Trattamenti superficiali delle fibre (apprettatura)

- Aumentare la bagnabilità della fibra rispetto alla matrice
- Creare un legame forte all’interfaccia fibra-matrice
- Aumentare l’efficienza di trasferimento degli sforzi dalla matrice alla fibra

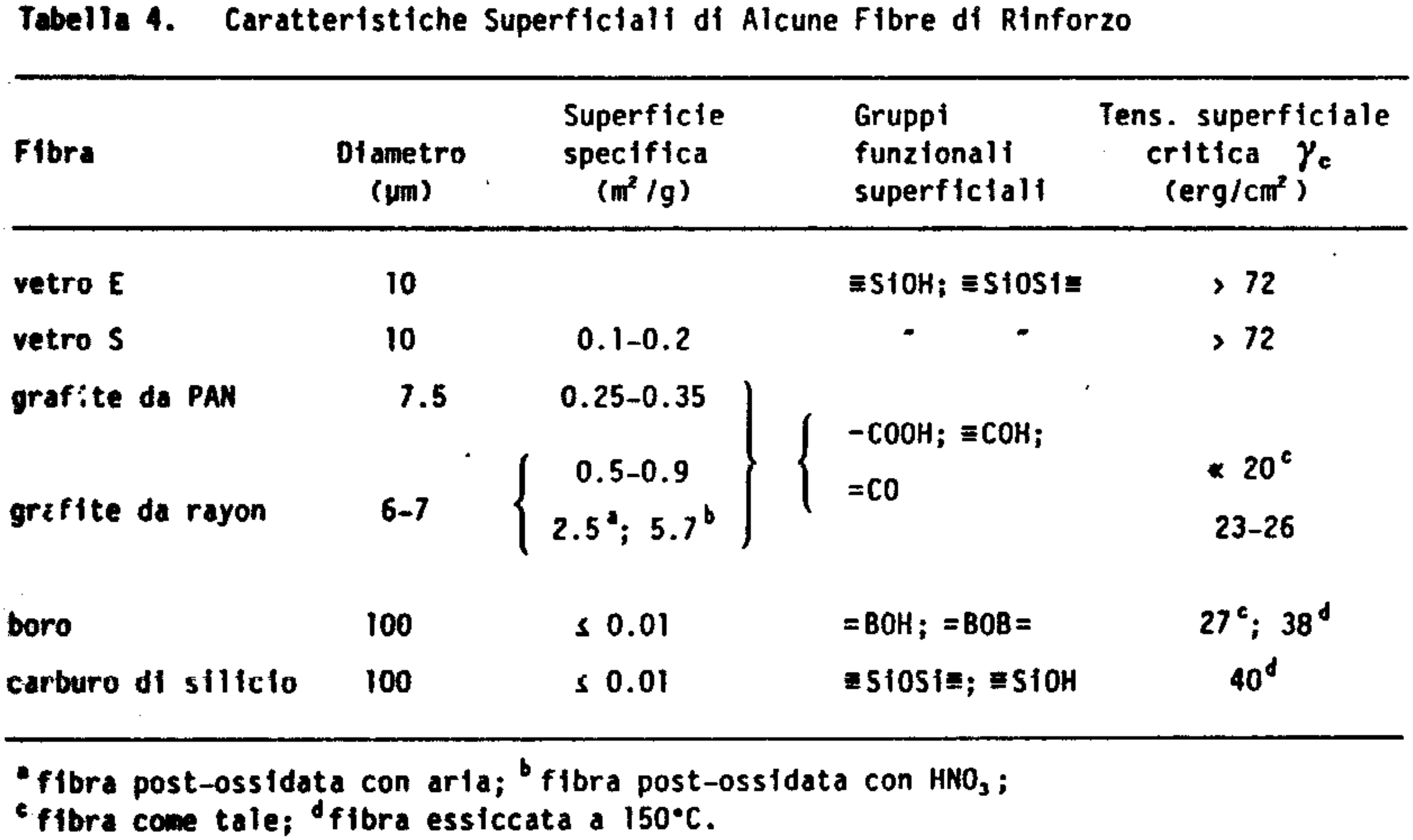

Tabella 4. Caratteristiche Superficiali di Alcune Fibre di Rinforzo

Fibra	Diametro (μm)	Superficie specifica (m^2/g)	Gruppi funzionali superficiali	Tens. superficiale critica γ_c (erg/cm^2)
vetro E	10		≡SiOH; ≡SiOSi≡	> 72
vetro S	10	0.1–0.2	" "	> 72
grafite da PAN	7.5	0.25–0.35	–COOH; ≡COH; =CO	≪ 20^c
grafite da rayon	6–7	0.5–0.9 2.5^a; 5.7^b		23–26
boro	100	≤ 0.01	=BOH; =BOB=	27^c; 38^d
carburo di silicio	100	≤ 0.01	≡SiOSi≡; ≡SiOH	40^d

[a] fibra post-ossidata con aria; [b] fibra post-ossidata con HNO_3;
[c] fibra come tale; [d] fibra essiccata a 150°C.

