Corso di Laurea Magistrale in Ingegneria dell'Innovazione del Prodotto

a.a. 2022-23

Anno I – Semestre I

Tecnologia dei materiali polimerici

Lezione 25

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FASE #1: La scelta del prodotto

PRINTED CIRCUIT BOARD, PCB

- La produzione annuale di rifiuti elettronici (E-Waste) ha una crescita del 10% annuo
- La produzione globale di E-waste è stata pari a 50 ton/anno nel 2016 [UN report]
- La maggior percentuale di questi rifiuti sono da ricondursi a PCBs
- I PCBs sono costituiti per il 70% da sostanze non metalliche,

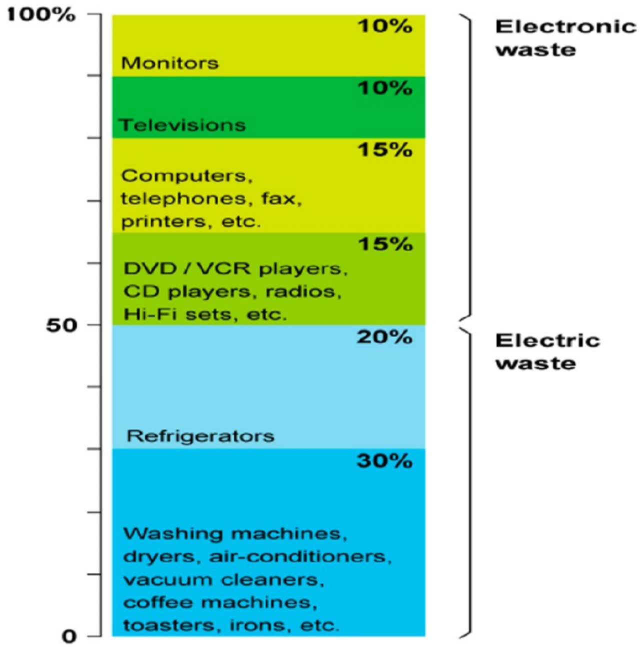


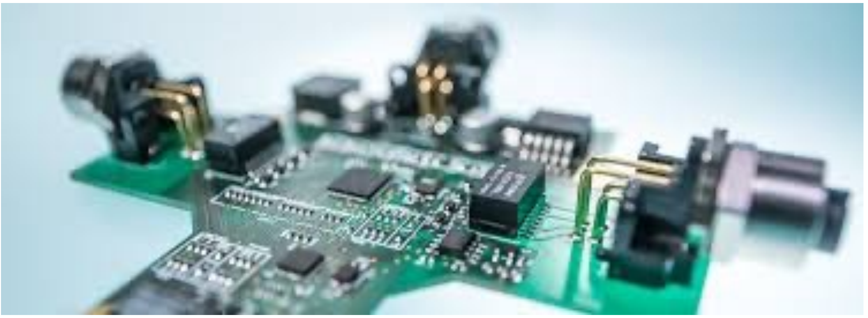
Fig. 1. Composition distribution of e-waste.

Home	Hospitals	Government	Private Sectors
• PC • TVs • Radio • Cell phone • Washing machine • Microwave oven • CD player • Fan • Electric iron etc.	• PC • Monitor • ECG device • Microscope • Incubator • X ray machine • MR etc.	• PC • CPU • Printer • Fax • Photocopy machine • Scanner • Fan • Tube light etc.	• PC • Boiler • Mixer • Signal conditioner • Incubator etc.

Fig. 2. Four main sources of e-waste.

[R. Qiu et al. / Journal of Cleaner Production 279 (2021) 123738]

STRUTTURA DI UN PCB



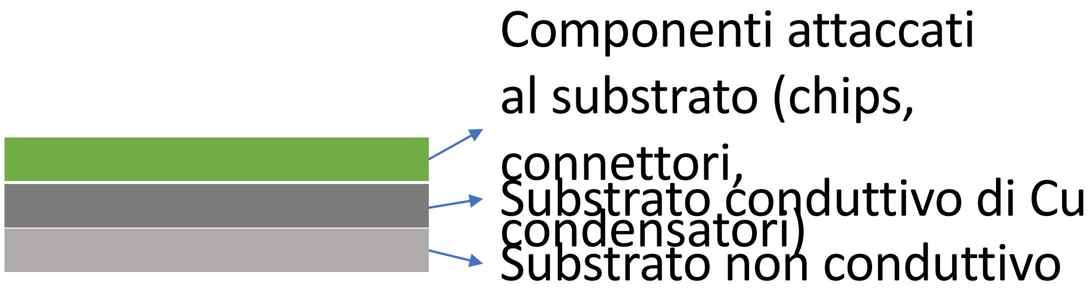


Table 2
PCB types, contents and properties.

Board/substrate	Single sided	Double sided	Multiple layered
Resın	Type	Color	Value
FR-2 (reinforcement)	Phenolic cellulose paper	Yellow/brown	Low value EEE (TV, home electronics)
FR-4 (reinforcement)	Epoxy glass fiber	Green	High value EEE (PC, phones)
Glass fiber/cellulose	FR-4	FR-4	FR-4
	FR-2	FR-2	FR-2
Cu substrate			
Solder	Sn, Pb		
Electronic components (IC)	Chips, ICs, relays	Connectors, capacitors	Resistors, switches

[M. Kaya / Waste Management 57 (2016) 64–90]

RICICLABILITA’

- La gran parte della ricerca è rivolta al recupero della componente metallica, in quanto essa contiene materie prime critiche
- Fino ad ora è stata rivolta scarsa attenzione al riciclo della componente non metallica (polime

