
	Outer diameter	mm	1.04	1.03
Insulation	Material	-	* 1	
	Minimum thickness	mm	0.40	0.40
	Average thickness	mm	0.48	0.52
	Outer diameter	mm	2.00	2.08
Twist	Color identification	-	Black x White	Black x White
	Material	-	* 2	* 3
Jacket	Average thickness	mm	1.21	1.15
	Outer diameter	mm	6.21	6.21

Note #1 : Irradiated cross-linked flame retardant polyethylene
 #2 : Irradiated cross-linked polyurethane
 #3 : Irradiated cross-linked flame retardant polyurethane

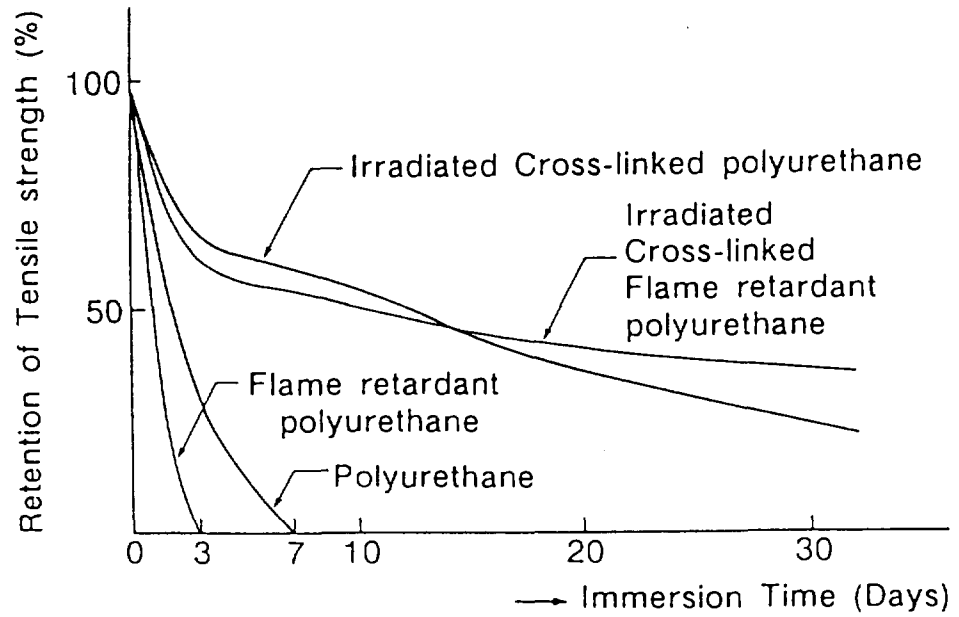


Fig. 5 100°C Hot water immersion test

Table 3 ASTM #2 Oil resistance at 100°C

Items		Unit	Type	
			BXRA	FRBXRA
Initial value	Tensile strength	Kg/mm ²	4.32	3.04
	Elongation	%	549	500
After 4 days of immersion at 100°C	Tensile strength	Kg/mm ²	4.06	3.15
	Elongation	%	632	542

Table 4 Brake fluid oil DOT3 resistance at 70°C

Items		Unit	Type			
			BXRA	Polyurethane	FRBXRA	FR-polyurethane
Outer diameter of the cable	Initial	mm	6.21	6.30	6.21	6.18
	Retention after immersion	%	142	melt-down	138	melt-down

