

# ADDITIVES and MODIFIERS for thermoplastic compounds



# THERMOPLASTIC COMPOUND

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- a “thermoplastic compound” is obtained by modifying a polymer, after the polymerisation phase, with the addition to the base resin of various additives and modifiers
- **The target** is to modify and enhance the performance of the base resin



# ADVANTAGES OF COMPOUNDING

The main benefit offered by a thermoplastic compound is the cost/performance optimization of the material for a specific application

the modification can have various effects:

- Modification of the aesthetics of the base resin (by adding colorants and pigments)
- Performance upgrade (for example mechanical performance improvement by adding glass fibres)
- to give additional and absolutely new properties to the base resin ( for example electrical conductivity )

# *Advantages of compounding*

- improved processing compared to the base resin (increased thermal stability during injection moulding, shorter cycle time)
- to increase the resistance of the base resin in the conditions applied to the thermoplastic components during service (by adding heat stabilizers, UV stabilizers, anti-oxidants ...)

**IN ANY CASE THE BASE REASON FOR USING A THERMOPLASTIC COMPOUND IS A COST REDUCTION**

**The cost of the thermoplastic compound plus the processing costs must be lower than the price offered by technical alternatives which can give an equivalent functionality**

# ADDITIVES

Additives can be divided in a few main categories based on their most important function:

- COLORANTS AND PIGMENTS
- FILLERS AND FIBERS
  - mineral fillers (talc, calcium carbonate, kaolin, mica .. )
  - glass fibres, carbon fibres
- STABILIZERS
  - anti-oxidants – heat stabilizers
  - UV stabilizers



# *additives*

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- PROCESSING AIDS

- releasing agents
- internal lubricants
- nucleating agents

- PROPERTY MODIFIERS

- elastomers
- flame retardants
- lubricating agents
- conductive fillers
- EMI shielding fillers
- magnetic fillers

# GLASS FIBRES

## Morphology and composition

Glass fibres are thin glass filaments (diameter 10-12 micron) obtained by spinning glass in the molten phase.

The **density** is  $2,54 \text{ g/cm}^3$

The average **length** of glass fiber is 5 mm

## *glass fibres*

The **composition** of glass "E" type is the following:

$\text{SiO}_2$	50-52%
$\text{CaO}$	16-25%
$\text{Al}_2\text{O}_3$	15-16%
$\text{B}_2\text{O}_3$	8-13%
$\text{MgO}$	0-6%



## *glass fibres*

- The raw material is defined “ **glass E** ”.  
‘E’ means “electrical” as the composition is selected in order to give good electrical properties to the thermoplastic compound.

After the spinning process a thin layer is applied to the fibres surface which is constituted of **specific chemicals able to produce an efficient bonding between the glass and the polymer**

# GLASS FIBRES: properties modification

Glass fibres enhance considerably the mechanical performance of the compound and particularly they affect:

- E modulus
- Tensile strength
- Stiffness at high temperature
- Fatigue resistance (cyclic loads)
- Creep resistance (deformation in the long term under constantly applied loads)

## ***Glass fibres: properties modification***

Moreover glass fibres affect other important properties:

- the **density** of the compound is increased
- the coefficient of linear **thermal expansion** is reduced (and more similar to that of metals)
- the **shrinkage** during the injection molding is reduced (warpage problems can be generated)
- the compound **fluidity** is lower
- the **flame resistance** is affected
- the **electrical properties** are modified



# GLASS FIBRES REINFORCED POLYMERS

- semi-cristalline polymers (PP, PA6, PA66, PBT, POM, PPS):  
by adding glass fibres an outstanding improvement of the mechanical performance is obtained
- Amorphous polymers (PS, ABS, PC, PPOm, PSU):  
by adding glass fibres only the E modulus and tensile strength are increased. The impact resistance is reduced by the addition of fibres.