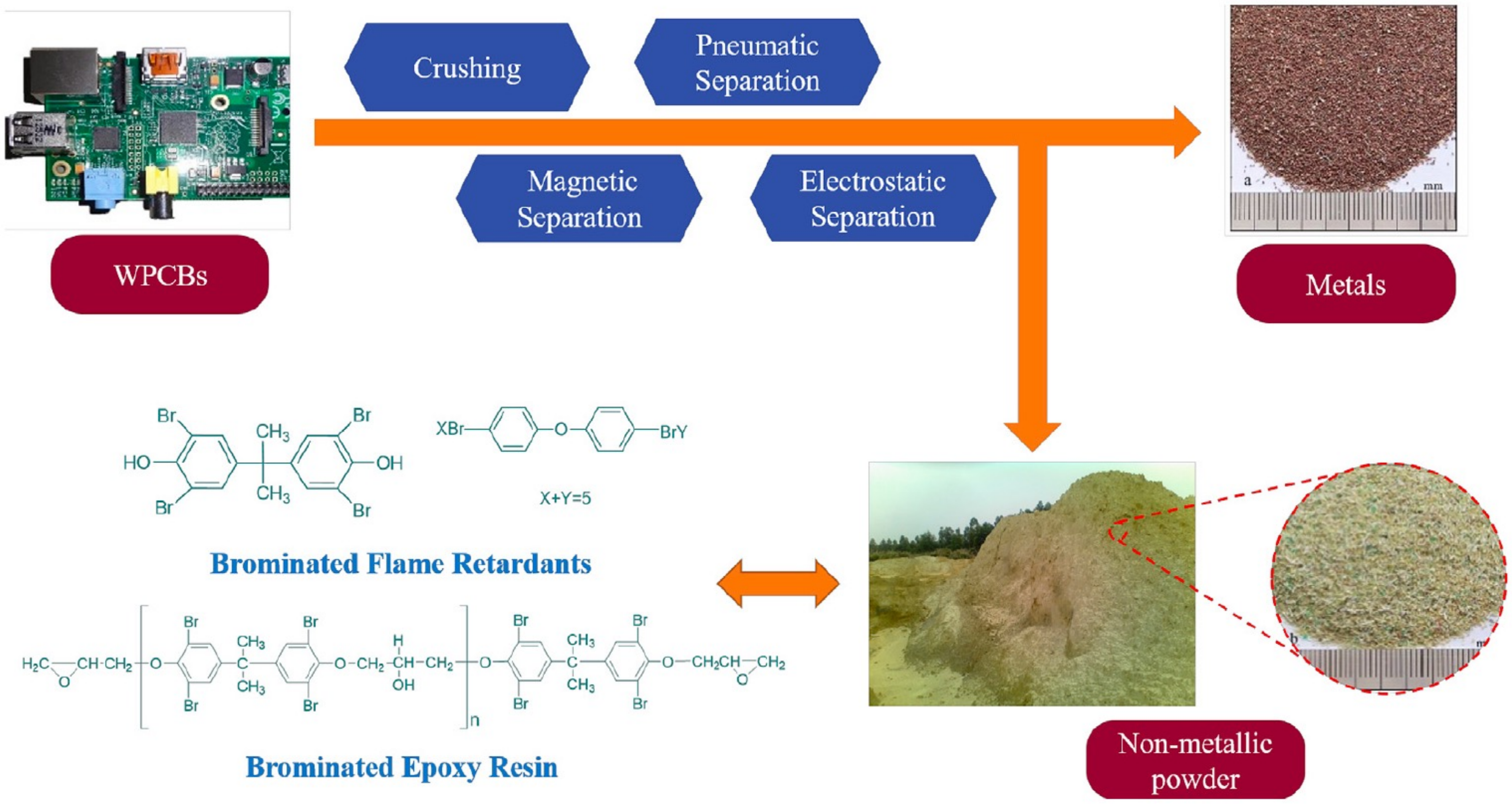
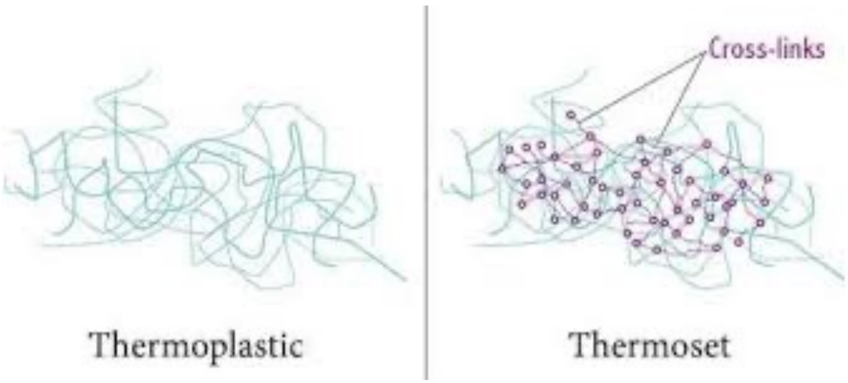
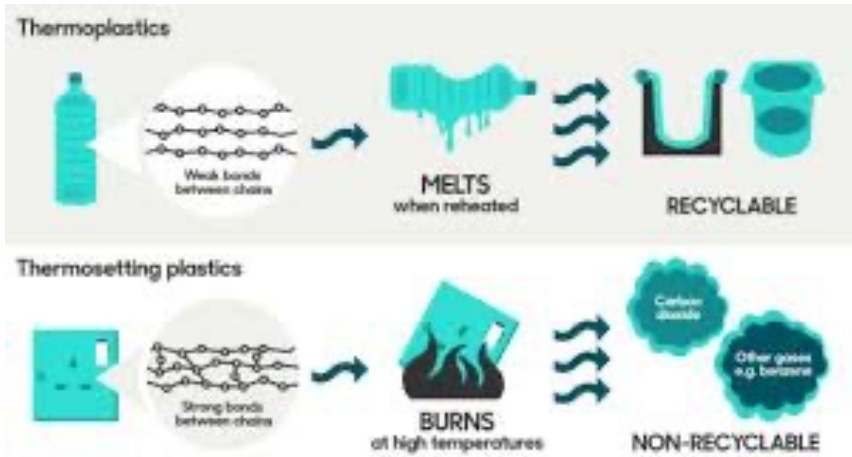


Fig. 1. Schematic diagram of non-metal powder production pathways and potential hazards of non-metal powder.

L’IDEA

- I substrati isolanti utilizzati sono termoindurenti: perché?
- Le resine termoindurenti, data la loro composizione chimica, non sono riciclabili secondo i metodi tradizionali di riciclo chimico e meccanico
- E’ possibile sostituire i substrati isolanti con polimero termoplastico riciclabile? Riducendo così l’impatto ambientale dei PCBs?
- Quali sono le condizioni operative in esercizio a cui devono rispondere questi substrati isolanti?





FUNZIONE DEL SUBSTRATO POLIMERICO

Isolare termicamente ed elettricamente il substrato metallico su cui viene stampato il circuito e saldati i componenti

- Il substrato isolante ed il substrato conduttivo sono accoppiati
- Il Cu è rivestito da una pellicola polimerica, che può essere attaccata chimicamente (di solito si usa diclorometano)
- Il circuito viene stampato sul substrato di Cu
- I componenti vengono saldati sulla piastra metallica, la quale si scalda
- In esercizio il PCBs è sottoposto a campi elettrici alternati con frequenze che possono arrivare anche a 10GHz nei dispositivi più performanti

- Devo tener conto delle proprietà termiche (Tg, CTE)
- Delle proprietà elettriche (costante dielettrica , fattore di dissipazione)
- Delle proprietà meccaniche, il componete in esercizio sarò sottoposto a cicli di fatica termica e possibile insorgenza di stress termici, creep?
- Quali sono le condizioni ambientali in cui opererà il componente? T, umidità ecc.
- Esistono normative?

