RAW MATERIALS HANDBOOK

TOPFIBRA

EFFECTIVE FILAMENT WINDING® PIONEERS

RAW MATERIALS HANDBOOK

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AIM OF THIS HANDBOOK

Glass fibre Reinforced Plastics (GRP) are composite materials which consist of a layered reinforcement and the matrix that binds the layers together.

The properties of the composites are strongly influenced by the properties of their constituent materials, the distribution of these materials, and the interaction amongst these materials.

The matrix serves to: bind the glass fibres together, transfer loads to the fibres and protects them against the environmental attacks and damages during the handling. The matrix strongly influences several mechanical properties of the composites, such as the transverse modulus and strength, shear and compression properties.

The physical and chemical characteristics of the matrix (such as the polymerization temperature, viscosity and reactivity) influence which fabrication processes and which appropriate technological parameters are chosen. The materials for the matrix for a composite system are selected with of all these factors taken into the consideration.

The reinforcing components (glass fibres in GRP) generate the mechanical strength.

The aim of this Raw Materials Handbook is to:

- define the type of the raw materials and the characteristics of the raw materials that are suitable to be used in the filament winding technology;
- provide a guide for the selection of the raw materials and to ensure that they comply with the suggested specifications.

RESIN SYSTEMS

RESIN SYSTEMS

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1 POLYMERIZATION OF THE POLYESTER RESINS

Polymerization is a chemical reaction which is involved in the process of converting polyester resins from their liquid state into the solid state.

The chemical elements involved in the polymerization reaction are:

1. polyester resin;
2. styrene (in which the polyester resin is dissolved);
3. initiators;
4. promoters.

2 RESINS

The polyester resins, used in the manufacturing of the composite materials, are classified as:

- **Orthophthalic resins**, which are the general-purpose resins used in the water conveying and sewerage applications. They are used for manufacturing laminates which do not undergo strong chemical attacks or weathering.

  From the thermal point of view, orthophthalic resins are employed at ambient or medium-low temperatures. They should not be used for the construction of the internal liner of a fiberglass pipe.

- **Isophthalic resins** offer the most suitable end-use in the manufacturing of pipes conveying waste liquids, drinking water and seawater, above or below ground. They are more resistant to corroding substances present in the ground, to most salts, and to medium concentration of the oxidizing acids.

  Isophthalic resins are always used for the internal liner of the pipe. They are also used for the transportation of hot water up to 80°C (for example in heating systems), as well as for the transportation of water in cooling systems, sea water outfalls from power plants, desalination plants, etc.

- **Vinylester resins** combine a greater resistance to chemicals with a high mechanical strength, which is also true at high temperatures.

- **Bisphenolic resins** have lower mechanical properties compared to vinylester resins, but they are characterized by a high resistance to the chemicals.

A wide variety of subtypes exist for each of the resin types given above. The resin producers usually supply the Chemical Resistance Tables and suggestions for the use and curing of each resin.

2.1 Mechanical Characteristics of the Cured Polyester Resins

In the following table you can find the properties of the different polymerized polyester classes. However, the reported data provides only the approximate reference values because they can vary with the polymerization temperature cycle and the curing system used.

Characteristics	Units of measure	Orthophthalic	Isophthalic	Bisphenolic flex type	Vinylester
Density 25°C	g/cm³	1.2	1.2	1.12	1.12
Barcol hardness	-	35±5	>40	>35	>35
Glass trans. temp.	°C	>110	>120	>120	>130
Heat distortion temp.	°C	>90	>95	>90	>98
Elongation at failure	%	2.5±0.5	>2	>3	>3
Tensile strength	N/mm²	80±10	>90	>60	>80
Tensile modulus	″	>3,800	>3,900	3,100	3,300
Flexural strength	N/mm²	110	>130	>120	>120
Flexural modulus	″	3,800	>3,000	3,100	>3,000
Volume shrinkage	%	9±0.5	9±0.5	7±1	7±1
Water absorption	% at 20 °C	<0.5	<0.2	<0.1	<0.1
Water absorption	% at 100 °C	<2	<1	<0.5	<0.5

Table 1: proprieties of the polymerized polyester classes

NOTE: The type, arrangement, and fibres content, determine the strength of GRP and guarantee the required mechanical properties. The selection of the thermosetting resin determines the chemical, electrical and thermal performance of the GRP product. However, the most significant contribution of the resin relates to the ‘life’ of the composite, since the resin must protect the reinforcement.

2.2 Properties of the Liquid Resins

The most important properties of the liquid resins used in the manufacturing process are their viscosity, reactivity, gel time, the peak temperature and the peak time of the reaction. These characteristics determine the operability of the resins and will be now explained in detail.

Viscosity

Viscosity depends on the molecular weight and percentage in weight of a monomer and is very sensitive to the temperature: the viscosity decreases as the temperature increases.
It is a very important characteristic because it contributes to the following factors:

- ease and effectiveness of mixing with the catalyst, accelerators and inhibitors (always in very low percentages with regard to the resin);
- ease for pumping;
- air encapsulation;
- optimum reinforcement wettability.

The reduction of the resin viscosity, in order to fit the process requirements, can be made by adding styrene in small amounts or by operating the process temperature.

Operating the process temperature is preferable, because increasing the amount of styrene may lead to a reduction of the resin elongation at the break. On the other hand, if the viscosity of the resin is too low, it will cause the resin to drip from the laminates.

For the Continuous Filament Winding (CFW) process, a viscosity range between 250 and 400 cPs @25°C is recommended. The ISO 2555 and ASTM D 1200 methods cover the determination of the viscosity, which is accurately reported in the Quality Control Handbook.

Resin Reactivity

Resin Reactivity is a parameter set which describes the polymerization reaction, and it varies based on the type and the percentage of the accelerator, catalyst and inhibitor, with the temperature and with the mass-volume ratio of the sample.

Gel Time

The polymerization reaction starts after the components are mixed. The velocity of the reaction also depends on the temperature. The polymerization reaction runs from the viscosity increase until the gel point. The gel point is the initial gelatinous state, developed during the polymerization of a thermosetting resin and it is the irreversible point at which a polymer changes from liquid to semi-solid. At the gel point the viscosity is very high (103- 105 Pas*sec) and at this stage it is no longer possible to adequately carry out some of the technological operations, such as the reinforcement, fillers impregnation and mixing of the catalysts and promoters. The gel time is the time interval between the resin mixing and the gel point occurrence. The gel time values are strongly dependent on the factors such as the ambient temperature, resin viscosity and catalysis, which are better explained below.

Time-to-Peak

The polymerization process is an exothermic reaction, therefore, it means that it releases energy in the form of the heat. The time interval, between the resin catalysis and the point of reaching the maximum temperature in the reactive mixture, is defined as time-to-peak.

Peak Temperature

The Peak Temperature is the maximum temperature reached by the catalysed resin during the polymerization reaction. The ASTM D 2471 method covers the determination of the gel time, peak temperature and time-to-peak for a thermoset resin. It is accurately reported in the Quality Control Handbook.

These resin reactivity parameters are very important for carrying out the correct procedure of the technological operations and for the final quality of the composite pieces.

In the Manufacturing Handbook you can find the recommendations concerning the resin reactivity parameters.

2.3 Resins for the Liner Production

In the fiberglass pipes manufacturing process, a chemical resistant resin must be used to make the liner an impermeable layer and thus secure the integrity of the inner wall of the pipe or the coupling.

Two resin types that are recommended for the manufacturing of the liner are the isophthalic resin and the vinyl ester resin.

The choice between those two resins is strongly dependent on the category of the transported fluid.

The elongation at break of the resin should remain within the limits of 4% - 6% in order to prevent any possible cracking of the liner with the subsequent fluid spillage under service. The Table 1 shows the recommended resins for the liner production.

Product	Description	Supplier
Palatal A 400-155V	Isophthalic resin	DSM
CE 66 N4	Isophthalic resin	CAM-ELIAF
Atlac 430	Vinyl ester resin	DSM

Table 2: Recommended resins for the liner manufacturing.

The properties of the recommended products may vary from batch to batch, which means it is necessary to perform laboratory tests to verify the quality of the resins before starting any production.

2.3.1 Purchase Criteria for the Liner Resins

2.3.1.1 Isophthalic Resin

PHYSICAL PROPERTIES OF THE LIQUID RESINS

Property	Test method	Unit	Specifications
Appearance			Clear
Viscosity as received (25°C)	ISO 2555/ASTM 1200-94	mPa* s	350 - 500[1]
Acid number	ISO 2114-74	MgKOH/g	Max. 15
Shelf life at 25°C		Months	Min. 4

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[1] The styrene monomer is added to the polyester resin to reach a viscosity value of 300 ± 25 cP.