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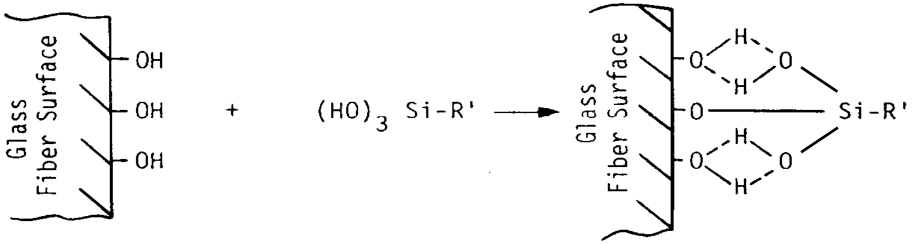
Trattamenti superficiali delle fibre di vetro

Impiego di agenti di accoppiamento (*coupling agents*)

- ☆ Aumentare la resistenza all'interfaccia fibra-matrice attraverso legami chimico-fisici
- 🕐 Proteggere la superficie della fibra da umidità e fluidi reattivi

Trattamento con *organosilani* in soluzione acquosa

$$R'\text{-}Si(OR)_3 + 3\,H_2O \rightarrow R'\text{-}Si(OH)_3 + 3\,ROH$$



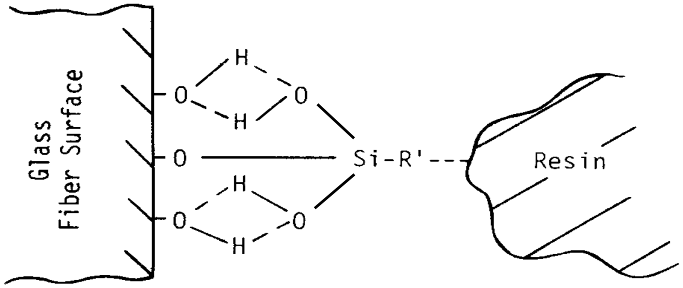


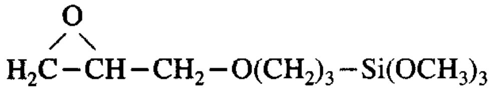
Table 2.13 Recommended Silane Coupling Agents for Glass Fiber-Reinforced Thermoset Polymers

With epoxy matrix:

1. γ-Aminopropyltriethoxysilane

   $H_2N-(CH_2)_3-Si(OC_2H_5)_3$

2. γ-Glycidyloxypropyltrimethoxysilane



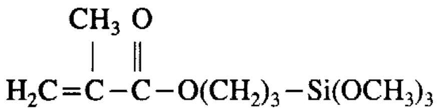
   $$\overset{O}{H_2C-CH}-CH_2-O(CH_2)_3-Si(OCH_3)_3$$

3. *N*-β-Aminoethyl-γ-aminopropyltrimethoxysilane

   $H_2N-CH_2-CH_2-NH-(CH_2)_3-Si(OCH_3)_3$

With polyester and vinyl ester matrix:

1. γ-Methacryloxypropyltrimethoxysilane



   $$H_2C=\overset{CH_3}{\overset{|}{C}}-\overset{O}{\overset{\|}{C}}-O(CH_2)_3-Si(OCH_3)_3$$

2. Vinyl triethoxysilane

   $H_2C=CH-Si(OC_2H_5)_3$

3. Vinyl tris(β-methoxyethoxy)silane

   $H_2C=CH-Si(OCH_2-CH_2-O-CH_3)_3$

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Trattamenti superficiali delle fibre di carbonio

Superficie chimicamente inattiva. Sono necessari trattamenti per

- ☆ Formare gruppi funzionali superficiali capaci di legarsi chimicamente alla matrice
- 🕐 Aumentare l'area superficiale (creazione di micropori o cavitazioni)

Trattamenti ossidativi con formazione di gruppi superficiali acidi (gruppi carbossilici, fenolici, idrossilici)

❶ In fase gassosa con gas contenenti ossigeno (aria, O_2, CO_2, O_3, ecc.) a $T \geq 250°C$ e in presenza di catalizzatori

❷ In fase liquida (HNO_3, NaClO, ecc.)

Trattamenti non-ossidativi con ricoprimento della fibra con un polimero organico avente gruppi funzionali capaci di legarsi chimicamente alla matrice.

❶ Copolimeri stirene-anidride maleica

❷ Copolimeri metilacrilato-acrilonitrile

❸ Poliammidi

Deposizione per elettropolimerizzazione (le fibre di carbonio rappresentano uno degli elettrodi, immersi in una soluzione acida di monomeri

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Surface treatments of carbon fibers

Anodic oxidation

Almost all CFs produced are used as reinforcements for resin matrix composite materials. These have therefore been treated by anodic oxidation to improve their adhesion with the resin matrix, following carbonization or high-temperature treatment because anodic oxidation has advantages over other oxidation techniques in rate, uniformity, and controllability of the degree of oxidation. Although a number of electrolytes could be used for the anodic oxidation, alkaline electrolytes, for example, sodium hydroxide and ammonium bicarbonate, are recommended to be used because the degradation products formed on the fiber surface dissolve in an alkaline aqueous solution leaving no residues, which simplifies the fiber washing, unlike in acidic solution. In acidic solution, the degradation products remain as residues on the fiber surface, without dispersing or dissolving into the solution.

Plasma treatment

*In addition to anodic oxidation, there are many methods available to alter the surface chemistry of CFs in an attempt to promote chemical bonding between the fiber and resin in composite materials. Among them, **plasma treatment** is noticeable from the point of view of treatment time as short as 15-30 s, which is very close to that needed for anodic oxidation treatment, and for being usable to introduce amine groups onto CF surfaces.*