Gruppo	MySelf		
Nome del componente	Rigid Printed Circuit Board-PCB		
Funzione del componente [1]	A printed circuit board (PCB) mechanically supports and electrically connects electrical or electronic components using conductive tracks, pads and other features etched from one or more sheet layers of copper laminated onto and/or between sheet layers of a non-conductive substrate.		
Materiali con cui è realizzato [2]	Al base (heat sink) Copper+Etchable Solder Mask (electric circuit), insulating substrate of Glass Fiber Reinforced Epoxy (Dielectric Layer)		
A. CONDIZIONI OPERATIVE	NORMALE	MIN	MAX
Temperatura di servizio (°C) [2]	30	5	235-255 for 10 s [welding]
Vita in servizio			
Tipo di carichi	The PCB is expected to be handled, to resist to accidental fall, to support the circuit components	<10 MPa Bending/compression/tensile During loading	<5MPa Load due to circuit components
Durata del carico		Short-Term	Long-Term, during the all life-time
Stress indotti termicamente Fatica TERMO-MECCANICA	Shear stress 10-20 MPa		
Sollecitazioni elettriche	Frequency: From 10 MHz to 4 GHz		
B. AMBIENTE [3]	Sostanze chimiche methylene chloride resistance (MCR), MCR between 0.01 percent and 0.20 percent.	Umidità moisture absorption value between 0.01 percent and 0.20 percent	Infiammabilità UL94 state that specimens cannot burn for longer than 10 seconds with flaming combustion.
Luce solare diretta no	Luce solare indiretta no	Disposizioni sullo smaltimento	Rifiuto di fine vita
C. RICHIESTE DI PROGETTO	Fattore di sicurezza	Tolleranze	Finitura
	Riciclabilità	Disassemblaggio a fine vita	H_m (KJ), CO_{2eq} (mol/unit)
D. TEST DI PERFORMANCE	Includere se c'è una richiesta di performance specifica		
F. APPROVAZIONI	Normativa UL94	Classificazione	
	Categoria (alimentare, medica, militare, aerospaziale, elettrica etc.)	Elettrica	
G. Aggiungere qui qualsiasi informazione utile a comprendere la funzione del componente, le condizioni di esercizio in termini di temperatura, carichi e «abusi» a cui la parte deve sottostare			

[1] https://en.wikipedia.org/wiki/Printed_circuit_board
[2] https://www.mclpcb.com/pcb-material-selection-guide/
[3] https://redstarworldwide.com/printed-circuit-boards-guide/

FASE#2: DEFINZIONE DI VINCOLI ED OBIETTIVI

VINCOLI

PROPRIETA' TERMICHE	Epoxy+Fibre di Vetro
Tg [°C]	-
CTE [$10^{-6}K^{-1}$]	<40
Infiammabilità	Non infiammabile o Autoestinguent e
PROPRIETA' ELETTRICHE	
ε	3.5-5.5
tanδ	0.001-0.02
PROPRIETA' MECCANICHE	
E [GPa]	15-30
σ_Y [MPa]	>20 MPa
ν	0.4
PROPRIETA' CHIMICHE	
Resistenza al DicloroMetano CH_2Cl_2	0.01-0.2%
[illegible]	[illegible]

OBIETTIVI

- Utilizzo di un polimero termoplastico
- Riciclabile, o a ridotti H_m e $CO_{2,\ eq}$
- Capacita' del substrato di lavorare alle alte frequenze, fino a 4GHz

ANALISI DEI VINCOLI E CURVE DI TRADE-OFF

1. PROPRIETA' TERMICHE

Durante le operazioni di saldatura si verificano picchi di temperatura per brevi tempi (decine di
Quali sono le conseguenze sulle caratteristiche del materiale?

T<Tg La struttura è stabile, possibile innesco di fenomeni di degradazione
T>Tg Cambiamento delle microstruttura con conseguenze sulle proprietà meccaniche ed elett

T<Tg, CTE coefficiente di dilatazione termica lineare dipende unicamente dalle vibrazioni degli atomi intorno alla loro posizione di equilibrio
T>Tg, CTE cambia significativamente

1. PROPRIETA' TERMICHE

CTE del Cu 17 W/mK

$\nu_{polimero}$=0.38-0.4

$$\alpha = \frac{1}{l}\left(\frac{\partial l}{\partial T}\right)_P = \left(\frac{\partial \ln l}{\partial T}\right)_P$$

$$\varepsilon_{z,termica} \approx \frac{\Delta l}{l_0} = \alpha \cdot \Delta T$$

$$\varepsilon_{z,meccanica} = \frac{\sigma}{E}$$

$$\sigma_{TERMICO} = E \cdot \alpha \cdot \Delta T$$

Per due piastre vincolate vale:

$$\sigma_{x\ termico} = \sigma_{y\ termico} = \frac{E \cdot (\alpha_{POLIMERO} - \alpha}{1 - 2\nu}$$