CURING PROPERTIES

Property[2]	Test method	Specification
Gel time (from 25° C to 35 °C) (1,0 % CO (1%) (NL49P) +1.0 % MEKP (9.0 % active O) (Butanox M50)	ASTM D 2471-99	8 - 16 min
25°C – Exothermic peak	ASTM D 2471-99	< 35 min
Exothermic peak	ASTM D 2471-99	<190 °C

MECHANICAL AND PHYSICAL PROPERTIES OF THE CURED RESINS

Property	Test method	Unit	Specifications
Barcol hardness	ASTM D 2583	934-1	Min 40
Tensile strength	ISO/R527-2	MPa	Min. 70
Tensile modulus	ISO/R527-2	MPa	Min. 3500
Elongation at break	ISO/ R537-2	%	Min. 4.0
Flexural strength	ISO 178	MPa	Min. 120
Flex. modulus	ISO 178	MPa	Min. 3600
Heat distortion temp.	ISO 75-A	°C	Min. 80

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[2] The reported properties are related to the resin with viscosity of 300 ± 25 cP.

2.3.1.2 Vinylester resin

PHYSICAL PROPERTIES OF THE LIQUID RESINS

Property	**Test method**	**Unit**	**Specifications**
Appearance			Clear
Viscosity as received (25ºC)	ISO 2555 ASTM 1200-94	mPa*s	350 - 550[3]
Shelf life at 25ºC		Months	Min. 5

CURING PROPERTIES

Property[4]	**Test method**	**Specification**
Gel time (from 25º C to 35 °C) (1.0 % CO (1%) (NL 49P) +2.0 % MEKP (8.6 % active O) (Butanox LPT)	ASTM D 2471-99	10 - 15 min
25°C – Exothermic peak	ASTM D 2471-99	< 35 min
Exothermic peak	ASTM D 2471-99	<190 ºC

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[3] The styrene monomer is added to the polyester resin to reach the viscosity value of 300 ± 25 cP.

[4] The reported properties are related to the resin with viscosity of 300 ± 25 cP

MECHANICAL AND PHYSICAL PROPERTIES OF THE CURED RESINS

Property	Test method	Unit	Specifications
Barcol hardness	ASTM D 2583	934-1	Min. 35
Tensile strength	ISO/R527-2	MPa	Min. 80
Tensile modulus	ISO/R527-2	MPa	Min. 3300
Elongation at break	ISO/ R537-2	%	5 – 6 %
Flexural strength	ISO 178	MPa	Min. 125
Flexural modulus	ISO 178	MPa	Min. 3100
Heat distortion temp.	ISO 75-A	ºC	Min. 100

Please note: this data is relevant specifically for the selection of the optimal resins from those present on the market and, as an extension, the selection of the appropriate supplier.

These curing properties can be different when used during the production process, because they depend on the ambient temperature and the production speed. Thus, it is necessary to perform the preliminary laboratory tests for each type of the production in order to select the optimal composition, following the recommendations of the Manufacturing Handbook.

2.4 Resins for the Structural Layer Production

The recommended resins for the production of the structural layer are shown in Table 3.

Product	Description	Supplier
Synolite 1503–N-3	Orthophthalic resin	DSM
CE 99 N4	Orthophthalic resin	CAMELYAF

Table 3: The recommended resins for the manufacturing of the structural layers

The properties of the recommended products may vary from batch to batch, which means it is necessary to perform the laboratory tests to verify the quality of the resins before starting the production.

2.4.1 Purchase Criteria for Structural Layer Resin

2.4.1.1 Orthophthalic resin

PHYSICAL PROPERTIES OF THE LIQUID RESINS

Property	**Test method**	**Unit**	**Specifications**
Appearance			Clear
Viscosity as received (25ºC)	ISO 2555 ASTM 1200-94	mPa* s	300 - 400[5]
Acid number	ISO 2114-74	MgKOH/g	Max. 30
Shelf life at 25ºC		Months	Min. 4

CURING PROPERTIES

Property[6]	**Test method**	**Specification**
Gel time at 25 ºC 1% CO (1%) (NL49P) +1,1% MEKP (9.0 % active O) (Butanox M50)	ASTM D 2471-99	10 - 20 min
25°C – Exothermic peak	ASTM D 2471-99	< 40 min
Exothermic peak	ASTM D 2471-99	<190º C

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[5] The styrene monomer is added to the polyester resin to reach the viscosity value of 300 ± 25 cP.

[6] The reported properties are related to the resin with viscosity of 300 ± 25 cP

MECHANICAL AND PHYSICAL PROPERTIES OF THE CURED RESINS

Property	Test method	Unit	Specifications
Barcol hardness	ASTM D 2583	934-1	Min 40
Tensile strength	ISO/R527-2	MPa	Min. 70
Tensile modulus	ISO/R527-2	MPa	Min. 3500
Elongation at break	ISO/ R527-2	%	Min. 3.0
Flexural strength	ISO 178	MPa	Min. 120
Flex. modulus	ISO 178	MPa	Min. 3600
Heat distortion temp.	ISO 75-A	ºC	Min. 75

Please note: the above data is relevant specifically for the selection of the optimal resin of those present on the market and, as an extension, the selection of the appropriate supplier.

The above reported curing properties can be different when used during the production process, because they depend on the ambient temperature and the production speed. Thus, it is necessary to perform the preliminary laboratory tests for each type of the production in order to select the optimal composition following the recommendations of the Manufacturing Handbook.

2.5 Resins for the Special Applications

For the application during the hand lay-up and the fittings production, the same resins are recommended, as reported earlier.

3 INITIATORS (Catalyst)

The polymerization reaction is activated by the so-called initiator. The initiator decomposes and produces the chemical species called radicals, which start the polymerization, reacting with the polyester resin and styrene.

The radical species production is a process activated by the temperature.

Most common substances, which are used to initiate the polymerization reaction, are the organic peroxides which differ one from another by the activation temperature. If the activation temperature is not reached, the polymerization reaction either does not start or it is very slow.

Table 4 shows some of the peroxides, commonly used for the production of the composites.

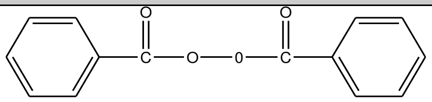
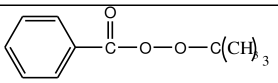
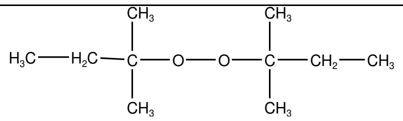
Peroxide name	Peroxide formula	Activation Temperature (°C)
Benzoyl Peroxide		90 - 130
Ter-butyl Perbenzoate		135 - 165
Methyl Ethyl Ketone Peroxide	 $H_3C-H_2C-\overset{CH_3}{\underset{CH_3}{C}}-O-O-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-CH_3$	30 - 60[7]

Table 4: Peroxide commonly used for the composites production

The organic peroxides are generally classified according to their reactivity and are divided between peroxides with:

- low reactivity;
- medium reactivity;
- high reactivity.

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[7] The lower activation temperature is related to the presence of a promoter.

The low, medium and high reactivities are related to a low, medium and high resin polymerisation rate respectively. The reactivity depends on the total active oxygen content: the greater the total oxygen content,[8] the higher the peroxide reactivity.

The choice of the initiator category is closely dependent on the ambient temperature, the pipe wall thickness and the process speed.

For thin and medium wall thickness laminates and high/medium process speeds, the high/medium reactive catalysts should be used.

The low reactive catalysts should be used for making the thick wall laminates in order to manufacture particular parts, such as fittings, by the hand lay-up process and in the locations with a high ambient temperature.

The initiators must be utilised in quantities no less than 1%, but no more than 2.5%.

If the quantity is below 1%, the final product can have poor mechanical, elastic and chemical resistance properties. If the quantity is above 2.5%, a strong exothermic reaction occurs which leads to an increase in fragility and eventual possibility of delamination.

3.1 Approved Initiators

Table 5 shows the initiators that are recommended for the pipe fittings and sleeves, produced with the Continuous Filament Winding technology (CFW).

Product	Description	Supplier
High reactive initiators		
Butanox M 60	Methyl ethyl ketone peroxide Total active oxygen: 9.8-10 %	AkzoNobel
Medium reactive initiators		
Butanox M 50	Methyl ethyl ketone peroxide Total active oxygen: 8.8-9.0 %	AkzoNobel
Low reactive initiators		
Butanox LPT	Methyl ethyl ketone peroxide Total active oxygen 8.4-8.6 %	AkzoNobel

Table 5: Recommended initiators for the pipes, fittings and sleeves, produced with the CFW technology

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[8] The concept of the active oxygen content is used for comparing the relative concentration of the peroxide groups in formulations.