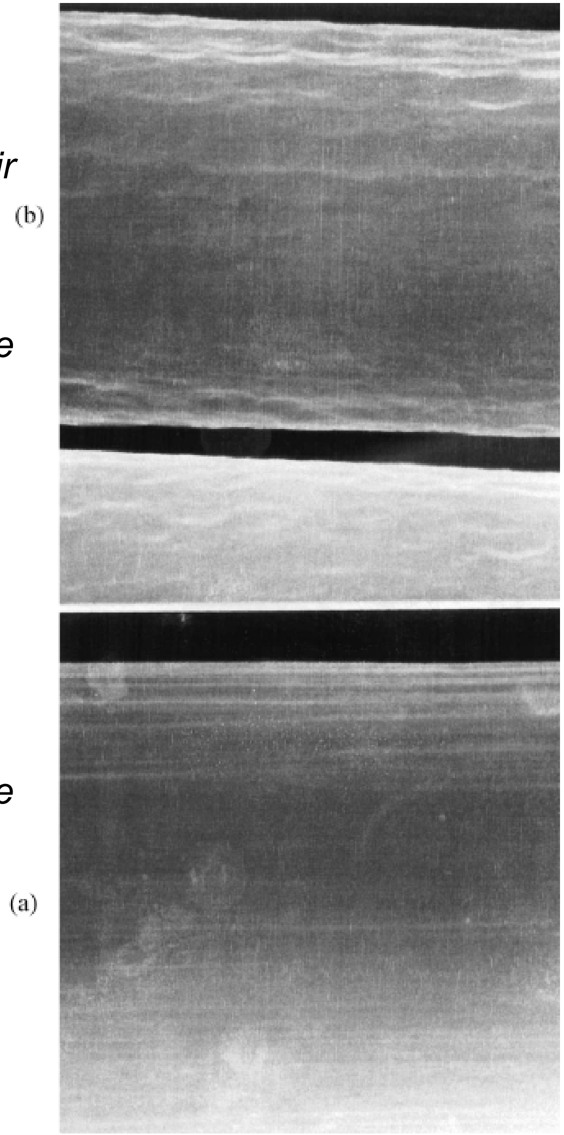

Figure 7 Surface of Besfight HT anodically oxidized in sulfuric acid solution. (a) Washed with water. (b) Washed with alkaline solution and then with water (after Shindo, 1983).

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Trattamenti superficiali delle fibre di Kevlar 49

Analoghe alle fibre di carbonio

➊ *Filament surface oxidation* o *plasma etching*: riduce la resistenza a trazione ma migliora la resistenza trasversale (*off-axis*) del composito (dipende dall'adesione interfacciale fibra-matrice.

➋ Formazione di gruppi reattivi (amminazione superficiale con plasma di NH_3, formazione di gruppi $-NH_2$) sulla superficie della fibra

Effetto dei trattamenti superficiali sulle proprietà meccaniche dei materiali compositi

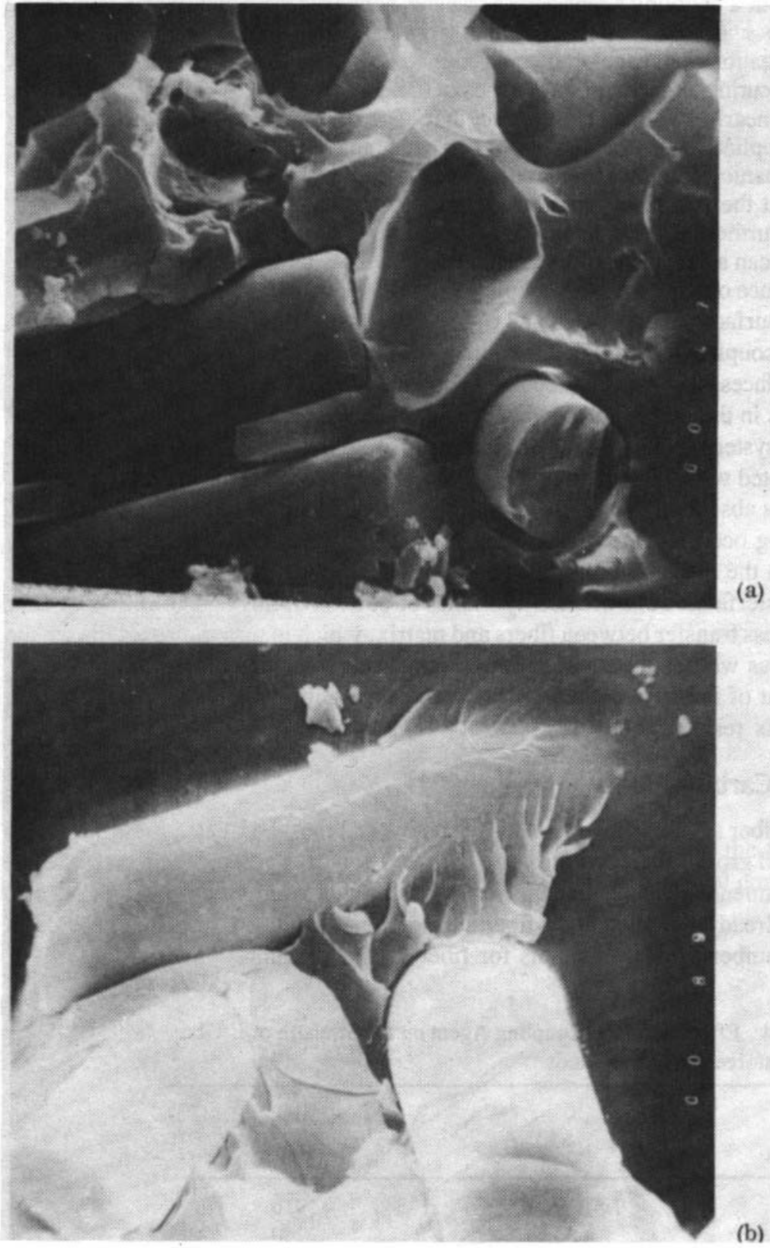

Figure 2.33 Photomicrographs of fracture surfaces of E-glass-epoxy composites demonstrating (a) poor adhesion with an incompatible silane coupling agent, and (b) good adhesion with a compatible silane coupling agent.