# Glass fibres length:

## Standard fibers (chopped):

Length 5 mm

- the glass fibres encounter a mechanical break-down during the compounding phase resulting in 1,5 mm fibre length in the compounded granules
- Additional break-down is generated during the injection molding so that the fibres length in the molded component is about 0,5 mm

## Short fibres (milled)

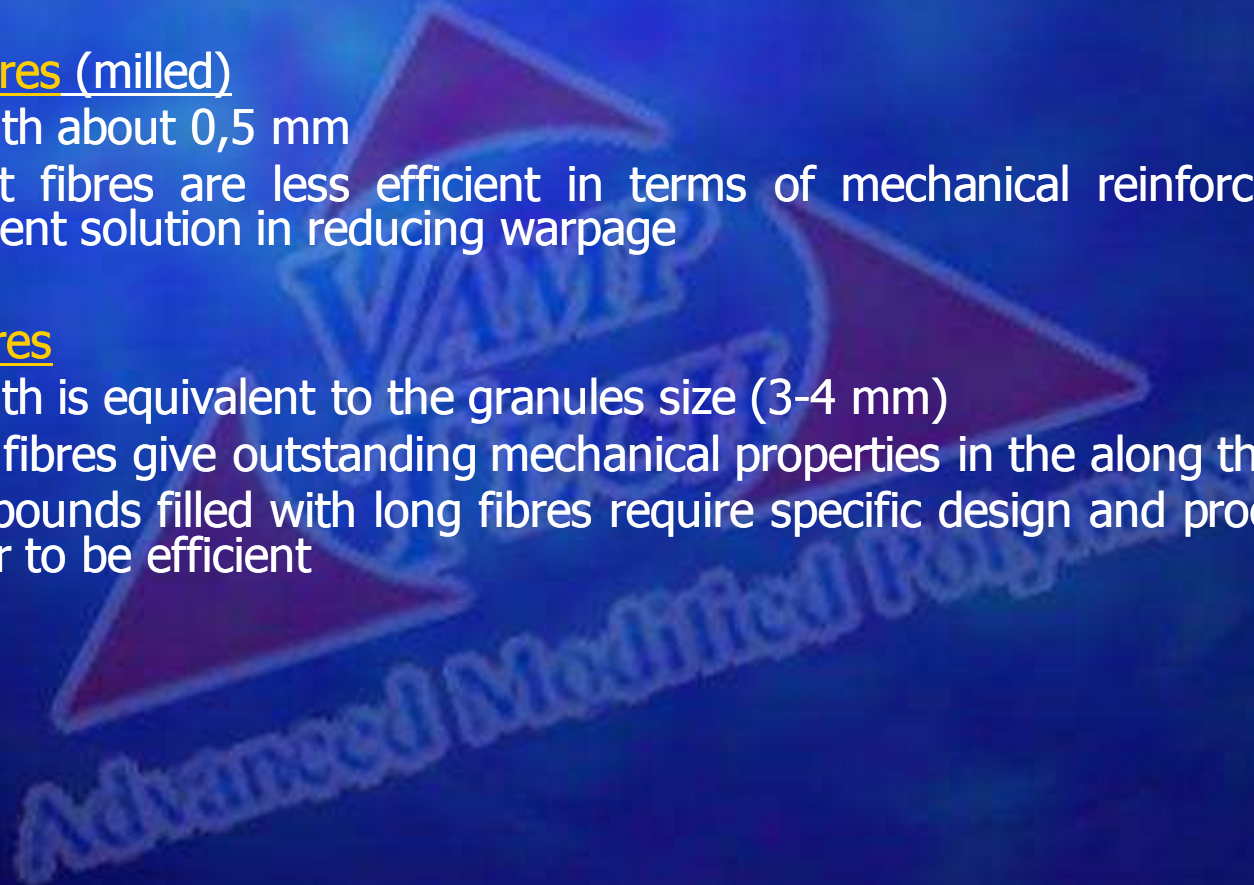
Length about 0,5 mm

- Short fibres are less efficient in terms of mechanical reinforcement but offer an efficient solution in reducing warpage