4 PROMOTERS (Accelerators)

In order to speed up the decomposition of the peroxide, the compounds, called "promoters" (or accelerators), are added to the resin system. Typical accelerators for the peroxide catalysts are:

Metallic Salts: these accelerators are used to activate the peroxide at ambient temperatures, at which the decomposition of the peroxides takes place very slowly.

Aromatic Amines: these accelerators activate the peroxide in combination with metallic salts when it is necessary to speed up the polymerisation reaction to achieve a high production speed. They may also be used at the ambient temperature conditions, below the standards.

Aliphatic Amides: these accelerators are used to activate the peroxide in combination with metallic salts when it is necessary to speed up the polymerisation reaction for a high production speed. They may also be used at the ambient temperature conditions below the standards. The use of the aliphatic amides instead of the aromatic amines is preferred, because they are less toxic and less dangerous to handle, while the final properties of the laminate remain unchanged.

4.1 Approved Promoters

Product	Description	Supplier
Metallic salts promoters (Accelerators or Primary Promoters)		
NL-49P (Co 1%)	1% Co in aliphatic ester	AkzoNobel
NL-51P (Co 6%)	6% Co in aliphatic ester	AkzoNobel
Aromatic amines promoters[9] (Secondary Promoters)		
NL-63-10P	N-N Dimethylaniline 10% in aliphatic ester	AkzoNobel
Aliphatic amide promoters (Secondary Promoters)		
Promoter D[10]	N,N-Diethylacetoacetamide	AkzoNobel

Table 6: Recommended promoters for the pipes, fittings and sleeves produced with the CFW technology

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[9] The aromatic amines and the aliphatic amides are not used for the special parts production by hand lay-up technology (fittings).

[10] Promotor D should be added in 10% concentration of a styrene solution to ensure right dosage.

5 CATALYSIS EFFECTS ON THE POLYMERIZATION REACTION

Figure 1 shows the temperature versus time, recorded during a polymerization reaction of a polyester resin using a peroxide initiator and a metallic salt as the promoter. In particular, different compositions have been monitored, using the same amount of the promoter and varying the peroxide quantity.

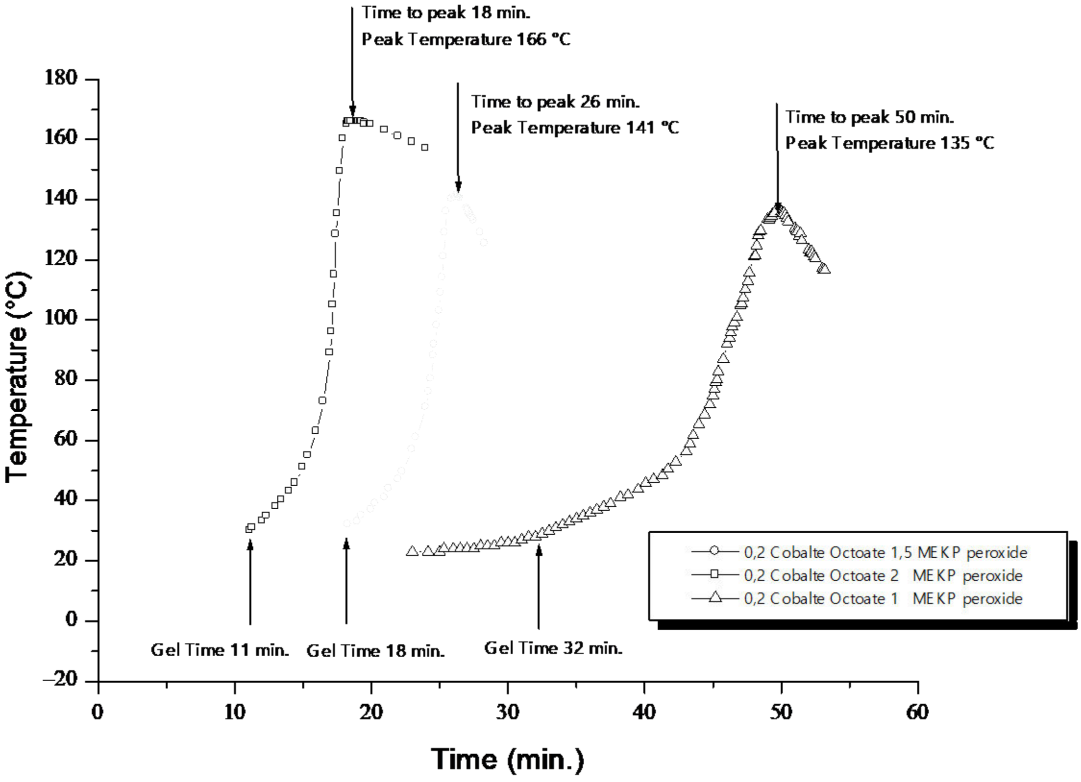

Figure 1: Resin reactivity parameters obtained while varying the amount of the initiator

As can be seen in Figure 1, the amount of the initiator, affects the polymerization reaction rate, which means it affects the gel time, peak temperature and time-to-peak.

In particular, increasing the amount of the initiator has the following effects:

- gel time decreases;
- time-to-peak decreases;
- peak temperature increases.

Figure 2 shows the temperature versus time, recorded during a polymerization reaction of a polyester resin, using a peroxide initiator and a metallic salt as the promoter. In particular, different compositions have been monitored using the same initiator amount and varying the promoter quantity.

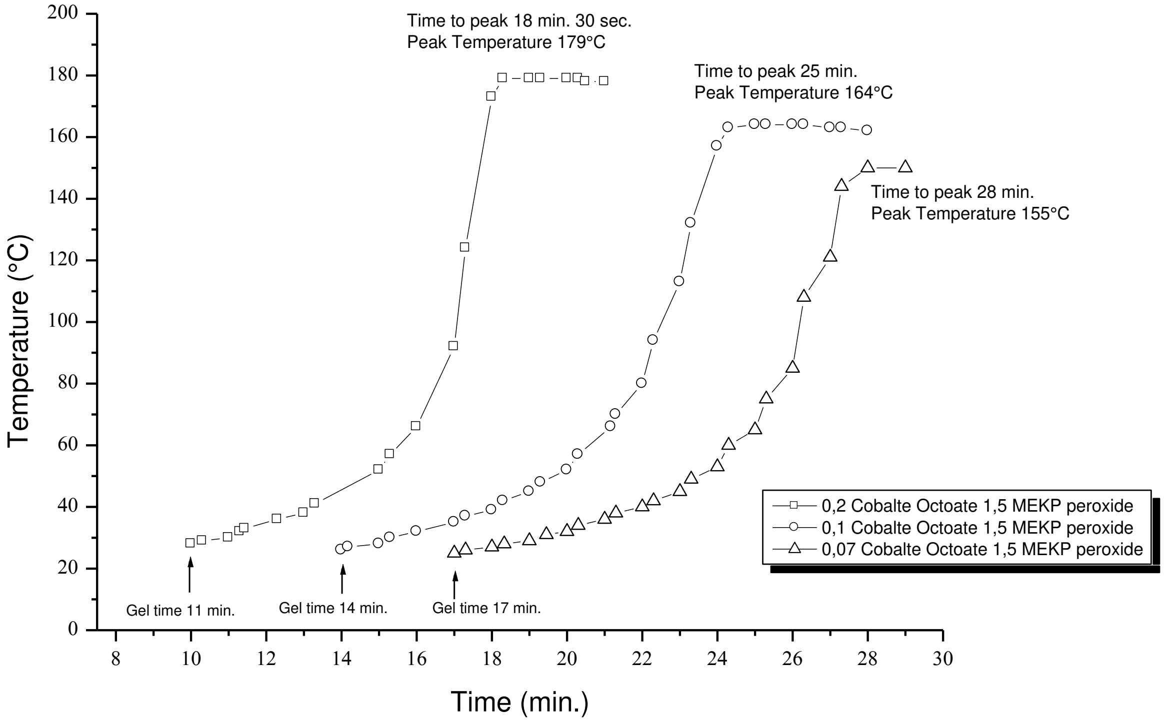

Figure 2: Resin reactivity parameters obtained varying the amount of catalyst

As seen in Figure2, the amount of the promoter also affects the gel time, the time-to-peak and the peak temperature values.

In particular, increasing the amount of the promoter has the following effects:

- gel time decreases;
- time-to-peak decreases;
- peak temperature increases.