Tabella 6. Carico di Rottura di Taglio Longitudinale di Compositi a Matrice Epossidica e con Rinforzo Unidirezionale di Fibre.

Fibra	Trattamento superficiale	Contenuto di fibre (% in vol.)	Carico di rottura di taglio (MPa)	
			immediato	dopo ebollizione in acqua (2 h)
vetro E	nessuno	60	91	17.5
vetro E	amminosilano	62	101	94
boro	nessuno	70	56	27
boro	CH_3OH bollente	72	67	65
carburo di silicio	nessuno	71	37	16.5
carburo di silicio	ossidazione + amminosilano	65	102	-
grafite	nessuno	50	29	27.5
grafite	HNO_3	43	52	48

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Incorporazione delle fibre nella matrice

➊ Incorporazione della fibra nella matrice per formare direttamente il manufatto finale

Hand lay-up
Spray-up
Filament winding
Pultrusion

➋ Incorporazione della fibra nella matrice per preparare fogli pronti per lo stampaggio (*ready-to-mold sheets*) che possono essere stoccati ed utilizzati in un secondo momento per formare strutture laminate

Stampaggio in autoclave
Stampaggio per compressione

Produzione di PRE-IMPREGNATI (*prepregs*)
Produzione di *Sheet Molding Compounds* (SMC), *Bulk Molding Compounds* (BMC)

Prepregs

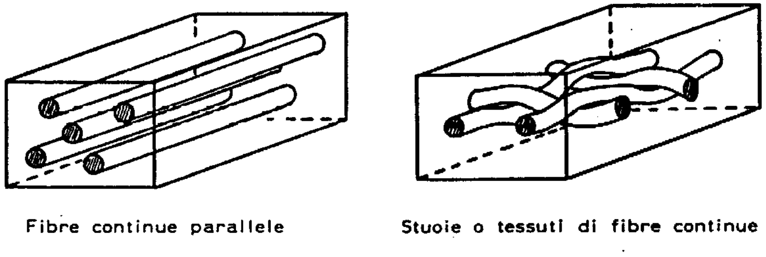
Nastri o strisce di fibre continue unidirezionali o tessute impregnate di resine (in genere resina epossidica).

Regolazione della viscosità attraverso una scelta calibrata dei reagenti e/o un avanzamento controllato della polimerizzazione fino ad un limite di moderata appiccicosità e fluidità (*B-stage*).

Fabbricazione di laminati piani o curvi

- sovrapposizione di più strati a diversa orientazione reciproca
- compattazione per compressione meccanica o pneumatica
- indurimento

Larghezza: 25-500 mm
Spessore*: 0.10-0.25 mm
Resina: 30-45% wt
** dopo indurimento*


Fibre continue parallele
Stuoie o tessuti di fibre continue

Morfologia interna di prepregs

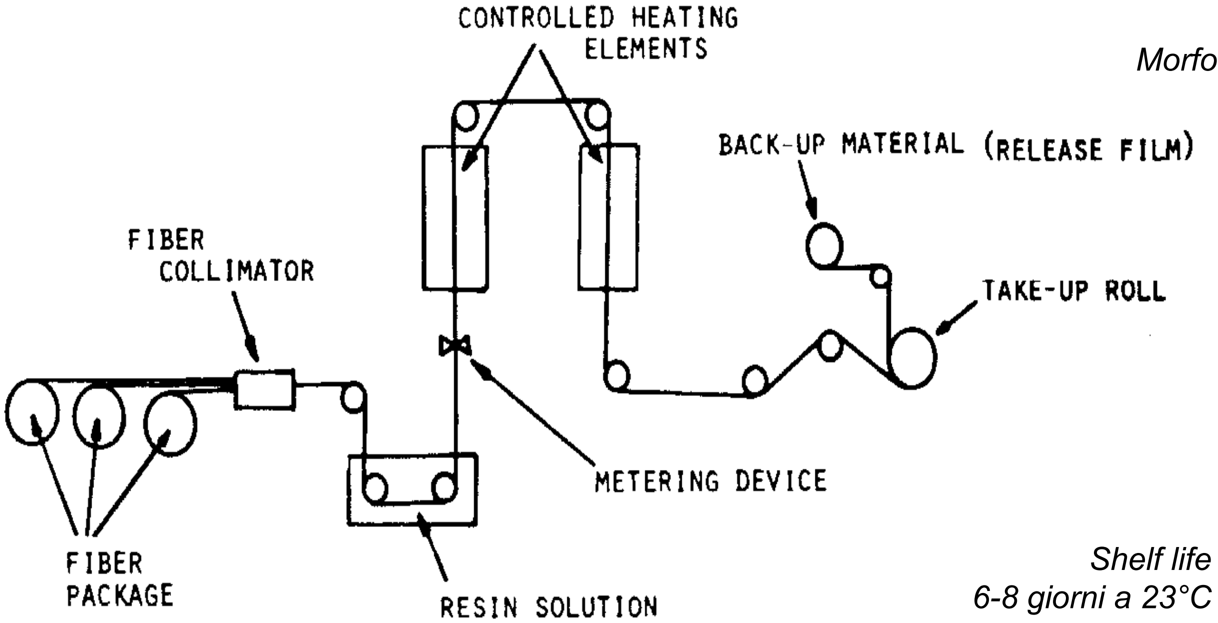


Figure 2.34 Schematic of prepreg manufacturing.

Shelf life
6-8 giorni a 23°C
6 mesi a -18°C

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Prepregs

The precursor necessary for any lay-up operation is known as “prepreg” (contraction of “preimpregnated materials). Prepreg consists of combined unidirectional fibers or woven fabrics with a resin matrix to produce a uniform lamina structure.