2. PROPRIETA' MECCANICHE

$$\sigma_{TERMICO} < \sigma_Y$$

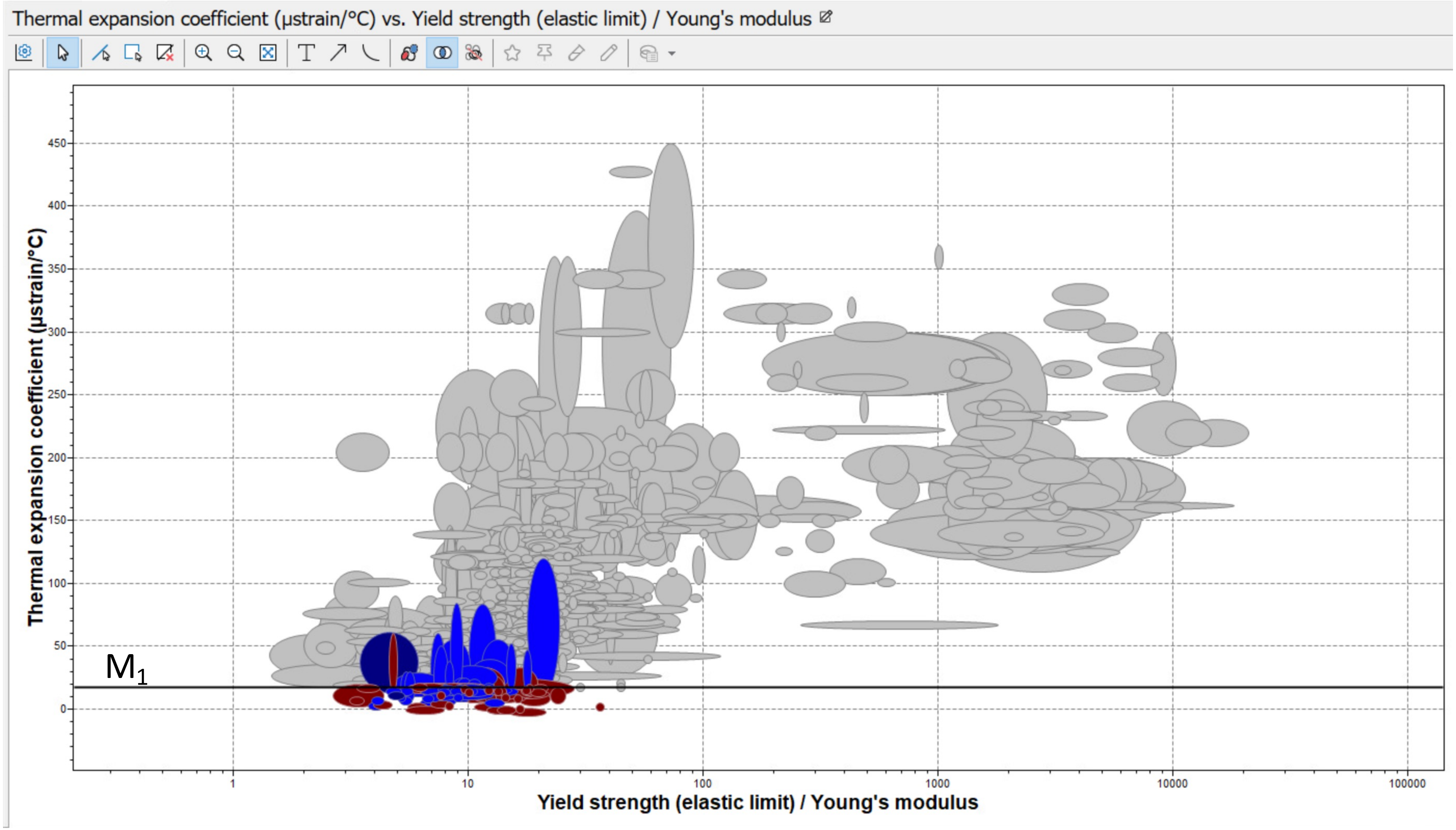
$$\frac{E \cdot \Delta\alpha \cdot \Delta T}{1 - 2\nu} < \sigma_Y$$

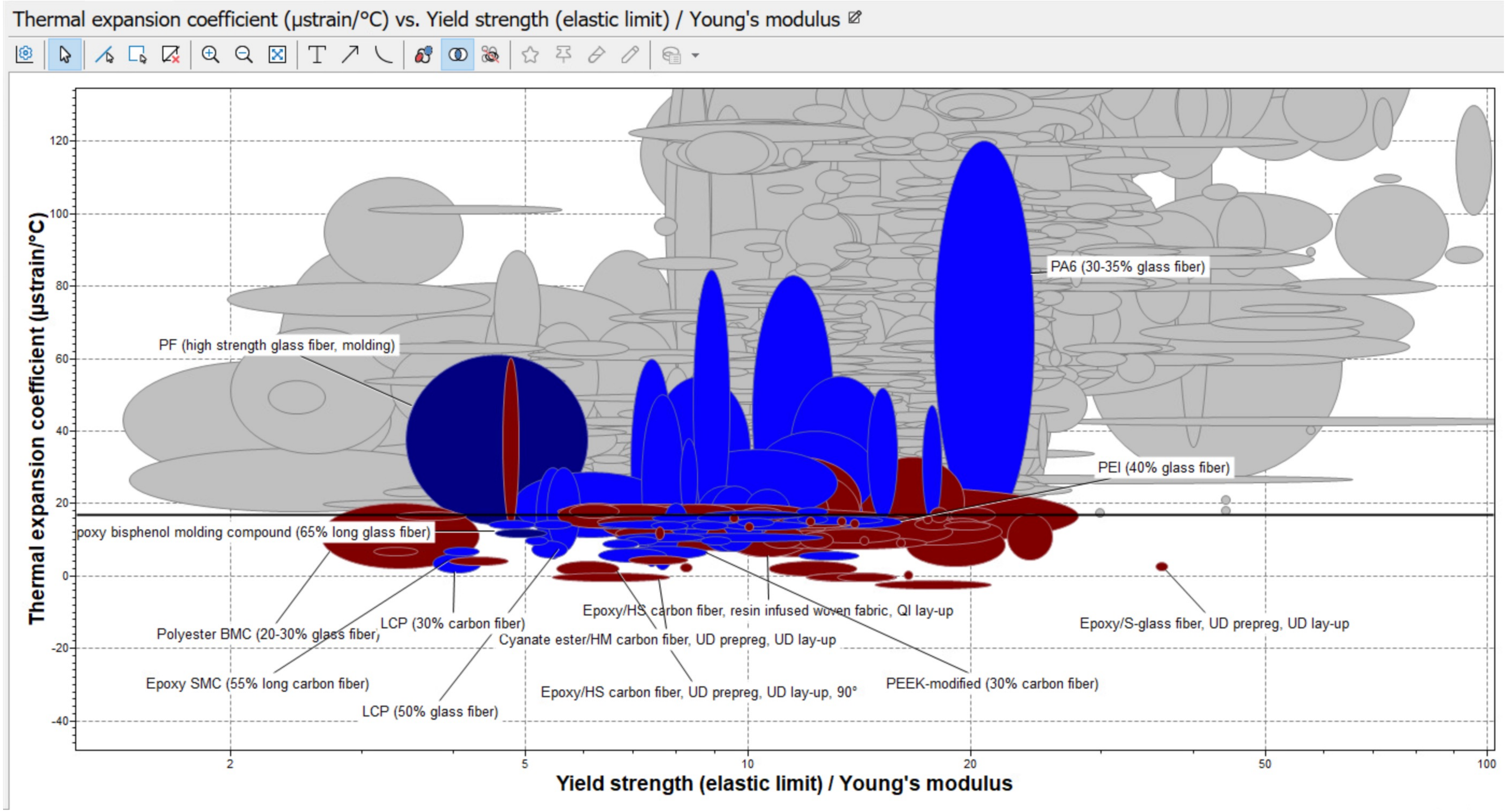
$$\Delta\alpha < \frac{\sigma_Y (1 - 2\vartheta)}{E \cdot \Delta T}$$

$$\boldsymbol{\alpha_{POLIMERO} < k \cdot \frac{\sigma_y}{E} + 17}$$

$k = \frac{1-2\upsilon}{\Delta T}$=0.001

M_1=cost=α_{Cu}


Thermal expansion coefficient (µstrain/°C) vs. Yield strength (elastic limit) / Young's modulus
Thermal expansion coefficient (µstrain/°C)
Yield strength (elastic limit) / Young's modulus
450
400
350
300
250
200
150
100
50
0
1
10
100
1000
10000
100000
M1