It is important to know, that changing the catalyst and the initiator amounts accordingly, it is possible to obtain the optimum reaction parameters for the used production speeds (see Manufacturing Handbook).

However, the numbers shown in the above reported graphs should be considered as purely indicative data. They have only been reported with the purpose of showing the qualitative effects of the reactive mixture composition on the reaction parameters.

The data and the graphs can change because the resins, initiators and catalysts that are available on the market can vary.

6 INHIBITORS

In polyester resin that is used for the manufacturing of the fibreglass products, the chemical species called the inhibitors are present. The addition of the inhibitors to the resin is made by the resin manufacturers and has a dual purpose:

- firstly, to increase the shelf life of the liquid resin. The resin shelf life is the maximum storage time beyond which the chemical and physical properties of the resin are altered. The standard volume of inhibitor guarantees a resin shelf life of 4-6 months;

- and secondly, to modulate the resin reactivity. The inhibitors are the chemical species able to react with the radicals generated by the initiators. In particular, a peroxide radical tends to react with an inhibitor molecule rather than with a polyester or styrene molecule. That means that the polymerisation reaction does not start until all of the inhibitor is consumed by the reaction with the radical species. The time range between the resin catalysis (with the addition of the promoter and the initiator) and the start of the polymerisation reaction is called the induction time. Therefore, greater or lesser amounts of the inhibitor can affect the gel time and the time-to-peak. These effects are particularly important in the resin selection phase. On the market we can find a wide range of the polyester resins similar in their chemical structure but different in the inhibitor content and, therefore, their reactivity properties.

Usually, it is not necessary to add further amounts of inhibitor, when taking into account those already present in the resin itself.

The addition of the inhibitor is recommended only in exceptional cases such as:

- at the very high ambient temperatures;
- long lasting hand lay-up operations;
- long lasting winding operations;
- production of the GRP pipes with thick walls.

The products normally used are: a styrene solution with 10% of the hydroquinone, or a styrene solution with 10% of the p-ter-butyl catechol. The latter is preferred, because it is heat sensitive and therefore effective in gel time regulation, according to the process requirements, but with little effect on the gel-to-peak time.

7 STYRENE

Styrene is a reactive solvent for the unsaturated polyester resins. Being the reactive solvent, it means that:

- styrene acts as a solvent, decreasing the viscosity of the unsaturated polyester resin;
- styrene is a reactive monomer, i.e. it participates in the polymerisation reaction of the polyester resin.

The addition of the styrene to the resin is carried out by the resin manufacturers using an amount of styrene which determines the chemical, physical and mechanical characteristics of the product of the cross-linking.

It is possible to add small amounts of styrene during the manufacturing operations to adjust the viscosity value to reach the desired values. This operation may be necessary if the ambient temperature is low or if the resin has an initial viscosity which is too high for the filament winding process.

Please note that the allowed additional quantity of styrene, without changing the resin basic properties, should be limited to a maximum of 5%. Greater amounts of styrene may lead to the decrease of the resin elongation at break.

The styrene monomer that is used should have a purity that is not lower than 99.5% and any impurities must not include:

- benzaldeyde;
- toluene;
- xylol.

Generally, the styrene contains:

- an inhibitor (hydroquinone) in quantity that is not greater than 1%;
- dimers and trimers in quantities that are not greater than 5%;
- water content that should not be greater than 1% and should visually appear colourless.

8 ATTACHMENTS AND REFERENCES

The Product Data Sheets and the Material Safety Data Sheets

The attached Product Data Sheet (PDS) and the Material Safety Data Sheets (MSDS) are supplied only as an indication, since they are often updated by the Manufacturers.

The Material Safety Data Sheets may vary for different countries, the ones supplied are generally referred to the European Community.

We suggest periodical checks of the Manufacturer's websites for the availability of updates of PDS and MSDS.

Manufacturers

DSM:	http://www.dsm.com/
	http://www.dsm.com/en_US/html/drs/home.htm
CAMELYAF:	http://www.camelyaf.com/
AkzoNobel:	http://www.akzonobel.com/
	http://www.akzonobel-polymerchemicals.com/
	http://www.akzonobel-polymerchemicals.com/ProductSelector/

8.1 Resins for the internal liner

DSM Palatal A 400-155V-PDS

DSM Palatal A 400-155V-MSDS

DSM Atlac 430-PDS

DSM Atlac 430-MSDS

CE 66 N4

8.2 Resins for the structural layer

DSM Synolite 1503-N-3-PDS

DSM Synolite 1503-N-3-MSDS

CE 99 N4

8.3 Catalysts

8.4 Accelerators – Promotors

GLASS REINFORCEMENTS

GLASS REINFORCEMENTS

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1 GLASS FIBRE

Besides the quality of the resin, there are two decisive factors for obtaining an excellent final result:

- the types of the glass employed;
- using the different types of glass in the most appropriate way possible in order to exploit their structural properties to the fullest.

Glass fibres are obtained with the silica glass based melting mixtures of inorganic materials at temperatures varying between 1300°C and 1600°C. Under these conditions, the cross-linked structure of the silica is destroyed, its continuity is interrupted and its structure is modified by the introduction of other oxides.

The fibres are formed by drawing and rapidly cooling the molten material exiting from a large number of very accurately dimensioned holes in a heated platinum alloy die, in the form of threads. A constant head of glass is maintained under the accurate temperature control, to produce the required diameter strand to tight tolerances when the fibres are wound onto a high speed mandrel, running at several thousand meters per minute.

From this basic thread, by direct or indirect operations, various commercial forms of reinforcements are obtained and appropriately designed to meet all the technical and technological requirements.

The reinforcements used in the manufacturing of the industrial products, such as vessels, silos and pipes, are made from three different types of glass compositions:

- **“C” glass**, which displays very good properties of the chemical inertness to corrosive environment;
- **“E” glass**, which is not so resistant to corrosion but displays a very high mechanical strength;
- **“ECR” glass**, which is similar to the E-glass, but it doesn’t contain boron and fluorine. Due to the removal of these components, the chemical resistance (including water-resistance, acid-resistance and alkali-resistance) is greatly improved. When compared to the E-glass fibers, the ECR-glass shows higher temperature resistance, better dielectric strength, lower electrical leakage, and higher surface resistance.

1.1 Typical Chemical Compositions

The following table shows the typical compositions of the "C" glass and the "E" glass (the values are in % per weight:

Component	"C" glass	"E" glass
SiO_2	64.8	54.5
B_2O_3	4.9	7.9
CaO	14.1	17.7
MgO	3.2	4.1
F_2	/	0.2
K_2O	0.5	0.1
Na_2O	8.2	0.5
Al_2O_3	4	14.9
Fe_2O_3	0.3	0.1

1.2 Physical and Mechanical Properties

The physical and mechanical properties of the "C" and the "E" glass are shown in the following table:

	Unit	C glass	E glass
Tensile strength at 22°C	N/mm^2	/	2,400
Young's modulus	N/mm^2	/	73,000
Elongation at break	%	/	4.5
Specific gravity	g/cm^3	2.53	2.60
Creep	-	Absent	Absent
Hysteresis	-	Absent	Absent
Filament diameter	mm^{-3}	10	10-23
Coeff. of thermal expansion	m/m° C	$7.1*10^{-6}$	$5*10^{-6}$

2 SURFACE TREATMENTS

The main function of the surface treatment (also called “size” or “sizing”) is to protect the glass filaments during the fibres manufacturing and during the transformation into the reinforced polymer. The functions of the main components of the size formulations are:

- Film former: provides the adhesion between the filaments forming the strands and prevents the adhesion between the strands during the winding operations;
- Lubricants: they protect the filaments from abrasion;
- Antistatic agents: they help avoid the formation of the electrostatic charges during the manufacturing and the use of the fibres;
- Coupling agent: provides the adhesion between the fibres and the polymeric matrix.

The mix of these components is used in the water solution in a concentration of 6 ÷ 10% with well-defined ratios in regard to the type of the glass and the type of the matrix.

2.1 Coupling Agents

The coupling agent enhances the adhesion between the reinforcement and the matrix and improves the wettability of the reinforcement, thus making the impregnation operations easier. The selection of the best coupling agent is fundamental in order to guarantee a good stress transmission from the matrix to the reinforcements and the optimum mechanical behaviour of the composite.

The employed coupling agent depends on the composition of the reinforcement and the resin itself. The most widely used coupling agents are silanes.