## Long fibres

Length is equivalent to the granules size (3-4 mm)

- long fibres give outstanding mechanical properties in the along the flow direction
- compounds filled with long fibres require specific design and processing conditions in order to be efficient



# GLASS BEADS

**Glass beads** can be used as filler of thermoplastic compounds in order to obtain:

- low warpage and good dimensional stability
- good surface finishing
- good scratch resistance

*note:*

*mechanical performance of glass beads filled compounds is poor compared to those reinforced with glass fibres*



# CARBON FIBRES

- Morphology and composition

Carbon fibers are composed by pure carbon

- Production

The carbon fibres are produced by carbonizing PAN fibres (poly acrylonitrile) in high temperature ovens where sequential chemical reactions are obtained

At a later stage a thin layer is applied to the fibres surface in order to obtain an efficient bonding between the fibers and the polymer

- General properties

the natural colour of carbon fiber filled compounds is black.  
Carbon fiber average length is 6 mm, their density is  $1,82 \text{ g/cm}^3$

# *Carbon fibres*

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Carbon fibres are **more efficient than glass fibres** and particularly:

- E modulus (**stiffness**) results to be much higher
- **tensile strength** is improved
- **density** is lower
- the **thermal expansion coefficient** is appreciably reduced and is similar to that of metals

# Carbon fibres

- the **surface resistivity** is reduced to a much lower magnitude that is from  $10^{14}$  to  $10^3$  ohms (carbon fibres are conductive)
- tribologic properties (**self-lubrication**) are improved
- It is not possible to obtain flame retarded compounds when carbon fibres are used



# CARBON FIBRE REINFORCED POLYMERS

- Even if all the base resin can be reinforced by using carbon fibres the high cost of these fillers is limiting their use in those polymers which can offer high technical performance as **PA6, PA66, POM, PC, PPS**
- some of the most relevant **applicazioni** are:
  - components requiring high mechanical performance
  - sport accessories
  - informatic technology (antistatic components)
  - antistatic products for explosive environments (**ATEX directive**)
  - medical applications & others

# OTHER REINFORCING FIBRES

## ■ Aramidic fibres

Main properties are:

- low density
- excellent tribologic properties
- electrical insulation

## ■ Stainless Steel fibres

their main property is the capability to give to injection molded parts excellent shielding properties to electromagnetic interference (EMI).

Stainless steel fibres are generally used for the production of boxes containing electronic devices which can be damaged by electromagnetic waves

# PA 66 – Glass fibres reinforced

	<b>UNITS</b>	<b>PA 66 unfilled</b>	<b>PA 66 30%</b>	<b>PA 66 50%</b>
- <b>Density</b>	<b>g/cm<sup>3</sup></b>	<b>1,13</b>	<b>1,36</b>	<b>1,58</b>
- <b>Longitudinal shrinkage</b>	<b>%</b>	<b>1,75</b>	<b>0,25</b>	<b>0,15</b>
- <b>IZOD notched impact</b>	<b>kJ/m<sup>2</sup></b>	<b>4,5</b>	<b>11,5</b>	<b>16,0</b>
- <b>Tensile strength</b>	<b>N/m<sup>2</sup></b>	<b>85</b>	<b>175</b>	<b>215</b>
- <b>E Modulus</b>	<b>MN/m<sup>2</sup></b>	<b>3.100</b>	<b>8.500</b>	<b>15.000</b>
- <b>Vicat (49 N)</b>	<b>°C</b>	<b>240</b>	<b>255</b>	<b>258</b>
- <b>HDT at 1,81 MN/m<sup>2</sup></b>	<b>°C</b>	<b>90</b>	<b>255</b>	<b>258</b>
- <b>Thermal Expans. Coeff. (linear)</b>	<b>K<sup>-1</sup></b>	<b>8x10<sup>-5</sup></b>	<b>3x10<sup>-5</sup></b>	<b>1,5x10<sup>-5</sup></b>
- <b>CTI</b>	<b>V</b>	<b>&gt;600</b>	<b>500</b>	<b>500</b>