Prepregs can be prepared with either thermoplastic or thermosetting matrices. The advantage of thermosets lies in their low molecular weight and low glass transition temperature prior to reaction. These enable thermosetting composites to conform to different shapes easily (**drape**) and to allow stacks of plies to stick together (**tack**).

Main processes:

- solution-dip impregnation
- hot-melt impregnation

Carbon fiber prepreg

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Prepregs

Prepregging by **solution-dip impregnation**

In the solution-dip process, low viscosities are obtained by the addition of solvent to the polymeric resin prior to impregnation

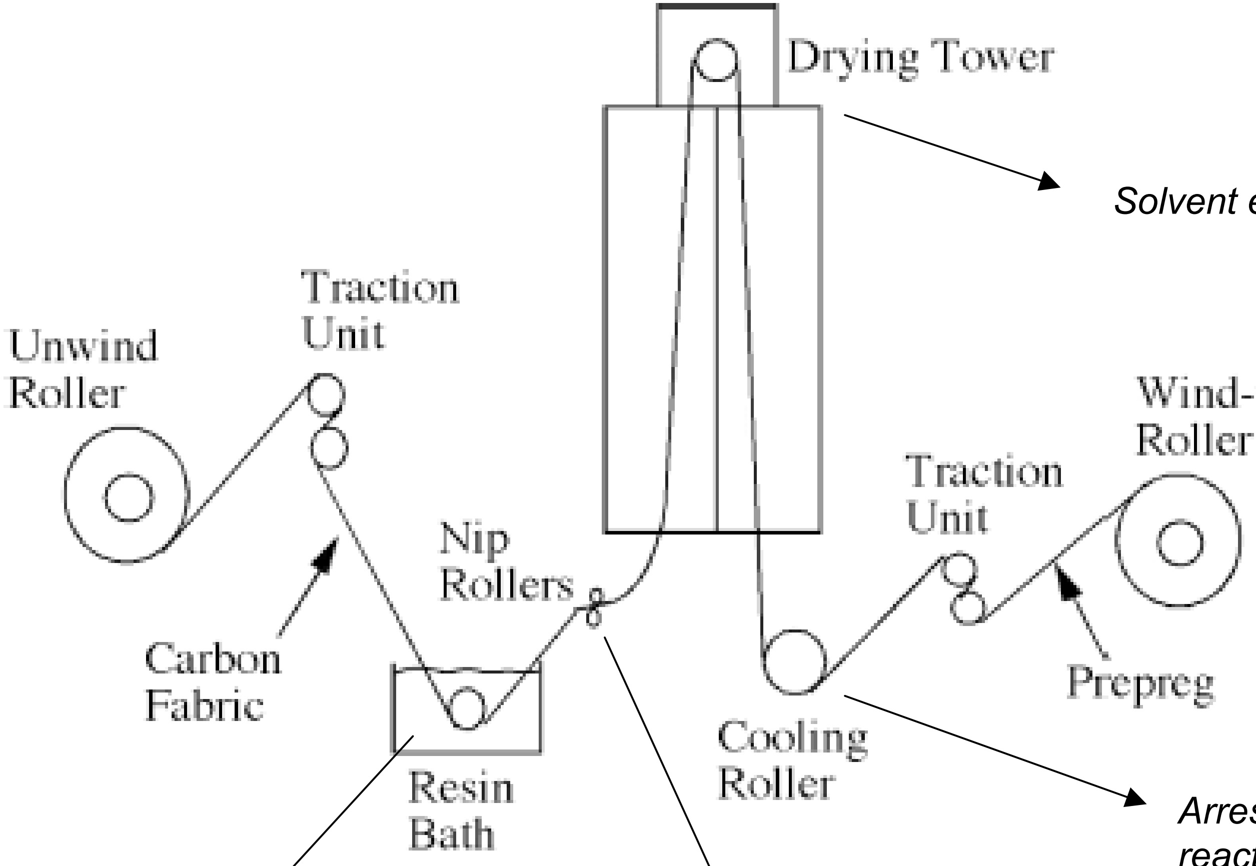

Figure 7 Schematic of a solution-dip prepregging process.

Solvent elimination

The prepreg is combined with a fresh backing film which is usually made out of a thermoplastic (PE or PP)

Arrest of resin flow and of chemical reaction of the resin matrix.

The viscosity of the solution is adjusted by monitoring both temperature and solvent content.

Control of the resin content and prepreg thickness

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Prepregs

Prepregging by **hot-melt impregnation**

The prepregging process can be divided into three areas:

- preimpregnation zone (fibers are aligned and the resin filmed, either on-line or separately);
- impregnation zone *per se* (the resin is forced into the fiber bed)
- postimpregnation zone (the product is treated for storage and handling)