The ideal coupling agent is a molecule containing two kinds of chemical groups, one of which reacts to adhere to the reinforcement, while the other binds to the resin, as shown in the Figure 3:

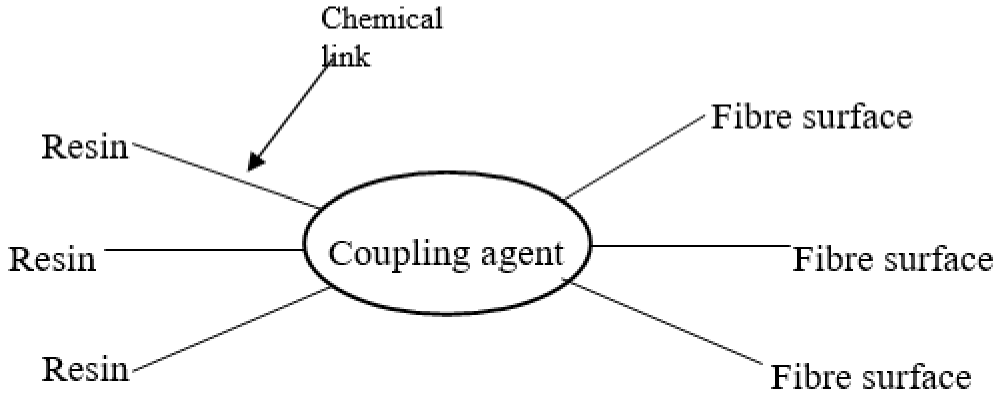


Figure 3: The sketch of the reaction involved between the coupling agent, the reinforcement and the resin

The reinforcements that are available on the market are already silane-coated, so they can be used immediately, without further processing.

Please note: before the purchase of the reinforcements it is necessary to preventively ask the supplier about the superficial treatment that makes the fibers suitable to one matrix typology instead of another. On the market, we can find reinforcements with good wettability for the phenolic, polyester, vinylester and epoxy resins.

3 REINFORCING MATERIALS FOR THE FILAMENT WINDING PRODUCTION

The reinforcements used in our industrial production process are:

- surfacing veils made from "C" glass;
- mats of chopped strands made from "E" glass;
- rovings for chopping;
- rovings for winding;
- woven rovings.

The development of the processing technologies has made other raw materials commonly used as well and now, even if they are not based on the glass fibres, they form an integral part of the structures of the GRP laminates.

For this reason, it seems more appropriate to mention these materials amongst other reinforcing materials and not consider them as the auxiliary materials. These materials are:

- synthetic surfacing veils;
- squeezing nets.

3.1 Surfacing Veils

This type of material is generally used to add reinforcement to the surface of a laminate, and thus, to:

- provide a resin-rich finish with the improved chemical and weathering resistance;
- ensure an adequate bond between the resin-rich surface layer and the bulk laminate;
- contribute towards preventing the formation of the hair cracks in the gel coat;
- contribute towards masking the pattern of the underlying reinforcement;
- provide a degree of elasticity for the surface layer, improving the impact resistance and the abrasion resistance.

In CFW production lines, the surfacing veil is used in the first ply of the laminate, which is in contact with the corrosive fluids, as well as in the last ply. In both cases, the surfacing veil has the principal functions of improving the resistance to the external agents/corrosive fluids, as well as providing the surface finish.

The surfacing veil is also used for making fittings by the hand lay-up lamination method. In this case, the surfacing veil is also in contact with the conveyed fluid. For this specific application, surfacing veils of the 1000 mm width can be applied.

3.1.1 Glass Surfacing Veils

The very fine fibres forming the surfacing veil (also called “surfacing mat” or more often only “surfacing”) consist of the type "C" glass, which has the best inertness to chemicals and is distributed in such a way that it forms a felt, which can be readily wetted with the resin.

“ECR” glass surfacing veils can also be used for the reinforcement of the internal liner, combining higher strength and good chemical resistance.

The fibres forming the felt should be continuous, to prevent the possibility of the infiltration of the corrosive liquids by the capillary action.

The band of surfacing veil in the dry state should have the tensile strength of at least 0.1 N/mm2 to allow automatic application.

3.1.2 Synthetic Surfacing Veils

When the solutions, which have to be contained or conveyed, include the substances which are aggressive to the glass, such as fluorides, it is recommended to replace the "C" glass of the surfacing veil with the synthetic fibres in the form of the chopped strands of the continuous fibres.

Moreover, the synthetic veils have excellent tensile and elongation properties that allow GRP fabricators to fully utilize the increased resilience and toughness of the corrosion resistant resins: C-glass veils are composed of the glass filaments with a break elongation of about 2.5% - 4.5%, which is less than the 5 – 7% range of the tensile elongation of the resilient corrosion resistant resins.

When under the thermal and mechanical stress an elongation to the same extent as the matrix is requested. The inability of the glass surfacing mat to elongate to the same extent as the surrounding resin matrix can contribute to the premature failure of the resin-rich corrosion barrier of the GRP. In this case, the use of a synthetic surfacing veil is suggested.

Synthetic surfacing veils are generally made with the polyester or synthetic fibres, such as polyacrylonitrile, where the bonding agent is soluble in the styrene to assure a good wettability. The length of the fibres is normally about 5 to 10 mm and they are arranged isotropically on a plane.

3.1.3 Recommended Surfacing Veils

The recommended suppliers and trade names for the surfacing veils are shown in the following table:

Supplier	Trade name	Material	Thickness basis weight
Glass Veil			
OCV	M524-C33	C-Glass	33 g/m^2
OCV	M524-ECR30A	ECR-Glass	30 g/m^2
OCV	M524-ECR30S	ECR-Glass	30 g/m^2
Freudenberg	Viledon TDB-T1790 C	C-Glass	30 g/ m^2
Freudenberg	Viledon TDB-T1798	ECR-Glass	30 g/ m^2
Synthetic Veil			
Freudenberg	Viledon T 1702	Polyester	26 g/m^2
Nexus	039-10	Polyester	31-37 g/m^2

OCV = OCV Reinforcements, division of Owens Corning incorporating Saint Gobain – Vetrotex since July 2007.

For an appropriate selection of the surfacing veil geometry we recommend following these recommendations:

- for all types of bobbins, the internal support should have the internal diameter of 76 mm and the external diameter of maximum 400 mm;
- in the production processes with the steel band width of 40 mm, it is necessary to use a surfacing veil that is 50/60 mm wide, while in case of a 60 mm wide steel band, a surfacing veil that is 70/80 mm wide must be used;
- note, that before acquiring the product, it is important to check with the supplier for the availability of the dimensions of materials used by the Topfibra machines.

3.2 Roving for Chopping

This reinforcing material is obtained by cutting the continuous “E” or “ECR” glass rovings in order to manufacture the isotropic reinforced structures. In the TOPFIBRA CFW plants, this reinforcement is applied using special cutters, however, the spray-up technology is also possible.

The fibres employed should have the following characteristics:

- excellent predisposition for being chopped and dispersed;
- low build-up of electrostatic electricity to avoid the accumulation of fibres on the machine parts and lumps falling on the mandrel;
- good parallelism of fibres;
- low fuzz deposit build-up in contact points;
- fast wet-out, requiring a small amount of resin.

The recommended binder is based on the silane. In the overall evaluation, it is also necessary to remember the characteristics of the impregnation, which has to be complete, and also the translucency of the laminate.

In the TOPFIBRA CFW production lines, the rovings for chopping (the commonly used term is “chopped”) are used for the manufacturing of:

- the inner liner. The chopped presence assures a homogeneous stress transfer mechanism to the structural layers;
- the structural wall in order to provide the axial resistance;
- the external layer with a light resin excess. Here, the chopped roving prevents resin from cracking.

3.2.1 Recommended Roving for Chopping

The recommended types of roving for chopping are shown below.

Supplier	Trade Name	Product	Silane Compatibilized for
OCV	P 246 Advantex	ECR-Glass	Polyester resin, vinyl ester resin
OCV	P 246E	E-Glass	Polyester resin, vinyl ester resin
OCV	Advantex 495 E	ECR-Glass	Polyester, vinyl ester resin
CPIC Fiberglass	ER - 10P - 2400	E-Glass	Polyester Resin
Fiberex	605-J-2400	ECR-Glass	Polyester, vinyl ester resin

CPIC = Chongqing Polycomp International Corp.

Please note: the spools need to be the internally unwinding spools type. The weight of the roving strand used for chopping is always 2400 tex. Tex is a unit of measure for the linear mass density of fibers and is defined as the mass in grams per 1000 meters. Most commonly used tex, also for continuous winding are 600, 1200, 2400 and 4800 tex.

3.3 Roving for the Continuous Winding

This reinforcement consists of the continuous rovings of the “E” or “ECR” glass and is used in the winding operations to obtain anisotropic structures.