# PC – Glass fibres reinforced

	UNITS	PC unfilled	PC 20% FV	PC 30% FV
- Density	g/cm <sup>3</sup>	1,20	1,35	1,44
- Longitudinal shrinkage	%	0,60	0,40	0,30
- IZOD notched impact	kJ/m <sup>2</sup>	80,0	12,0	13,5
- Tensile strength	N/m <sup>2</sup>	58	105	135
- E Modulus	MN/m <sup>2</sup>	2.200	5.400	8.500
- Vicat (49 N)	°C	146	147	148
- HDT at 1,81 MN/m <sup>2</sup>	°C	131	139	140
- Thermal Expans. Coeff. (linear)	K <sup>-1</sup>	7x10 <sup>-5</sup>	3x10 <sup>-5</sup>	2,5x10 <sup>-5</sup>
- CTI	V	225	155	155

# FIBRES Reinforcement

## Glass fibres vs. Carbon fibres

	UNITS	PA 66 30% GLASS FIBRES	PA66 30% CARBON FIBRES
- Density	g/cm <sup>3</sup>	1,38	1,28
- Tensile strength	MN/m <sup>2</sup>	180	215
- E Modulus	MN/m <sup>2</sup>	8.500	17.000
- IZOD notched impact	kJ/m <sup>2</sup>	13,0	7,0
- Thermal Expans. Coeff. (linear)	K <sup>-1</sup>	3x10 <sup>-5</sup>	1x10 <sup>-5</sup>
- Volume resistivity	Ohm cm	10 <sup>13</sup>	10 <sup>3</sup>

# Fibres Reinforcement: **DISADVANTAGES**

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Glass and carbon fibres offer outstanding advantages in terms of mechanical performance of thermoplastic compounds.

However the **potential risk of warpage** problems (which are due to **differential shrinkage** along the flow and transversal to the flow) must be taken into consideration in the design stage.



# MINERAL FILLERS

Mineral fillers are widely used in compounding of thermoplastic materials as they offer several **advantages**:

- **Low cost**
- **Good dimensional stability** of molded parts

This property of mineral filled compound is mainly due to the **Aspect Ratio** of the fillers.

The low length/thickness ratio (which is extremely high for glass fibers) allows to get **uniform shrinkage** which results in a low warpage of the molded parts.

# MINERAL FILLERS

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**Propries** of mineral filled compounds are affected by:

- **amount (percentage)** of mineral fillers
- **dimensions** of mineral filler particles
- **morphology** of the filler
- chemical **composition** of the filler surface
- **impurities** present in the fillers

# MINERAL FILLERS :

## COMPOSITION AND PROPERTIES

	COMPOSITION	MORPHOLOGY	DENSITY (g/cm <sup>3</sup> )	Aspect Ratio
<b>Calcite</b>	Calcium carbonate	Granules	2.7	3
<b>Caolin</b>	Aluminum silicate	Lamellar	2.6	10 – 50
<b>Mica</b>	Al and K silicate	Lamellar	2.8	> 50
<b>Talc</b>	Magnesium silicate	Lamellar	2.7	30
<b>Wollastonite</b>	Calcium silicate	Fibrous	2.9	> 50
<b>Glass Fibres</b>			2.6	> 500



# Other Mineral Fillers

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- Additional mineral fillers used for polymer modification are:

- Calcium Carbonate
- Barite (barium sulfate)
- Mica (aluminum silicate)

Advanced Modified Polymers

# MINERAL FILLERS: FILLER PERFORMANCE COMPARISON

	UNITS	PA66 30% Talc	PA66 30% Calcium Carbonate	PA66 30% Caolin	PA66 30% Wollastonite
Density	$g/cm^3$	1.36	1.36	1.36	1.37
Linear Shrinkage(L)	%	0.7	1.1	1.2	1.1
Transversal Shrinkage (T)	%	0.7	1.1	1.2	1.1
IZOD notched impact	$kJ/m^2$	3,5	2,5	5,0	2,5
CHARPY unnotched impact	$kJ/m^2$	30	14	>300	20
Flexural strength	$MN/m^2$	110	105	140	130
E Modulus	$MN/m^2$	6200	4000	4700	4600
HDT at 1,81 $MN/m^2$	$^{\circ}C$	165	85	90	135