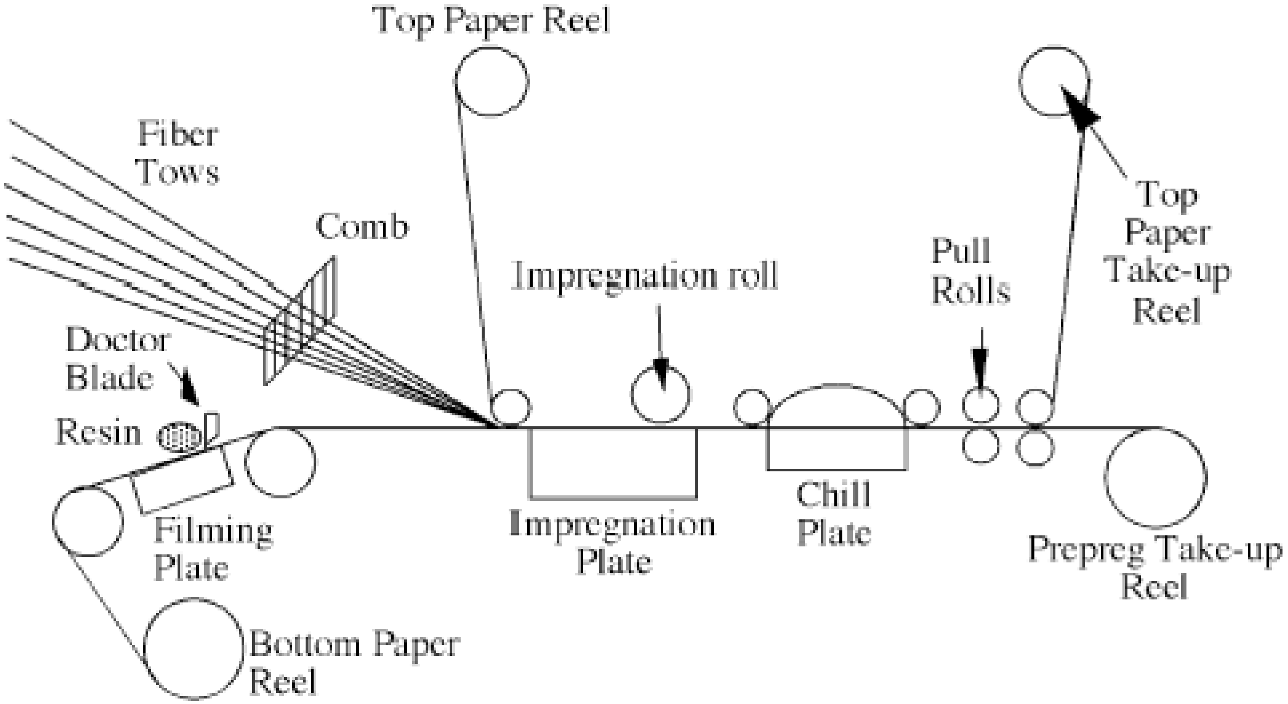

Figure 8 Schematic of a hot-melt film-impregnation prepregging process using doctor blades.

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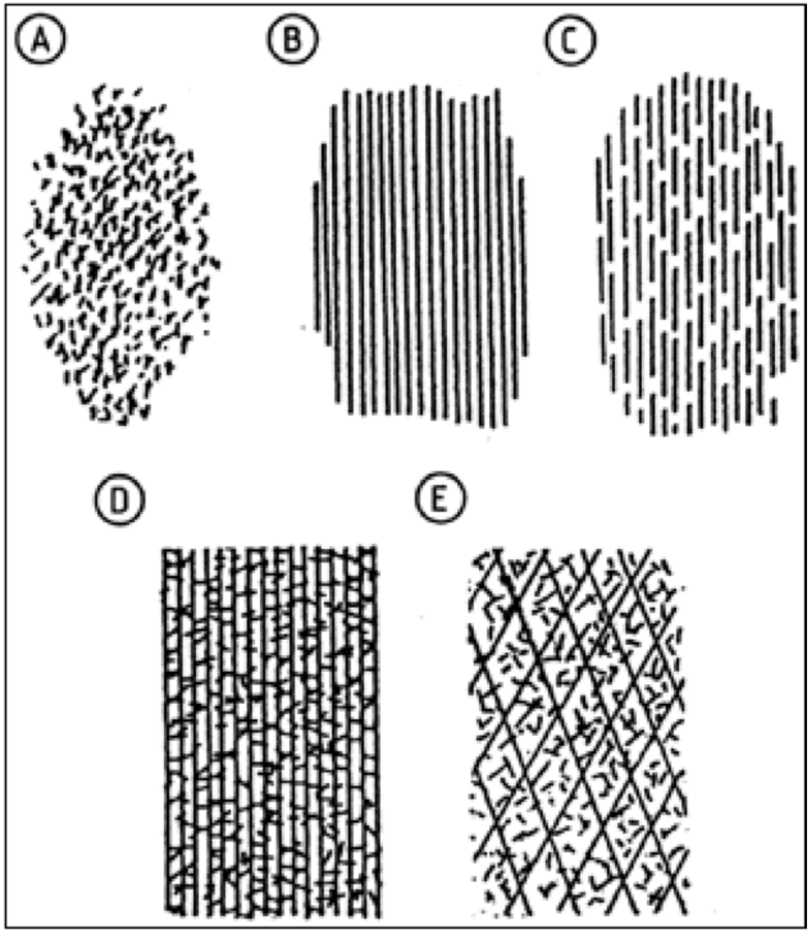
Sheet Molding Compounds (SMC)

Sottili fogli o lastre di fibre premiscelate con una resina termoindurente (in genere resine poliestere insature o vinilestere)

- **SMC-R**: contengono fibre discontinue distribuite in modo casuale (random)
  SMC-R30 → Contenuto di fibra del 30% wt
- **SMC-CR**: contengono uno strato di fibre continue unidirezionali sopra ad uno strato di fibre discontinue distribuite in modo casuale (SMC-C40 R30 → Contenuto di fibra continua del 40% wt e di fibra discontinua del 30% wt)



- **XMC**: contengono fibre continue incrociate (angolo 5-7°) ed eventualmente uno strato inferiore di fibre discontinue distribuite in modo casuale

Fiber reinforcement structures of various sheet molding compounds
A) SMC-R
B) SMC-C
C) SMC-O
D) SMC-CR
E) XMC