The roving for winding should have the following properties:

- parallelism of fibres;
- suitable protection against the dampness and impact;
- low build-up of the electrostatic charges;
- ease of impregnation;
- translucency of the laminate produced;
- the absence of fuzzing through pay out system.

3.3.1 Recommended Roving for Winding

The recommended roving for winding are reported here:

Supplier	rade name	Available tex	Silane compatible with
OCV	R25H	600-1200-2400- 4800	Epoxy, Polyester, Vinylester
CPIC/Fiberglass	ER-469 2400 tex	600-2400	Polyester
OCV	RO99 - P192	600-1200-2400- 4800	Epoxy, Phenolic, Polyester, Vinylester

Please note: the spools need to be the internally unwinding spools type.

Figure 4 and Figure 5 show the roving for chopping and a roving for winding:

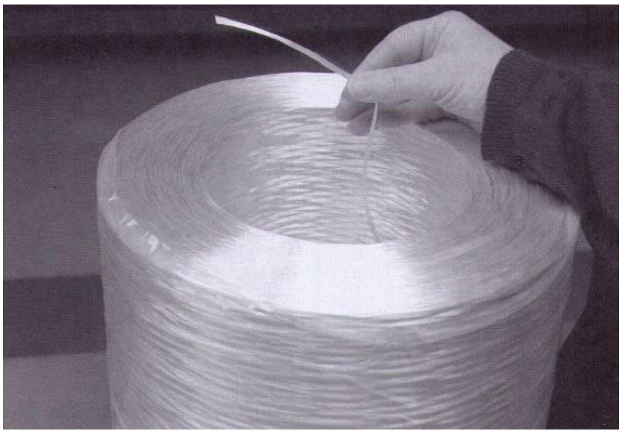


Figure 4: Roving for winding

Figure 5: Roving for chopping

3.4 Woven Roving

The woven rovings are made of the continuous rovings, woven at the right angle to each other, with and of equal density in both directions (balanced woven rovings). The characteristics of the employed rovings should be equal or superior to those described for the winding rovings.

This kind of reinforcement is used in the hand lay-up operations for manufacturing fittings. The layers of the woven roving alternate with layers of the mats in order to improve the mechanical strength of laminates, as compared to the ones which can be obtained using only layers of mats.

3.4.1 Recommended Woven Roving

The recommended type of the woven roving is shown below:

Supplier	**Trade name**	**Product description**	**Weight (g/m^2)**	**Weight uniformity (g/m^2)**	
				0°	**90°**
OCV	WR 500 P-125	Woven roving 0°/90°	528	288	240

3.5 The Mat of the Chopped "E" Glass Fibres

This kind of the reinforcement, called generally “chopped strand mat” (CSM), is used in the hand lay-up operations, such as the manufacturing of fittings, the application of the branches, localized reinforcements, repairs and butt joints.

The main characteristics required of this material are:

- uniformity of weight per unit of surface;
- good solubility of the bonding agent;
- ease of impregnation and good translucency of the made laminates;
- high mechanical strength;
- suitable packing to protect the glass from dampness.

These characteristics are generally obtained with mats based on the “E” glass fibres treated with a silane binder and bonded with a polyester bonding agent. The recommended type is a mat with a medium binder content (3 to 6% range) based on a high solubility binder for assuring a complete wet out in a short time.

This reinforcing material is a felt, which can be rolled up. It consists of the chopped threads, arranged in an isotropic manner, where the length of the fibres varies between 20 and 50 mm.

In the CFW manufacturing lines, mats are used to joint pieces of pipes in the production of fittings by the hand lay-up technology.

3.5.1 The Recommended Chopped Strand Mat

The recommended types of the chopped strand mat are shown here:

Supplier	Trade name	Notes	Weight (g/m^2)
OCV	M 123	For filament winding or continuous laminating ECR Glass – Available also in E glass	225, 300, 450
OCV	M534	For Hand Lay Up E Glass	300-600
OCV	M705	For Hand Lay Up ECR Glass	300-900
OCV	M 723A	For complex mould ECR Glass	300-900

3.6 Squeezing Nets

In order to obtain the inner liner without trapped air bubbles and with very compact and uniform plies, instead of rolling the laminate under construction, it is very often preferable to use a band consisting of a net of cotton or the polyester or acrylic synthetic fibres, wound with a tension of about 0.5 N/mm (of width), above the plies forming the liner. The result is better quality and time saving.

These squeezing nets made of cotton or synthetic fibres have a mesh size 1.5 to 2.5 mm and selvedge on both sides. The nets should be uniform, free of missing threads and should be supplied in rolls that are protected from damp. The length of the roll should be at least 200 meters, while the width depends on the dimensions of the product on which the squeezing net is applied, and on the equipment available for its application.

The properties and tolerances of squeezing nets should conform to:

maximum humidity:	1% by weight
ultimate tensile strength:	2 kg/cm
uniformity of mass:	±5%
solubility in styrene:	max. 5%(*)

(*) by weight after 1-hour immersion at the ambient temperature.

The nets are generally used during the construction of tanks and during the construction of the pipes produced with the automatic moulding machines, and during the reciprocal (Discontinuous) Filament Winding (DFW).

In the CFW process, the squeezing nets can be used to improve the compaction in the sand core layers.

4 REINFORCED POLYESTER CHARACTERISTICS

The average mechanical characteristics for the different types of the “E” glass reinforcements in a polyester matrix are shown in the following table.

The values refer to the perfectly impregnated laminates, manufactured with the correct glass/resin ratio. The values for the roving laminates have been determined in the direction of the fibres.

Characteristic	Unit	30% mat by weight	33% chopped by weight	70% roving by weight
Tensile strength	N/mm^2	95	110	700
Flexural strength	″	140	150	800
Tensile modulus	″	5,700	6,000	36,000
Flexural modulus	″	5,300	5,600	32,000
Poisson’s coefficient	-	0.3	0.3	0.55
Tensile elongation	%	2.5	2.5	2

The mechanical and the elastic properties of a glass reinforced laminate in a pre-established direction, depend on the glass-to-resin ratio, on the roving winding angle, and on the ratio between the different types of the reinforcements.

5 Attachments and References

The Product Data Sheets and The Material Safety Data Sheets

The attached Product Data Sheet (PDS) and the Material Safety Data Sheets (MSDS) are supplied just as an indication, since they are often updated by the Manufacturers.

The Material Safety Data Sheets may vary for different countries, the ones supplied are generally referred to the European Community.

We suggest periodical checks of the Manufacturer's website for the availability of the new updates of the PDS and the MSDS.

OCV:	http://www.ocvreinforcements.com/
Freudenberg:	http://www.freudenberg.com/
Nexus:	http://www.nexusveil.com/
CPIC Fiberglass:	http://en.cpicfiber.com/
Fiberex:	http://www.fiberex.com/

5.1 Surfacing Veil

OCV M524-C33.pdf

OCV M524-ECR30S

OCV M524-ECR30A

Freudenberg VILEDON T 1790 C

Freudenberg VILEDON T 1798 ECR

Freudenberg VILEDON T 1702 Polyester

Nexus 039-10 Polyester

5.2 Roving for chopping

5.3 Roving for hoop winding

5.4 Woven roving

5.5 Chop strand mat:

AUXILIARY RAW MATERIALS

AUXILIARY RAW MATERIALS

TABLE OF CONTENTS

1 GENERALITIES

The auxiliary raw materials, applied in the production of fibreglass pipes and tanks, are:

- polyester film release agent;
- wax release agents,
- inert fillers,
- primer for the resin-rubber system;
- silica gel;
- cements and putties;
- paraffin;
- absorbers for the ultraviolet rays;
- acetone solvent.

Of all the materials included in the general list above, only some of them are currently used in the CFW Manufacturing line, as specified further on.

2 RELEASE AGENT

2.1 Saturated Polyester Film (Mylar®)

Saturated polyester film is used to maintain the composite material separate from the steel band on the mandrel. It is also used to allow a good finish on the surface of the internal liner of the product.

The material is a thin film of a terephthalic-based, saturated polyester resin.

For the appropriate selection of the film geometry, the suggestions shown below should be considered:

- for the all types of rolls, the internal support should have an internal diameter of 76 mm and an external diameter of maximum 400 mm;
- in the production processes, with the steel band width of 40 mm, it is necessary to use a film with 50/60 mm width. If the steel band width of 60 mm is used, a film with 70/80 mm width must be used;

- the thickness of the material should be 24/30 µm. The film must be thin so it can be easily wrapped up on the mandrel steel band without wrinkling, in order to have a complete sealing of the steel band and a smooth finish of the internal liner;
- the characteristics of the film should not undergo any modification for 30 min after it has been immersed in styrene.