Thermal expansion coefficient (µstrain/°C) vs. Yield strength (elastic limit) / Young's modulus
Thermal expansion coefficient (µstrain/°C)
Yield strength (elastic limit) / Young's modulus
120
100
80
60
40
20
0
-20
-40
2
5
10
20
50
100
PA6 (30-35% glass fiber)
PF (high strength glass fiber, molding)
PEI (40% glass fiber)
poxy bisphenol molding compound (65% long glass fiber)
Epoxy/HS carbon fiber, resin infused woven fabric, QI lay-up
Epoxy/S-glass fiber, UD prepreg, UD lay-up
LCP (30% carbon fiber)
Polyester BMC (20-30% glass fiber)
Cyanate ester/HM carbon fiber, UD prepreg, UD lay-up
Epoxy SMC (55% long carbon fiber)
PEEK-modified (30% carbon fiber)
Epoxy/HS carbon fiber, UD prepreg, UD lay-up, 90°
LCP (50% glass fiber)

ANALISI DEI VINCOLI E CURVE DI TRADE-OFF

Dati Epoxy

$Tan\delta > 0.014$

$\varepsilon > 4$ ad 1GHz

f_{max} =4GHz

2. PROPRIETA' ELETTRICHE

La funzione del polimero è quella di isolare elettricamente il substrato metallico

Elevata resistività volumetrica

L'angolo di perdita deve essere tale da non determinare perdite di segnale e dissipazione termic

L' energia termica dissipata è data da:

$P=2\pi f \cdot V^2 \cdot \varepsilon \cdot \tan\delta$ [J]

$c_P \Delta T = H_m$ [J/Kg] → $P_s < H_m$

$P_s = \frac{P}{m}$ [J/Kg]

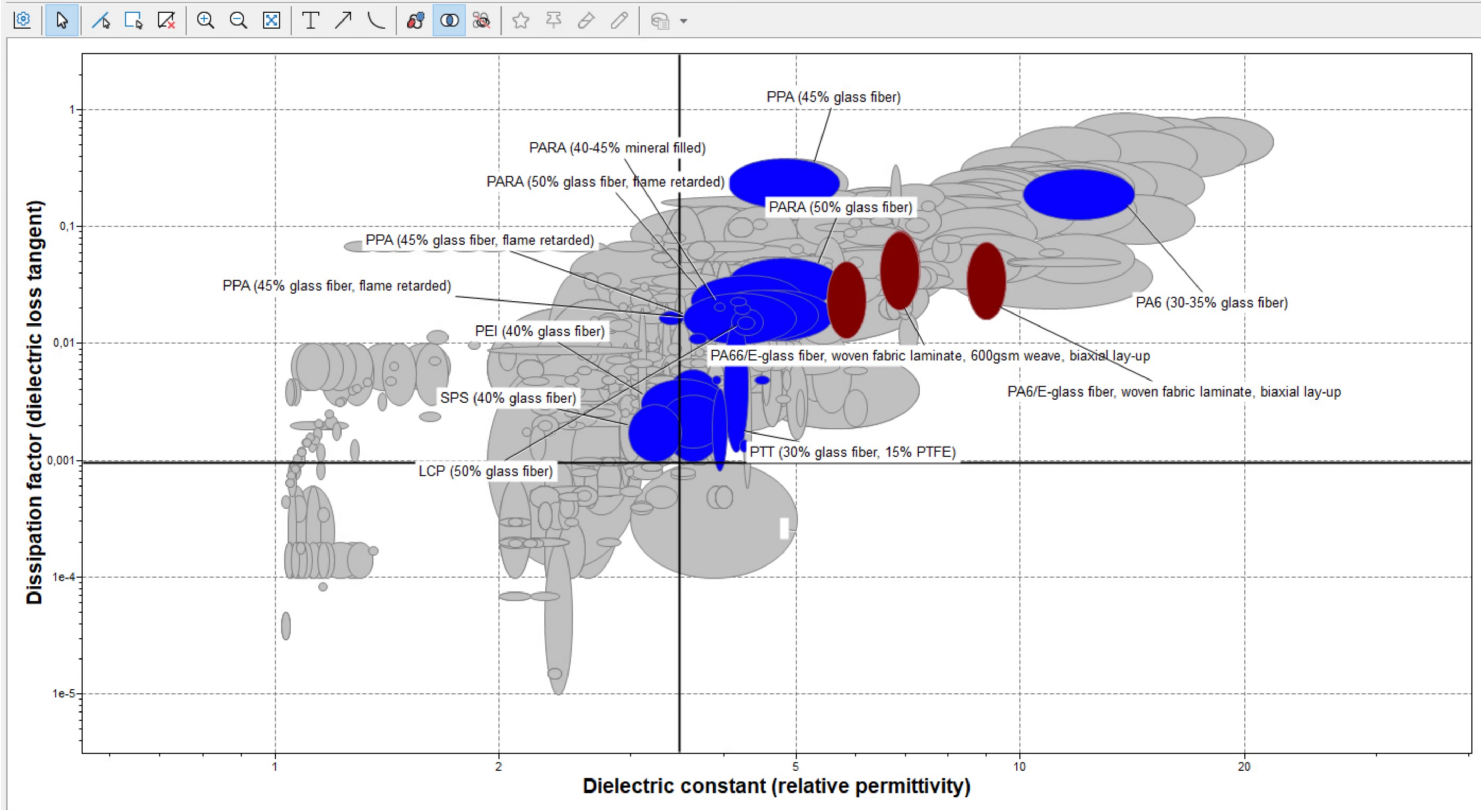
$2\pi f \cdot V^2 \cdot \varepsilon \cdot \tan\delta < m\, c_P \Delta T$