# PERFORMANCE: GLASS FIBRES vs. MINERAL FILLERS

	UNITS	PA6	PA6 30% M.F.	PA6 30% G.F.
Density	$g/cm^3$	1,14	1,37	1,36
Linear Shrinkage(L)	%	1,40	0,60	0,25
Transversal Shrinkage (T)	%	1,50	0,60	0,70
IZOD notched impact	$kJ/m^2$	4,5	3,5	11,0
CHARPY unnotched impact	$kJ/m^2$	5	5	12
Flexural strength	$MN/m^2$	105	110	240
E Modulus	$MN/m^2$	2700	6200	8100
HDT at 1,81 $MN/m^2$	$^{\circ}C$	110	165	175



# ELASTOMER MODIFIED COMPOUNDS

- Elastomer modified compounds offer excellent **impact resistance**.

The elastomers used in compounding are mainly acrylics or polyolefins.

*Note:*

*By using elastomer modification it is possible to avoid conditioning of molded parts produced with hygroscopic polymers like PA6 and PA66*

# PA 66 vs. ELASTOMER MODIFIED PA 66

	<b>UNITS</b>	<b>PA 66 unfilled</b>	<b>PA 66 Elastomer Mod.</b>
Density	<i>g/cm<sup>3</sup></i>	1.14	1.05
Linear shrinkage	%	1.5 – 1.8	1.4 – 1.7
IZOD notched impact +23° C	<i>KJ/m<sup>2</sup></i>	4,5	>50,0
-20° C		3,5	23,0
-40° C		2,5	17,0
CHARPY (unnotched)	<i>KJ/m<sup>2</sup></i>	>300	>300
Tensile strength at yield	<i>MN/m<sup>2</sup></i>	85	55
E Modulus	<i>MN/m<sup>2</sup></i>	2900	1800
HDT at 1.81 MN/m <sup>2</sup>	°C	90	65

Advanced

# PIGMENTS & COLORANTS

- coloring is a fundamental key for the success of thermoplastic compounds as it allows to obtain the requested color by **avoiding the very complex and expensive painting process**
- Coloring additives can be classified as follows:

## Pigments

Pigments are inorganic additives which are insoluble in the base resin

## Colorants

Colorants are organic or inorganic additives solubili nella resina di base. They are selected based on the thermal stability of the color resulting by the mixing process

### *Note:*

*Cadmium based pigments allow to get very brilliant colours with high UV resistance and good thermal stability. However they cannot be used for applications mentioned by the RoHS directive*



# Flame Retardant additives

the Flame Retardant Additives action is **to block or to delay the combustion process** causing the self-extinguishing of thermoplastic components as soon as the flame or the glowing wire are removed



# Flame Retardant Additives

	<b>PS</b>	<b>ABS</b>	<b>PPO<sub>m</sub></b>	<b>PC</b>	<b>PP</b>	<b>PA</b>	<b>PBT</b>
<b>Organic Chlorinated Halogens (Cl)</b>	X	X			X	X	X
<b>Organic Brominated Halogens (Br)</b>	X	X			X	X	X
<b>Polymeric Brominated Halogens (Br)</b>				X		X	X
<b>Melamine derivatives (N)</b>						X	
<b>Red Phosphorous (P)</b>						X	
<b>Polyphosphates (P e N)</b>			X	X	X		
<b>Aluminum Hydroxide (Al)</b>					X		
<b>Magnesium Hydroxide (Mg)</b>					X	X	
<b>Antimony trioxide (Sb)</b>	X	X		X	X	X	X