2.2 The Recommended Saturated Polyester Film

Trade name	Description	Supplier
Mylar 15A-HP	Polyester release film	Du Pont
Garfilm ER	Polyester release film	Coveme
Hostaphan RNK	Polyester release film	Mitsubishi

Before purchasing the release film, please check with the supplier for the availability of the sizes required for the manufacturing plant.

2.3 The Product Data Sheets

Mylar 15A-HP Product Data Sheet

Garfilm ER Product Data Sheet

Hostaphan RNK Product Data Sheet

2.4 Wax Release Agents

Wax release agents are used as an alternative to the release film in the following cases:

- to make the extraction of the polyester resin laminates from the moulds with a complex geometry easier;
- for the production with epoxy resins, because this resin type can stick to the polyester release film.

The wax release agent is the Carnauba wax (vegetable wax), diluted with trichloroethane. However, other types of waxes, such as paraffin wax or even beeswax can be used.

The wax should be in the form of a paste with a consistency of a pudding. It should be homogeneously dispersed in a very thin layer. After the application, the surface must be carefully polished.

The wax should be able to withstand the contact with styrene for at least 5 minutes without dissolving.

2.4.1 Recommended Wax Release Agents

Trade name	Description	Supplier
NU Ceara Wax	Carnauba wax	Huntsman
CR 80	Carnauba wax	Marbo

3 INERT FILLERS

The general effects that the inert fillers have on the liquid and cured resin properties, are listed here. Not all of them are applicable to each kind of filler.

The effects of the fillers on the liquid resin systems are:

- increase in viscosity;
- reduction of the exothermic peak.

The effects of the fillers on the properties of the cured resin systems are:

- reduced costs;
- resin systems are rendered opaque;

- increased resistance to impact;
- increased stiffness;
- increased compression strength;
- decreased flexural strength;
- reduce shrinkage;
- increase abrasion resistance;
- they impart self-extinguishing properties.

To improve the compression strength, the fillers should include:

- kaolin;
- calcium carbonate;
- calcium sulphate.

To obtain the self-extinguishing properties of the final product, the employed fillers should contain:

- aluminium hydrate;
- antimony trioxide.

To make the final product conductive, the fillers should consist of:

- finely micronized carbon black or even graphite and dissolved in the styrene or directly in the resin, to the form a paste with the consistency of pudding.

To improve the stiffness and obtain the cost reduction, the filler should consist of:

- the silicon dioxide (quartz sand).

When the special requirements use the necessary fillers, it should be noted that:

- the fillers should have a humidity not greater than 1 % by weight;

- calcium carbonate should not be used in the association with the self-extinguishing resins based on the halogenated products;
- the aluminium hydrate loses its effectiveness after a period of time;
- quartz sand should have, as a general rule, a grain size between 0.3 and 1 mm and a purity greater than 97%;
- use of the fillers modifies the physical and mechanical properties of the laminates.

3.1 Silica Sand in the CFW Process

Silica (SiO2) appears in the crystalline form as quartz (virtually pure silica sand) and when it is less pure, it appears in the form of sand.

The silica sand is mainly added to the structural part of the laminate in order to increase the thickness and the stiffness of the pipes with a minimal cost increase. In case of a low pressure pipe or “gravity pipe”, where the strength required to sustain the internal pressure is quite low, the pipe wall is less thick, while a thicker wall would be necessary to give the required pipe stiffness. The wall thickness is increased by means of adding silica sand, dispersed in the core layer of the pipe wall. At the same time, a certain amount of the resin needs to impregnate the silica sand.

In the Continuous Filament Winding process, the sand, together with the glass fibres and resin, is one of the main components of the pipe structural wall.

The correct type and grade must be chosen with care in order to maximize the benefits of using the sand. The main factors to be considered in the sand selection are the cost, the chemical composition (see ASTM-C 33), resin absorption, sand geometry, and particle distribution.

Resin absorption

Resin absorption in the laminate containing the silica sand depends on the void content in the pure sand. Void content is defined as the ratio between the volume of the voids and the total volume of a container filled with sand. The lesser the voids, the lesser will be the resin required to get a good impregnation and compactness of the mixture. The void content of the sand depends on the particle distribution and partially on the sand geometry.

Particle distribution

When the particle distribution (PD) is good, the sand grains of several sizes will be present in such proportions that the quantity of the smaller grains will fill as much voids as possible between the larger grains. Finding a natural sand with the optimum particle distribution is not simple, and to artificially "compose" such a distribution can be expensive.

Sand Geometry

The shape of the sand grains affects the characteristics of the sand in terms of the flowing and packing capacity and subsequently of the void content. The natural sands that have a spherical shape or ones with rounded corners are generally preferred to the sands obtained from crushing the larger grains. The crushed sands have irregular shapes and can be richer in very fine particles (powder).

3.2 Recommended Sand

The recommended properties of the washed, dried and graded sand for the polyester resin systems are shown in the next tables:

Chemical Characteristics:

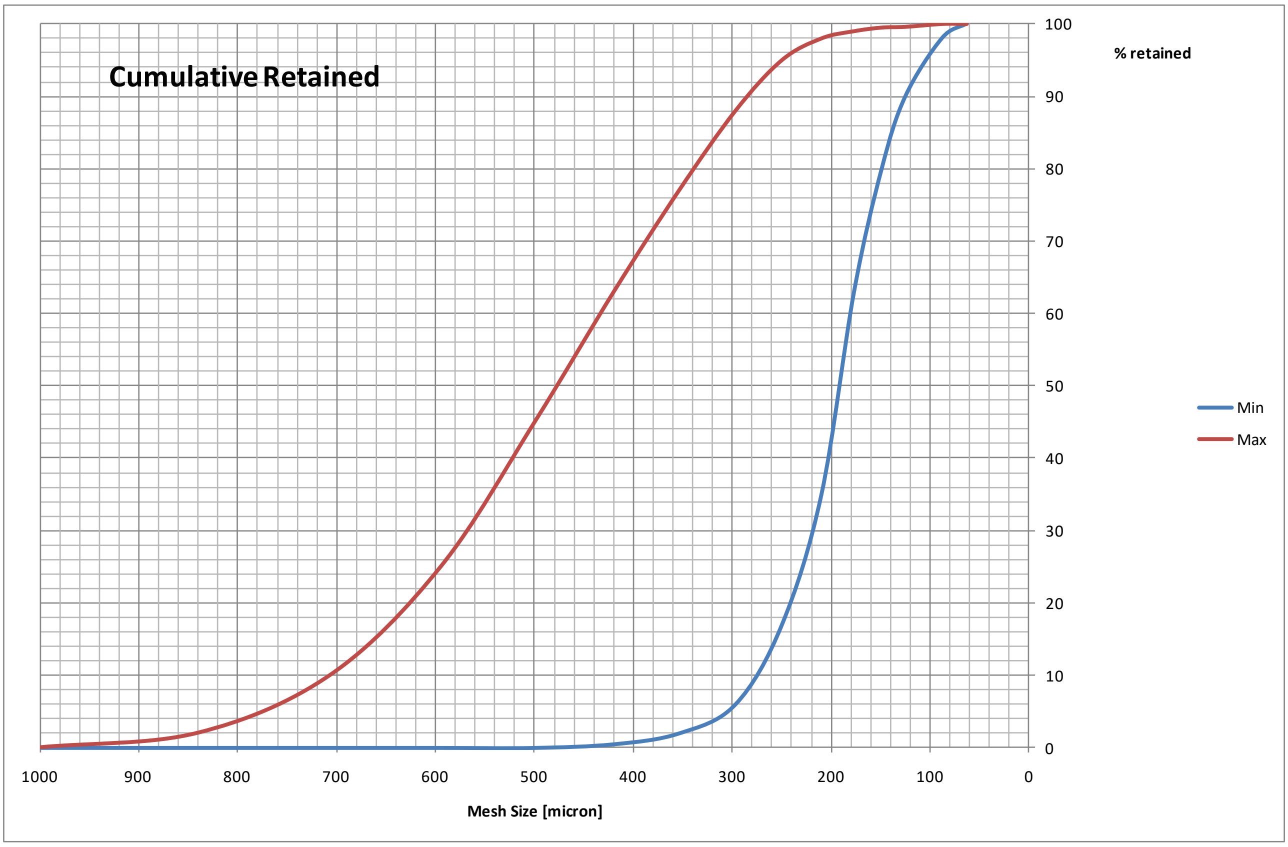
CHEMICAL CHARACTERISTICS	
SiO_2	98.1% min
Al_2O_3	1.1% Max
Fe_2O_3	0.1% Max
TiO_2	0.08% Max
CaO	0.06% Max
K_2O	0.5% Max
Na_2O	0.06% Max

Physical Characteristics:

PHYSICAL CHARACTERISTICS	
Absolute spec. gravity	2600 kg/m^3
Apparent spec. gravity	1500 kg/m^3
Humidity	Max 0.1%
Ignition loss	Max 0.3%

Particle Size Distribution:

The sand particle distribution shall be included within the limits reported below.