$\varepsilon \cdot \tan\delta < k c_P$

V [V]	10
F [s^-1]	4*10^9
ΔT [°C]	200
M [Kg]	0.02

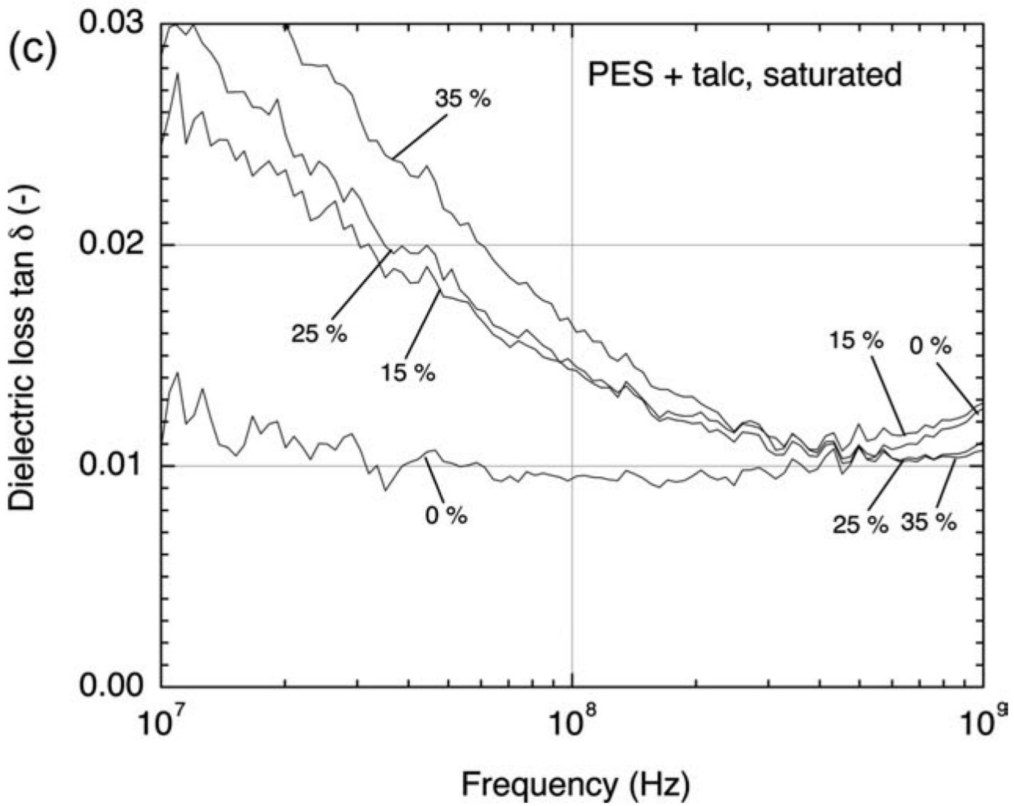
$K=\frac{m * \Delta T}{2\pi f V^2}$

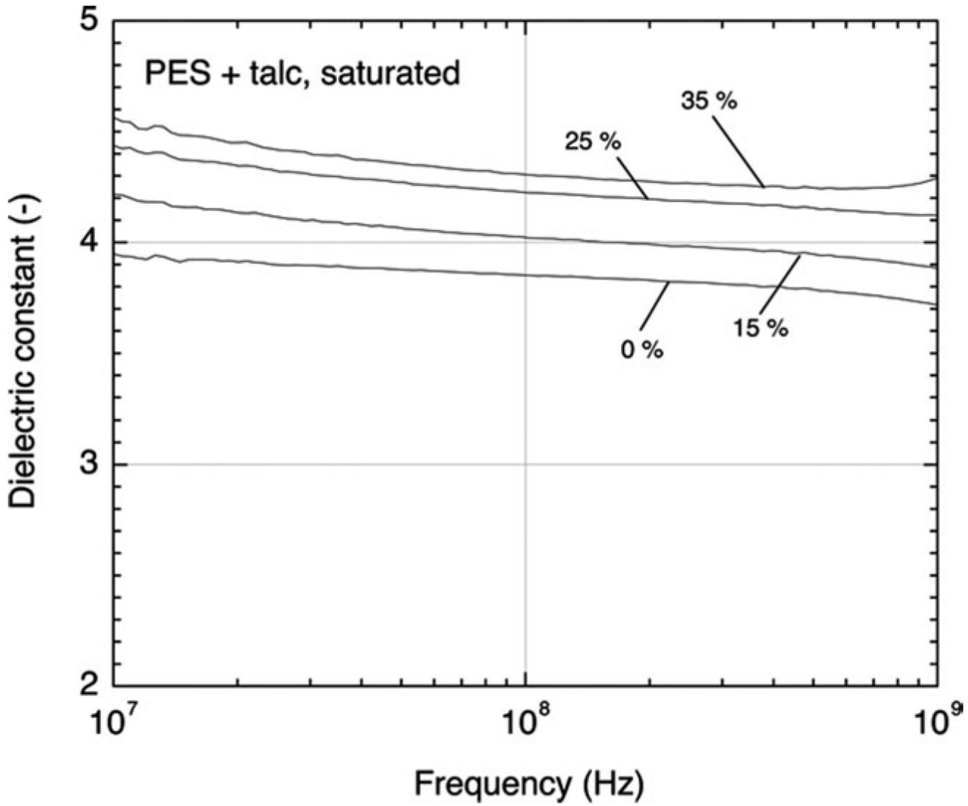
Dissipation factor (dielectric loss tangent) vs. Dielectric constant (relative permittivity)



ANALISI DEI VINCOLI E CURVE DI TRADE-OFF

3. EFFETTO DELL'UMIDITA' SULLE PORPRIETA' ELETTRICHE





OUTPUT FASE#2

- Definizione di Vincoli ed Obiettivi
- Individuazione degli Indici o delle soglie

VINCOLI

PROPRIETA' TERMICHE
XXX
XXX
XXX
PROPRIETA' ELETTIRCHE
XXX
XXX
PROPRIETA' MECCANICHE
XXX
XXX
XXX
PROPRIETA' CHIMICHE
XXX
XXX

OBIETTIVI

- OBIETTIVO#1
- OBIETTIVO#2
- ….

