

Part 4: Carbon fibre reinforced composites

Introduction

Carbon fibres first emerged in the aviation sector in the 1980s. Currently, in aircraft, composite structures that are reinforced with these materials are used in all the primary parts, including the wings and fuselage.

These fibres then progressively made inroads in the sports and industrial sectors from the 1990s. Currently, the range of carbon fibres available on the market is increasingly vast and they are starting to be used in mass market applications and in an increasingly varied range of niche markets, under the influence of two factors:

- On the one hand, prices have dropped significantly and there are an increasing number of suppliers.
- On the other, the demand is high for lightweight products that consume less energy (motor vehicles, aviation, wind energy, electronics, etc.)

Today, composites are still overshadowed by glass fibres (85%), but carbon fibres are experiencing strong growth. They reinforce epoxy matrices by 72%, polyester ones by 12% and phenolic ones by 9%.

The industrial landscape of carbon fibres

The specialist of the carbon fibre market, Ch. Red (Composites Forecasts & Consulting LLC), believes that the carbon fibre offer exceeds demand and that this

situation will persist for a few more years. Indeed, there are new entrants to the market and the productivity of existing plants has been improved; on the other hand, some client markets are still in doubt (wind turbine blades) or could experience a drop in business.

Suppliers of PAN-based carbon fibres in the form of thin strands (66% of the market) are as follows, ranked according to their capacity from highest to lowest: Toray Industries (Tokyo, Japan) – 31 %, Toho Tenax Co. Ltd. (Wuppertal, Germany) - 21%, Mitsubishi Rayon Co. Ltd. (Tokyo, Japan), Hexcel Inc. (Dublin, Calif.), Cytec Engineered Materials Inc. (Tempe, Ariz.) and Formosa Plastics Corp. (Taipei, Taiwan).

The suppliers of fibres with over 24,000 filaments are Zoltek Inc. (St. Louis, Mo.) – 53%, SGL Group (Wiesbaden, Germany) - 27 %, Toho, PR China, Toray and several new small Chinese producers. The total capacity for this type of fibre represents only 50% of the total capacity for thin strands.

New entrants such as Hyosung (S. Korea), Sabic (Saudi Arabia), DowAksa (Turkey), Alabuga Fiber (Russia) are focused on producing industrial fibres, the modulus of which is not so high: these fibres are aimed at alternative markets to the high-tech and aviation markets that are experiencing faster growth. However, they still lag way behind the longer-serving producers.

Several new carbon fibre manufacturing units are planned for the near future in China in particular. They are generally associated with acrylic fibre producers, which supply the precursors (PAN).

The global capacity for production of carbon fibres was 111, 785 tonnes in 2012. In 2016 it is set to reach 156,845 t and in 2020 set to reach 169,300t. In relation to these nominal capacities, actual production only represents a part, evaluated at 60% in 2012, 68% in 2016 and 72% in 2020.

There are several hundred commercial grades of carbon fibres, 80 to 90% of which are "standard" fibres; the remaining 10 to 20% are high or intermediate modulus fibres.

In terms of the demand, the total market for carbon composites should increase from \$ 14.6bn in 2012 to \$ 36bn in 2020 with an average growth of 13%/year, which would correspond to a demand of 110,000 tonnes of carbon fibre. Hence the overcapacity mentioned previously. This situation could contribute to keeping the prices at a competitive level.

The domains of application

A recent study undertaken by Lux Research reckons that the growth of the market for carbon composites (fibres, nanotubes, graphene) will be highest in the wind energy

sector and is forecasting growth levels of 16%/year by 2020 and a twofold increase within 5 years. The most promising sectors are aviation, wind farming and motor vehicles. The market for petrol and gas will experience a relatively slow growth - 5%/year - due to the level of conservatism in this area. Sports does not constitute a big sector in terms of volumes, but clients are prepared to pay for performance.

Aviation

Aeronautical structures are still the key application for high modulus carbon fibre composites, used as a substitute for aluminium in particular.

The military sector is in need of several different products - helicopters, satellites, rockets, jets, etc. - with stringent specifications regarding materials: the temperatures are extreme and the environments varied, from the radiation experienced by spacecraft to the ocean surroundings experienced by jets. The advances made have been - and are still being - passed on to the commercial aviation sector.

Thanks to the more resistant, more rigid fibres and more ductile resins, thermosetting composites have established themselves in the construction of structural components - fuselage, wings, substructures. 50% of the structure of the Boeing 787 or the A350 XWB uses composites, compared with 8% for the previous generation of aircraft. Composites are also used in the wings, tailplane and other components of aircraft of all sizes, flying machines or drones.

The demand for carbon fibres in the aviation industry in 2015 should represent over 13,000 tonnes, 60% of which will be in commercial aviation.

The aviation industry is growing and the future of composites is guaranteed in this area. But there is some uncertainty regarding the rate of growth that can be put down to delays and excessive costs that can lead to order cancellations which represent significant quantities of composites.

In the aviation sector, the composite parts are often the big structures (10m for example), which pose some very specific challenges to the designers:

- distortions due to temperature effects;
- distortions in the materials during manufacture;
- difficulties in measuring large that can be relatively flexible;
- handling problems when assembling the structures;
- profitability issues that are related specifically to the fibre placement operations.