Shape and Quality of the Sand Particles

Sand should be of a natural and river origin. The shape of the grains must be mainly spherical. Moreover, the sand should not contain any dust, which produces the following undesired effects:

- because of the highly superficial development, dust absorbs a very high amount of resin;
- dust can spread in the working environment, making the correct development of the technological operations difficult.

4 PRIMER FOR THE RESIN-RUBBER SYSTEM

For the construction of the pipe couplings, two alternatives are to be considered:

- couplings can be realized by using the grooving machine that makes the grooves on a piece of pipe previously manufactured for this purpose; the gaskets are subsequently inserted into the grooves;
- couplings can be realized by placing the gaskets on a steel mandrel, opportunely spaced out, and by the hand lay-up application of the reinforced resin.

In the second case, the direct application of the reinforced polyester on the rubber is not advisable. The reason is that even it offers the advantage of assuring the adhesion due to the reaction between the styrene contained in the polyester resin solution and the rubber, the disadvantages are the following:

- the reaction may alter the characteristics of the rubber, compromising its efficiency during the service;
- the efficiency and the constant quality of the adhesion are not assured, depending on the reaction which is influenced by the substances contained in the rubber (carbon black, acetylene black, sulphides) and by the working conditions (room temperature, resin reactivity).

For these reasons, an agent particularly fit for the natural and synthetic rubbers is used.

The product is supplied by “Bayer” and it consists of a solution of triphenylmethane-4,4’,4”-tri-isocyanate in ethyl acetate with an isocyanate (NCO) content of 9.3±2% and with a solid content of an approximately 27%.

It is a yellowish green, or reddish brown to dark violet liquid, with a density of approximately 0.99 g/m3 at the temperature of 23°C, where the colour and the product’s quality are unrelated. The flash point (DIN 51755) is –3°C and the viscosity at 23°C is approximately 3 mPa*s (Brookfield, spindle 1, 60 rev/min).

The product must always be kept in tightly closed containers. Moisture, including the air humidity, must be excluded whenever the contents are taken from a container or transferred from one container to another. Small quantities should therefore be taken, not from a large container but from a sized receptacle intended for the current use with the suitable closures, such as the screw caps, with the polyethylene seals.

5 FUMED SILICA (Aerosil®)

Fumed silica is used for either its thixotropic properties, or the capacity to obtain the suspensions with a high static viscosity and a low kinematic viscosity.

It is used in preparing putties, intended as fillers, in butt-and-strap joints, or in fittings.

It is best to restrict the use of the fumed silica to the cases of a real necessity, since its mixture with the resins leads to the fragility of the products.

Furthermore, the addition of the fumed silica to the bisphenolic and to the vinyl ester resins to improve the viscosity, essentially reduces the chemical resistance to the corrosive environments.

Fumed silica should be employed in quantities not greater than 2% by weight in order to render the resin thixotropic.

The fumed silica is a pure silicon dioxide, finely micronized. The maximum dimensions of the particles should be less than 5 microns.

6 PUTTIES

Putties are used as adhesives and/or filling compounds in the production of some of the fittings and in making of the butt-and-strap laminated joints. They are applied inside and outside the pieces to be joined, to provide the dimensional stability to the joint before the hand lay-up process.

Putties consist of the resins filled with various kinds of fillers, for example:

- fumed silica (Aerosil);
- talc, quartz, kaolin or calcium carbonate;
- micro spheres or glass flakes;
- milled glass fibres.

Putty resin typology depends on the resin used during the production; for an epoxy matrix an epoxy based putty is selected, for a polyester matrix a polyester based putty is used.

Putties should consist of the previously accelerated resins, thickened with the quantity of the required fumed silica to obtain the consistency of pudding.

Putties are prepared by slowly adding the fumed silica to the resin and then stirring the mixture to obtain a very viscous paste that will not slip down when applied to the vertical walls. The required quantity of the fumed silica is about 2% – 4%.

Several ready-to-use putties are available on the market in various formulations. The selection is made on the basis of the working condition and of the type of the resin used for the pipe production.

7 PARAFFIN

The polymerisation reaction of the polyester and vinyl ester resins can be inhibited from the oxygen. The final effect of this is an incomplete polymerisation of the outer layers. Thus, paraffin is added to the polyester and vinyl ester resins to enable a complete polymerisation of their surfaces in the contact with air.

Paraffin in particular tends to spread over the surface and so obviates the inhibiting action of the oxygen.

In the end, the application of paraffin in the resin of the outer plies, prevents the products from ageing and considerably reduces the pollution of styrene during the processing.

Paraffins are waxes (higher alkanes C.8 C.12) with a melting point of about 50°C, already dissolved in styrene. The solution of the paraffin should be newly prepared and be transparent, without suspended solids. The solution should have a 5% paraffin content.

This solution is used at a concentration of 5% in the resin, constituting the outer ply.

Like all waxes, paraffin acts as a release agent, therefore care should be taken that the surfaces containing paraffin are properly rubbed down before further plies are laid up.

Paraffin use is limited to the following cases:

- when it is necessary to use very slow catalyses for manufacturing special pieces by the hand lay-up technology at the ambient temperature;
- in the resin that is used to cover the gasket grooves of the sleeves and to reduce the friction effects during the sleeves coupling operations.

8 ABSORBERS FOR THE ULTRAVIOLET RAYS

These materials have a low molecular weight, are organic compounds, and are added in low percentages to the resin to prevent the penetration of the ultraviolet rays through the laminates.

The energy of the UV radiation with a wave length of 300-400 nanometres, equivalent to the 72-95 Kcal/mol, is sufficient to break the C-C covalent bond (70-170 Kcal/mol). The function of these compounds is to absorb the UV radiation in the 300-350 wave length range, transforming it into thermal energy.

Even when the cobalt soaps are used as accelerators and the natural colour of the cured resin provides the absorption of a great part of the UV spectrum, it is anyway always recommended to add to the top coat of the resin the compounds cancelling the effect of the ultraviolet rays.

The ultraviolet ray absorbers should be used for all the products that will be installed in the open. Because of cost reasons, these materials are not recommended for underground tanks and pipes, unless the storage period preceding the installation is longer than 12 months.

The suggested UV absorber is TINUVIN 320 by Ciba Geigy, which is used in a percentage of 0.2% by weight if added to the total quantity of resin, or 5% by weight if added to the resin of the outer ply.

9 ACETONE SOLVENT

Acetone is used as the personal cleaning product and for the cleaning of tools employed in the process. It should never be used to dilute the polyester resin.

Used acetone can be recovered and distilled with a satisfactory result and with a yield of about 50 - 70%.

The product is a technical acetone that should not contain, corrosive or toxic substances, detrimental to health.

This specification should also be compared to the local regulations regarding accidents and the illness prevention at work.

10 VARNISHES AND GEL COATS

Varnishes and gel coats are generally used for finishing the outer surfaces of the tanks and pipes, in order to improve their appearance and to protect the resins from weathering.

The products used are the polyurethane varnishes or gel coats, based on the polyester resins that have a good inertness to chemicals, with the inert fillers and various pigments.

The gel coats, forming the outermost ply, should contain 5% of the paraffin by weight. The polyurethane varnishes should be translucent with a low tendency towards yellowing, even after the heat treatment at 100°C. The varnish should be a two-component product with a high reactivity.

The "dust-dry" time should be less than 30 minutes long and the varnish should be dry to the touch within two hours at the ambient temperature.

Solvents used in the varnish should not be detrimental to the health and should comply with the local regulations that are in force regarding health at work. The gel coats should comply with our specifications for the chemically resistant resins.

The varnishes should have a hardness no less than 50 Barcol, and the adhesion to the laminates should be at least equal to 0.1 N/mm2. The thickness of each single coat of the applied varnish should be at least 100 microns.

When applied to a reinforced polyester laminate, the varnish should neither change appreciably, nor become yellow, nor crack after the immersion in the distilled water at 100°C for 100 hours.

The polyurethane varnishes can be used only when applied to tanks or other products intended for the indoor installation. For the tanks and pipes that will be installed outdoors, the use of the paraffined resin and the UV absorber is recommended.