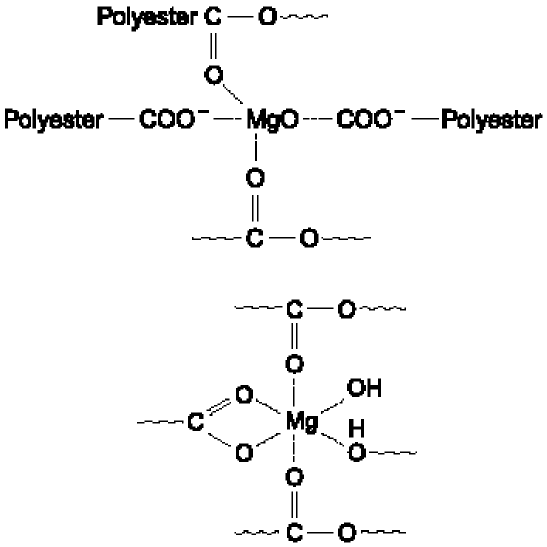
Sheet Molding Compounds (SMC)

Composizione

Table 2.16 Typical Formulation of SMC-R30

Material	Weight %	
Resin paste		70%
Unsaturated polyester	10.50	
Low shrink additive	3.45	
Styrene monomer	13.40	
	27.35	
Filler ($CaCO_3$)	40.70	
Thickener (MgO)	0.70	
Initiator (TBPB)	0.25	
Lubricant (zinc stearate)	1.00	
	42.65	
Inhibitor (benzoquinone)	Trace amount < 0.005 g	
Glass fiber (25.4 mm, chopped)		30%
Total		100%

Thickener (MgO) effects:



Filler ($CaCO_3$) functions:

- *Reduce cost*
- *Increases modulus*
- *Reduce mold shrinkage*
- *Control viscosity*
- *Produce smother surface*

Table 2.15 Properties of Calcium Carbonate-Filled Polyester Resin

Property	Unfilled polyester	Polyester filled with 30 phr $CaCO_3$
Density, g/ml	1.30	1.48
HDT, °C (°F)	79 (174)	83 (181)
Flexural strength, MPa (psi)	121 (17,600)	62 (9000)
Flexural modulus, GPa (10^6 psi)	4.34 (0.63)	7.1 (1.03)

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Sheet Molding Compounds (SMC)
Fabbricazione

Al termine della produzione i fogli SMC vengono sottoposti a processo di "maturazione" (inspessimento o aumento della viscosità) a 30°C per 1-7 giorni. I fogli SMC "maturi" possono essere immediatamente stampati oppure stoccati alla temperatura di –18°C

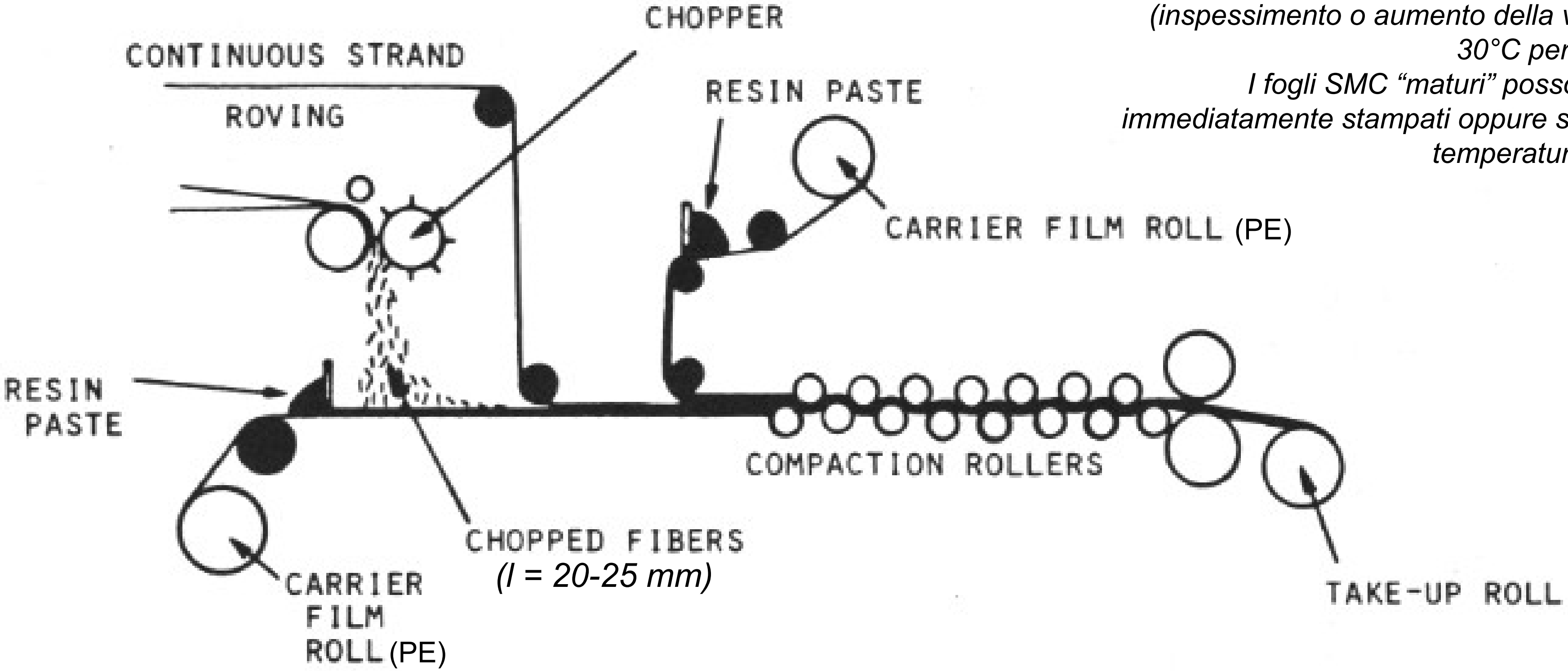

Figure 2.36 Schematic of a sheet molding compounding operation.