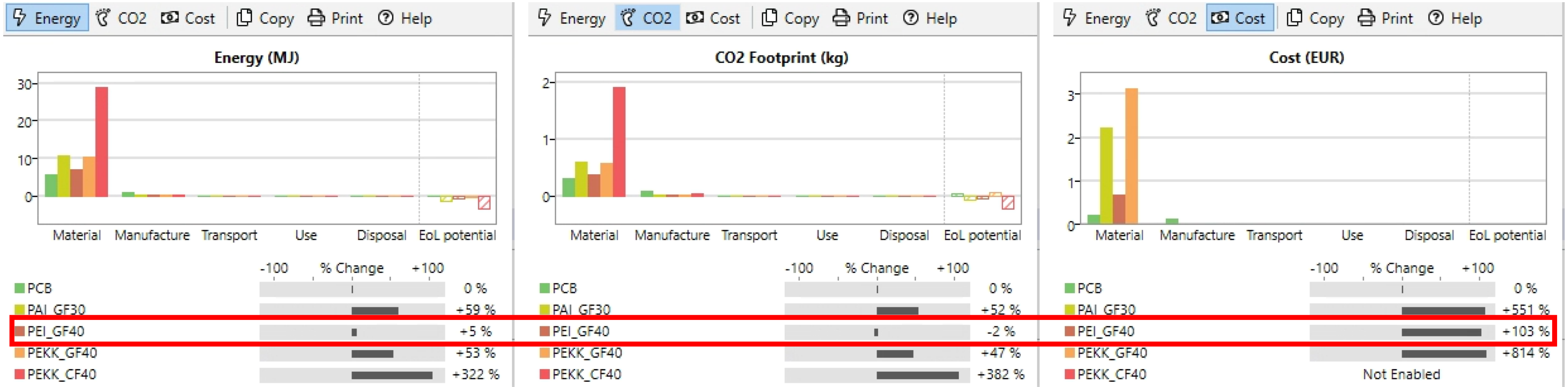
ANALISI DEI VINCOLI

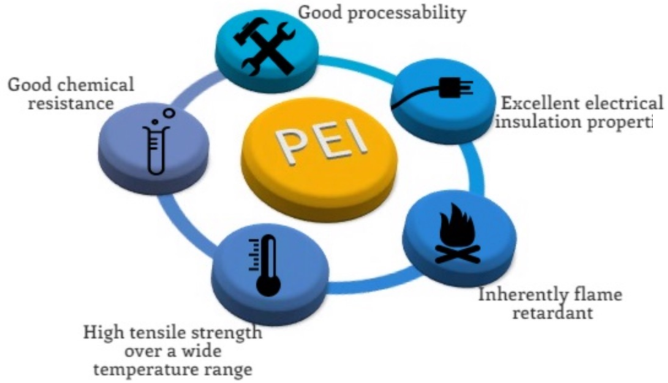
PROPRIETA' TERMICHE

PROPRIETA' MECCANICHE

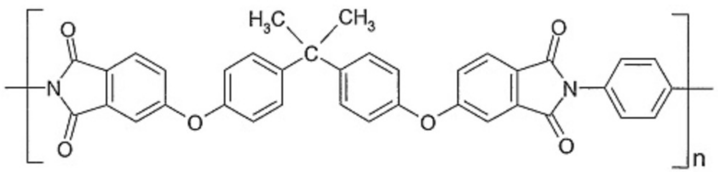
……

FASE #3: ECO-AUDIT





PoliEterImide



Molecular Structure of Polyetherimide (PEI)

This high-performance polymer also exhibits high tensile strength, good flame resistance and low smoke emission making it an ideal material of choice in automotive, **electrical,** medical and other industrial applications.

Principali caratteristiche del PEI

https://omnexus.specialchem.com/selection-guide/polyetherimide-pei-high-heat-plastic

- PEI is an **amorphous thermoplastic** resin with amber transparency
- The resin is characterized by **high deflection temperature** (200°C at 264 psi), high tensile strength and flexural modulus (480,000 psi), and very good **retention of mechanical properties** at elevated temperatures
- It has unique combination of high specific strength, rigidity, flexibility, exceptional dimensional strength etc.
- In addition, the resin exhibits **good electrical properties**, which remain stable over a wide range of temperature and frequencies (including microwave)
- It has good UV-light resistance and weatherability
- PEI is **inherently flame resistance** without the use of additives
- It has a high limiting oxygen index of 47, combined with NBS smoke chamber results which show the lowest specific optical density of any unfilled thermoplastic
- Polyetherimide is resistant to alcohols, acids, and hydrocarbon solvent but dissolves in partially halogenated solvents
- PEI also displays **good hydrolytic stability**
- Most of the PEI grades has a UL94 flame resistance rating of VTM-0, is FDA compliant, EU Food Contact Compliant, and ISO10993 compliant in natural color
- Polyetherimide resin is available in an unreinforced grade for general-purpose processing methods as a transparent resin and in standard and custom colors.

It is also available in:

Four **<u>glass-fiber-reinforced grades</u>** (10, 20, 30, and 40% glass),
- Bearing grades, and
- Several high-temperature grades

Glass reinforcement provides even greater rigidity and dimensional stability while maintaining many of the useful characteristics of basic PEI. The glass reinforcement yields a product with an exception strength-to-weight ratio and increased tensile strength.

Limitations Associated with PEI
- Very high cost. Applicable for highly demanding applications
- Low colorability
- Attacked by polar chlorinated solvents leading to stress cracking
- A long drying before processing is necessary
- Hot mold during injection molding

Applicazioni

- Automotive and Aerospace
- Electrical and Electronic
- Disposable & Reusable Medical Applications
- Metal Replacing for industrial applications & appliances

Electrical and Electronical Market

<u>Electrical / electronic</u> is the second most important market for Polyetherimide. In the telecommunications market, there is an increasing need for high heat resistant materials, especially for high-end connectors in the fiber optics segment. PEI resin offers **<u>high heat resistance</u>** as well as great flow for thin wall design.

• applications of Polyetherimide include:

Electrical switches and controls
•Electrical motor parts
•Printed circuit boards, and
•Connectors

Polyetherimide is also used in so-called **molded interconnect devices (MID)**. This is because of its unique plating capabilities. PEI allows the combination of electrical functions with the advantages of injection molded 3-D mechanical components.

The key trend influencing further use of polyetherimide in electrical / electronic applications is new product development. To meet the ongoing needs for **miniaturization in the electronics sector**, (increased packing densities and more lightweight carrier materials) ceramic-filled polyetherimide grades have been developed. These grades have excellent electrical and processing properties, and can also be easily metalized. They are suitable for applications such as:

- Circuit boards operating in the microwave range as well as internal aerials
- Electronic chips, and
- Capacitors

Ensinger

TECAPEI GF30 natural - Stock Shapes (rods, plates, tubes)

Chemical Designation
PEI (Polyetherimide)

Colour
amber opaque

Density
1.51 g/cm^3

Fillers
glass fibres

Main features
- high dimensional stability
- good heat deflection temperature
- high thermal and mechanical capacity
- high strength
- high creep resistance
- electrically insulating
- resistance against high energy radiation
- sensitive to stress cracking

Target Industries
- electronics
- semiconductor technology
- automotive industry
- mechanical engineering
- vacuum technology

Mechanical properties	parameter	value	unit	norm	
Tensile strength	5mm/min	135	MPa	DIN EN ISO 527-2	
Modulus of elasticity (tensile test)	1mm/min	5300	MPa	DIN EN ISO 527-2	1)
Tensile strength at yield	5mm/min	135	MPa	DIN EN ISO 527-2	
Elongation at yield	5mm/min	4	%	DIN EN ISO 527-2	
Elongation at break	50mm/min	4	%	DIN EN ISO 527-2	
Flexural strength	2mm/min, 10 N	195	MPa	DIN EN ISO 178	2)
Modulus of elasticity (flexural test)	2mm/min, 10 N	5500	MPa	DIN EN ISO 178	
Compression strength	1% / 2% 5mm/min, 10 N	18 / 39	MPa	EN ISO 604	3)
Compression modulus	5mm/min, 10 N	4200	MPa	EN ISO 604	4)
Impact strength (Charpy)	max. 7,5J	51	kJ/m^2	DIN EN ISO 179-1eU	5)
Notched impact strength (Charpy)	max. 2J	6	kJ/m^2	DIN EN ISO 179-1eA	
Ball indentation hardness		325	MPa	ISO 2039-1	6)

comment

(1) For tensile test: specimen type 1b
(2) For flexural test: support span 64mm, norm specimen.
(3) Specimen 10x10x10mm
(4) Specimen 10x10x50mm, modulus range between 0.5 and 1% compression.
(5) For Charpy test: support span 64mm, norm specimen.
(6) Specimen in 4mm thickness