# PA 66 25% Glass Filled UL94 V0

		<b>PA 66 25% FV</b>	<b>PA 66 25% FV (con alogeno organico)</b>	<b>PA 66 25% FV (con alogeno polimerico)</b>	<b>PA 66 25% FV (con fosforo rosso)</b>
<b>Densiy</b>	g/cm <sup>3</sup>	1,35	1,50	1,60	1,37
<b>IZOD notched impact</b>	kJ/m <sup>2</sup>	9,0	6,5	6,5	8,5
<b>E Modus</b>	KJ/m <sup>2</sup>	7000	8800	8800	7500
<b>Tracking Index (CTI)</b>	V	500	300	400	400
<b>UL94 1,5 mm</b>	-	HB	V0	V0	V0
<b>Hot runners</b>		YES	YES/NO	YES	YES/NO
<b>Surface Aesthetics</b>		++	-	+	++
<b>All colors</b>		+++	++	++	-
<b>Hot and Humid environment</b>		++	++	++	-



# Degradation process and STABILIZERS

- Polymers can be affected by degradation processes which are causing the macromolecular chains breakdown.  
The degradation processes are active during all the stages of the compound life and are **due to the combined action of heat, oxygen and light** which results in a reduction of the compound performance.
- The degradation processes can be divided in two main classes:
  - **thermal-oxidation processes** due to the combined action of heat and oxygen
  - **photo-degradation processes** due to UV radiations

# Thermal oxidation

- Thermal-oxidation can happen during the following stages:
  - 1 during the compounding stage (extrusion), due to the combined action of heat and mechanical stress
  - 2 during the injection moulding stage, due to shear stress, heat and oxygen
  - 3 during the life of the thermoplastic component (in service) due to the combined action of heat, oxygen and chemicals present in the environment

# Photo-degradation

- photo-degradation processes can happen **during the life of the thermoplastic component** due to the energy given by UV radiation on the surface of the plastic part
- the consequences of photo degradation are not the same for all the involved polymers and result in the following negative effects:
  - **Colour modification** for the moulded parts
  - Depolymerization (**decay of all the polymer properties**)
  - Cross-linking and Gel formation (**increased stiffness and brittleness**)



# Heat Stabilizers

- Heat Stabilizers are molecules which **interfere with the polymer degradation by stopping or delaying the degradation process.** Therefore the Heat Stabilizers action is to reduce to slow down the properties decay

- Heat Stabilizers can be divided in two classes according to their chemical activity:

## PRIMARY ANTI-OXIDANTS

they stop or delay the chemical reactions related to the polymer degradation.

## SECONDARY ANTI-OXIDANTS

they delay the degradation at a later stage

Heat Stabilizer type and quantity are defined based on the base polymer and service conditions

# UV stabilizers

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- UV stabilizers can be divided in two families:

## UV absorber

they absorb the UV radiation and convert it into heat

## Reactive UV stabilizers

they stop or delay the chemical reactions related to the polymer degradation

# Self-Lubricating ADDITIVES

- Thermoplastic compounds can sometimes replace metals in mechanical applications like gears, cams, bearings and slides where , together with competitive cost, low weight and good mechanical properties, **low friction coefficient and low wear are requested.**
- Some thermoplastic polymers (like POM) are intrinsically self-lubricated and offer low friction coefficient without the addition of specific additives
- Self-lubrication of thermoplastic compounds can be significantly improved by using specific additives



# Self-Lubricating ADDITIVES

## Molybdenum disulphide

- offers a moderate reduction of the friction coefficient
- it is used with semi-crystalline polymers (particularly polyamides) as it improves the surface crystallinity which results in lower wear and PV limit
- it is added in small quantities (1-3%) as it involves a drawback in terms of mechanical performance reduction