Nota: XMC preparati per filament winding

Incorporation of fiber into thermoplastic resins

Problem: incorporating fibers into high-viscosity thermoplastic resins and achieving a good fiber wetout are much more harder than those in low-viscosity thermosetting resins

Advantages: unlimited storing period

***Solution impregnation**: used for polymers that can be dissolved in solvent (typically amorphous polymers*

***Liquid impregnation**: coating of fibers with low molecular weight monomers or prepolymers (precursors)*

***Film stacking**: film stacking is used with woven fabrics or random fiber mats which are interleaved between sheets of unreinforced thermoplastic resins; prepregged sheets are obtained by using heat and pressure*

***Fiber mixing**: intimate mixing of thermoplastic filaments with reinforcing fibers*

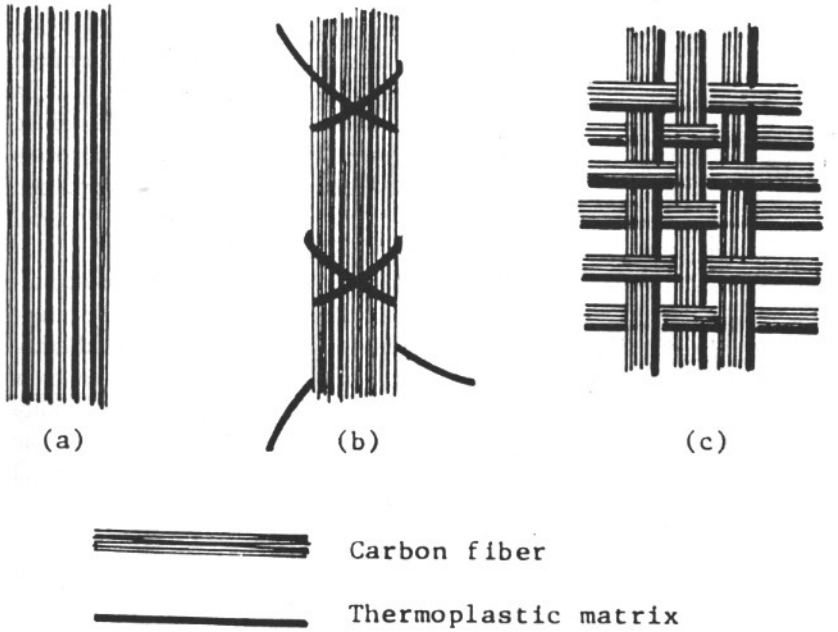

Figure 2.38 (a) Commingled, (b) wrapped and (c) coweaved fiber arrangements.

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Incorporation of fiber into thermoplastic resins

Hot-melt impregnation*: mainly used for semicrystalline thermoplastics (PEEK, PPS) for which there are no suitable solvents available for solution impregnation*

For good and uniform polymer coating on filaments, the resin melt viscosity should be as low as possible. On the other hand, high temperatures (low viscosity) may cause polymer degradation.

Hot-melt impregnated prepregs tend to be stiff and tack free (no stickiness) with problems in draping the mold surface and sticking the prepreg layers to each other.

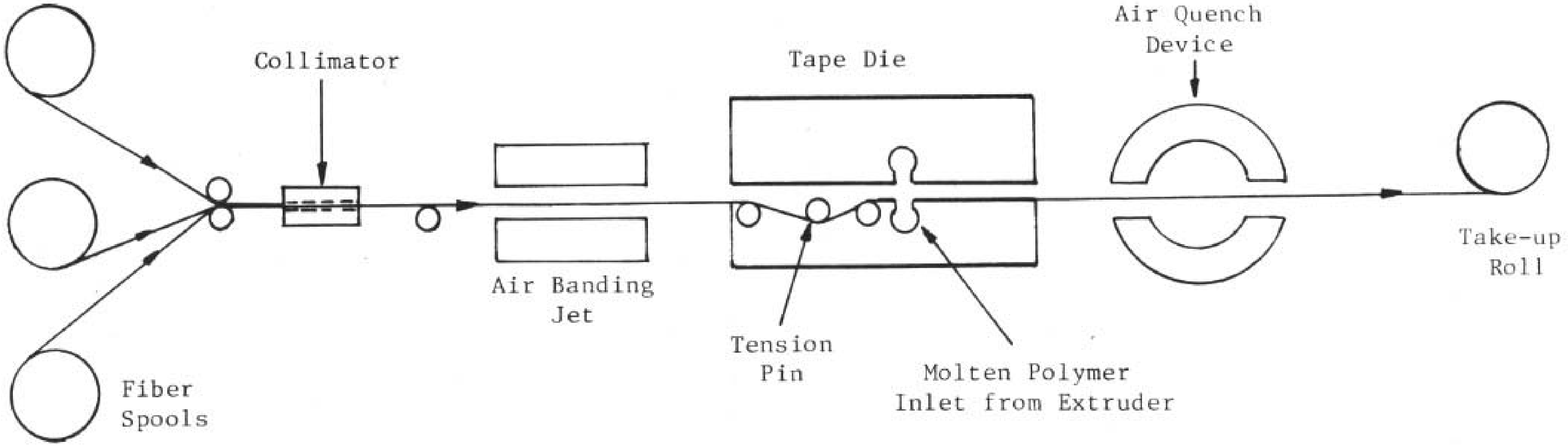

Figure 2.37 Hot melt impregnation of thermoplastic prepregs (adapted from Ref. 28).

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