Fig. 6 The Mechanism of Heat Shrinkable Tube

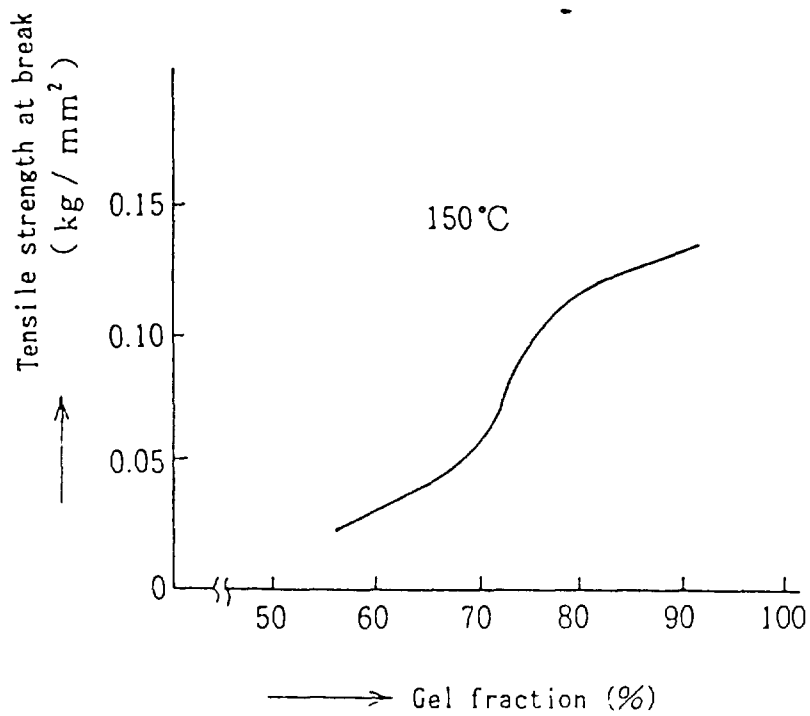
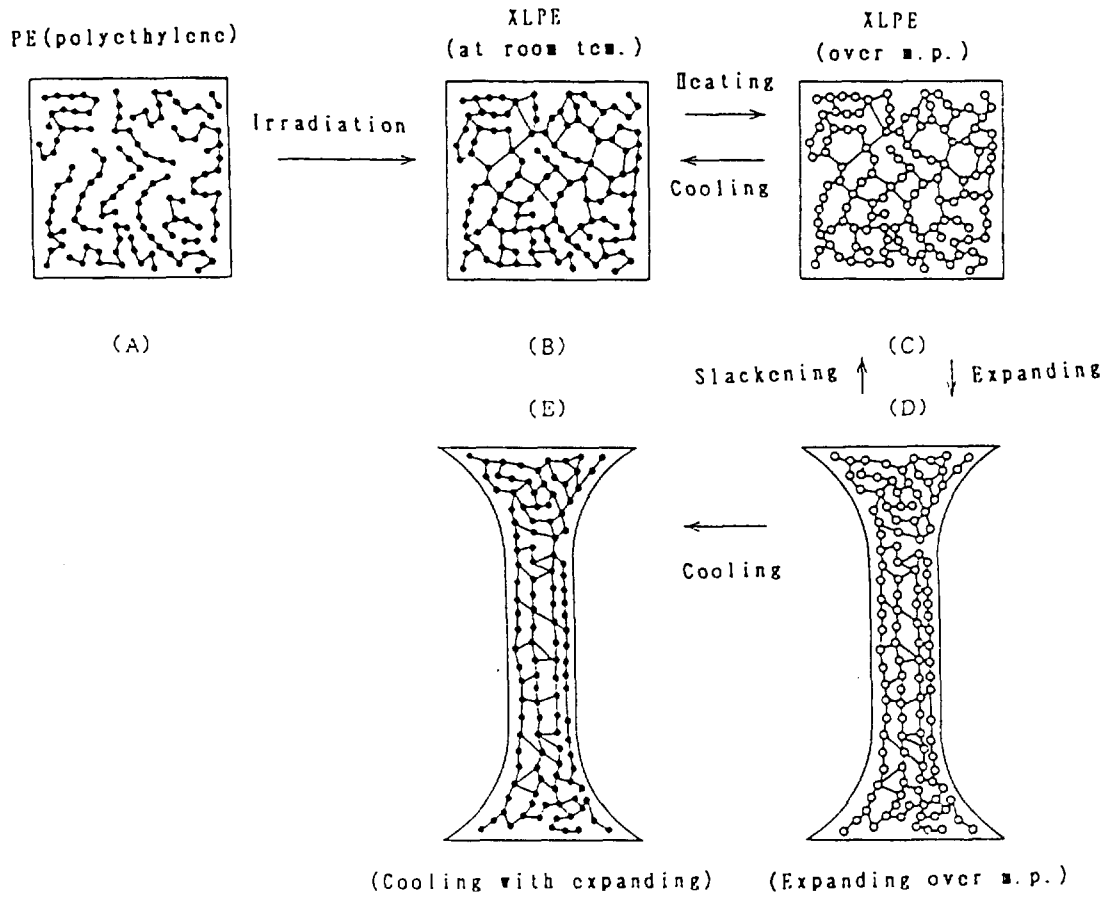


Fig. 7 Tensile strength at high temperature