Thermal properties	parameter	value	unit	norm		comment
Glass transition temperature		213	°C	DIN EN ISO 11357		(1) Found in public sources. Individual testing regarding application conditions is mandatory.
Melting temperature			°C	DIN EN ISO 11357		
Service temperature	short term	200	°C		1)	
Service temperature	long term	170	°C			
Thermal expansion (CLTE)	23-60°C, long.	3	10^{-5} K^{-1}	DIN EN ISO 11359-1;2		
Thermal expansion (CLTE)	23-100°C, long.	3	10^{-5} K^{-1}	DIN EN ISO 11359-1;2		
Thermal expansion (CLTE)	100-150°C, long.	4	10^{-5} K^{-1}	DIN EN ISO 11359-1;2		

Electrical properties	parameter	value	unit	norm		comment
surface resistivity		10^{14}	Ω	DIN IEC 60093		
volume resistivity		10^{14}	Ω*cm	DIN IEC 60093		

Other properties	parameter	value	unit	norm		comment
Water absorption	24h / 96h (23°C)	0.04 / <0.1	%	DIN EN ISO 62	1)	(1) Ø ca. 50mm, h=13mm (2) + good resistance (3) - poor resistance (4) Corresponding means no listing at UL (yellow card). The information might be taken from resin, stock shape or estimation. Individual testing regarding application conditions is mandatory.
Resistance to hot water/ bases		+		-	2)	
Resistance to weathering		-		-	3)	
Flammability (UL94)	corresponding to	V0		DIN IEC 60695-11-10;	4)	

Polymer Resources

Classic® Engineering Plastic Compounds

Friday, December 4, 2020

PRL PEI-G40

Polymer Resources Ltd. - *Polyether Imide*

Units English

Action | **Legend (Open)**

General Information

General		
Material Status	• Commercial: Active	
Availability	• North America	
Filler / Reinforcement	• Glass Fiber, 40% Filler by Weight	
Additive	• Flame Retardant	
Features	• Flame Retardant	• High Heat Resistance
RoHS Compliance	• RoHS Compliant	
UL File Number	• E113219	
Forms	• Pellets	
Processing Method	• Injection Molding	

ASTM & ISO Properties [1]

Physical	Nominal Value	Unit	Test Method
Density / Specific Gravity	1.60		ASTM D792
Melt Mass-Flow Rate (MFR) (337°C/6.6 kg)	3.0 to 18	g/10 min	ASTM D1238
Molding Shrinkage - Flow (0.125 in)	1.0E-3 to 3.0E-3	in/in	ASTM D955
Water Absorption (24 hr)	0.13	%	ASTM D570
Water Absorption (Equilibrium, 73°F)	0.90	%	ASTM D570
Mechanical	**Nominal Value**	**Unit**	**Test Method**
Tensile Modulus (0.125 in)	1.69E+6	psi	ASTM D638
Tensile Strength (Yield, 0.125 in)	25600	psi	ASTM D638
Tensile Strength (Break, 0.125 in)	25600	psi	ASTM D638
Tensile Elongation (Break, 0.125 in)	2.5	%	ASTM D638
Flexural Modulus (0.125 in)	1.69E+6	psi	ASTM D790
Flexural Strength (0.125 in)	34000	psi	ASTM D790
Impact	**Nominal Value**	**Unit**	**Test Method**
Notched Izod Impact (0.125 in)	1.8	ft·lb/in	ASTM D256
Unnotched Izod Impact (73°F, 0.125 in)	8.0	ft·lb/in	ASTM D4812
Reverse Notch Izod Impact (73°F, 0.125 in)	9.0	ft·lb/in	ASTM D256
Hardness	**Nominal Value**	**Unit**	**Test Method**
Rockwell Hardness (M-Scale)	114		ASTM D785
Thermal	**Nominal Value**	**Unit**	**Test Method**
Deflection Temperature Under Load (66 psi, Unannealed, 0.125 in)	418	°F	ASTM D648
Deflection Temperature Under Load (264 psi, Unannealed, 0.125 in)	413	°F	ASTM D648
Vicat Softening Temperature	450	°F	ASTM D1525 [2]
CLTE - Flow (-4 to 302°F)	8.0E-6	in/in/°F	ASTM E831
RTI Elec			UL 746
0.06 in	221	°F	
0.12 in	221	°F	
RTI Imp			UL 746
0.06 in	221	°F	
0.12 in	221	°F	
RTI Str			UL 746
0.06 in	221	°F	
0.12 in	221	°F	

Electrical	Nominal Value	Unit	Test Method
Volume Resistivity	1.5E+16	ohms·cm	ASTM D257
Dielectric Strength (0.0625 in, in Oil)	600	V/mil	ASTM D149
Dielectric Constant (1 kHz)	3.70		ASTM D150
Dissipation Factor (1 kHz)	2.0E-3		ASTM D150
Flammability	**Nominal Value**	**Unit**	**Test Method**
Flame Rating			UL 94
0.06 in	V-0		
0.12 in	V-0		

Processing Information

Injection	Nominal Value	Unit
Drying Temperature	290 to 300	°F
Drying Time	4.0 to 6.0	hr
Drying Time, Maximum	8.0	hr
Rear Temperature	630 to 750	°F
Middle Temperature	640 to 750	°F
Front Temperature	650 to 750	°F
Processing (Melt) Temp	640 to 750	°F
Mold Temperature	225 to 350	°F

Notes

[1] Typical properties: these are not to be construed as specifications.

[2] Rate B (120°C/h), Loading 2 (50 N)

Esempio di scelta delle materie prime

Ensinger: azienda europea, fornisce già il prodotto stampato (plates)

PRL-PEIG40: azienda Nord-America fornisce il pellet che va estruso o stampato

Conclusioni:

- ❖ I primi risultati della FASE#3 possono non essere soddisfacenti
- ❖ Può essere pertanto necessario reiterare il processo di selezione fino ad arrivare ad un risultato soddisfacente
- ❖ La selezione parte dalla definizione dei vincoli e degli obiettivi: l’analisi approfondita dei vincoli rappresenta la parte essenziale del processo di selezione
- ❖ L’Analisi di EcoAudit, per prodotti che non hanno una funzionalità specifica (ad esempio non prevedono il consumo di corrente elettrica), si concentra sull’impatto delle materie prime, trasporto e processo di produzione.
- ❖ Un’analisi accurata delle materie prime può potenzialmente modificare l’output dell’EcoAudit.