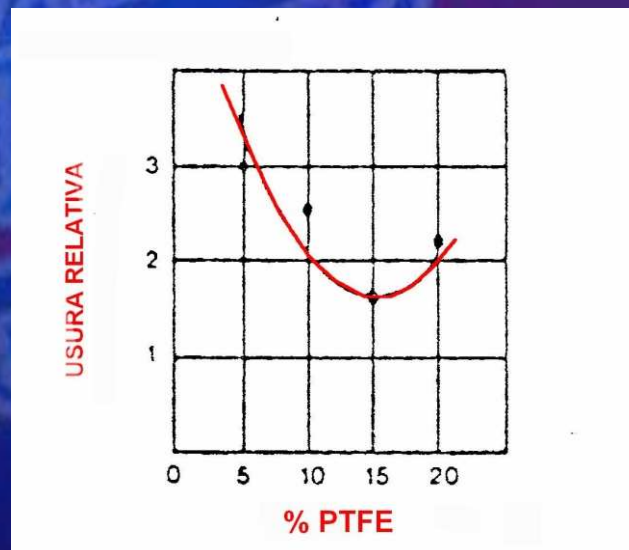
## Grafite

- offers a reduction of the friction coefficient
- improves the dimensional stability of the compound having the same effect of a filler and being added in high percentages to the base polymer (up to 30%).
- it is efficient for under the water applications

# Self-Lubricating ADDITIVES

## *Polytetrafluoroethylene (PTFE)*

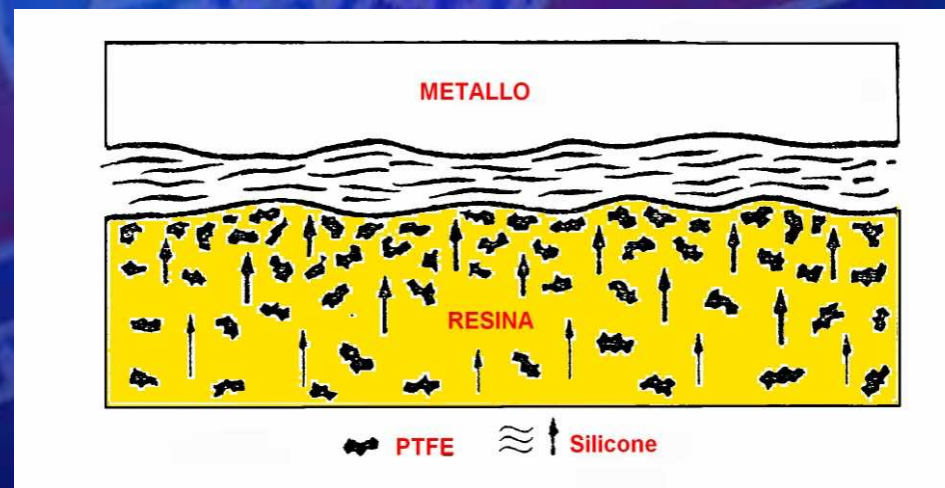
- it is the most efficient modifier as it has a very low friction coefficient (0,03)
- during the sliding process it PTFE generates a thin layer over the part surface which gives an outstanding lubrication
- PTFE offers the best performance when added to the base polymer in a percentage included in the range 15-20%



# Self-Lubricating ADDITIVES

## Silicon

- it is added to the base polymer in the state of **high viscosity oil**
- even if Silicon can be efficiently mixed with many polymers it **tends to migrate to the surface of the plastic part** generating a lubricating oil
- it is particularly **efficient at the start up and at high speed**
- it is generally used in small percentages (up to 2%) and it is often used in combination with PTFE





# ANTI-STATIC COMPOUNDS

- in order to reduce the electrical insulation intrinsically given by base polymers **conductive fillers and particularly carbon based fillers**. The amount of fillers is strongly affecting the surface resistivity

the target is to avoid high electrostatic loads on the surface the plastic parts

- In some applications and particularly for **Potentially Explosive Environments** it is fundamental to avoid electrostatic charges on the surface of thermoplastic components which may generate sparks and subsequently explosion  
The safety conditions of Potentially Explosive Environments are defined by the **ATEX directive**.