These issues are increasingly well-understood, but developments are still possible. Developments in the area of:

- multi-functional materials: structural, thermal conductors, resistant to varied environments;

- speeding up the baking times;
- speeding up the design times and design to market times;
- certification and qualification of materials;
- testing.

Thermoplastic composites are restricted to internal fittings. However, their toughness makes it possible to make lightweight designs. They are quick to put into use and they are robust. They have good FST (fire, smoke, toxicity) properties and can be recycled. And therefore, advances are continuing to be made in the area of structural parts such as the leading edges of the wing in polyphenylene sulfone or partitions in polyetherimide + carbon.

Motor vehicles

In 2050, there will be 2.5 billion vehicles in the world, which represents a production of 100,000 vehicles/year.

The ecological challenge is therefore considerable. In Europe, the objective for reducing emissions is to reach 125 g/km in 2015 and 95 g/km in 2020. We know that a 10% gain in mass makes it possible to reduce consumption by 7%. 200kg/vehicle must be saved by 2015-2020.

Reducing fuel consumption, decreasing greenhouse gas emissions, reducing material consumption, etc. Composites are at the forefront of the developments being made in this area, with Germany and Japan leading the way. It would be possible to save 50-60% in weight by replacing the steel used in electric vehicles and 30% by replacing the aluminium with carbon fibre composites.

The demand for composites in motor vehicles is very high. The Japanese manufacturer, Teijin, estimates that, in order to attain the objectives for reducing CO2 emissions, carbon composites will attain 5-7% of all new vehicles in 2020.

The low margins of the automotive sector and the lengthy development process have slowed down the introduction of carbon composites in motor vehicles, but the growth in the coming years will be significant, 17%/year. New designs such as the electric and hybrid vehicles provide opportunities to update many parts.

A decisive step in the process for introducing carbon-reinforced composites for their long-term use in the automotive industry was made with the launch of the BMWi3. This fully electric vehicle is fitted with a carbon fibre reinforced composite passenger cell. 30,000 units of this car will be manufactured each year and it is the product of a partnership between BMW and SGL Group that built a specific production plant for this application.

The development of composites in mass-produced vehicles (tens of thousands per year) will depend on the success of this model. In any case, designs will have to be revised, processes updated and automation will be needed.

- To ensure a high level of mechanical resistance, the alignment of the fibres must be controlled as well as the handling of the pre-shaped parts and their placement in the tools; until now the techniques used to achieve this were above all manual, slow and difficult to automate.
- The application techniques (RTM, compressions) that must be incorporated in the automated production lines designed for mass production must be optimised with this in mind. The cycle times that include impregnation times, polymerisation times and baking times must be shortened.

Consequently, for example, the German machine manufacturers, Dieffenbacher and KraussMaffei, have come together to develop such automated lines for the high pressure RTM process (HP-RTM). These systems include a preform manufacturing unit, a shaping press and a finishing station. Firms like BMW, Audi or Daimler are already equipped with these systems.

Globe Machine Manufacturing (US) developed a high speed out-of-autoclave sealed press. The cycle time is 17 mins. It goes from 0.2 to 25 bars at a rate of 5.5MPa/min and from 43°C to 288°C with direct heating and then to 482°C with indirect heating.

Plasan uses composites in the Corvette Stingray 2014. The prepreg carbon is placed in the machine and sealed with a 12.7mm-thick silicon film. The mould is loaded in the sealed chamber of the Globe press and pressure is applied using compressed air (< 10 bar) to compact the prepreg that is heated up by the machine.

Quickstep Composites (US) uses an automated resin infusion technique with quick polymerisation. The process called "resin spray transmission" (RST) starts with the resin being projected into the open mould. A carbon preform is then placed on the surface of the sprayed mould. The latter is closed and the part is polymerised. The machine is fitted with a quick heating and cooling system (30 °C to 40 °C/min). The cycle time is 10 mins, the costs of the machinery are low, the automation is simple to use and the parts manufactured in this way are category A parts.

- Current resins generally have cycle times that are too long and therefore incompatible with mass-production techniques. Suppliers are working to improve the materials and therefore increase the saturation speed of the preforms and the crosslinking times. Consequently, Momentive's Epikote/Epikure systems have been able to reduce their baking times from 90 mins in 2000 to 30 mins in 2009. They are currently down to 3-5 mins and should reach 2 mins in 2015. The viscosity of the resins is also a key factor since the percentage of fibres used in the structural parts is 50% or more, which makes impregnation difficult to achieve.
- The control techniques, used in the aviation sector, must be adapted as well as the design methods (especially in terms of impact resistance).

Wind energy

The wind energy industry, that is growing very rapidly, will be the first sector to use these products in the coming years, ahead of the aviation industry, and it will represent 60% of the entire market.

For 7-8 years now, wind energy, driven by the instability of petrol prices and public incentives, has been undergoing rapid growth; it is reasonable to imagine that this growth will continue into the future. We know that the production of commercial wind turbines has grown by a multiple of 115 in 20 years.

For economic reasons, turbines are increasingly large and increasingly powerful. The average height of the rotors has risen from 25m in diameter to over 80m, with some models reaching 123m for 5.0 MW, with a weight of 17700kg per blade. At the moment, 40,000 blades are being manufactured every year.

Blade production could reach 82,000 in 2019, 6% of which would be made of carbon composites.

The Wind turbines that use longer blades and have a swept area that is larger produce more power for a lower cost per kWh. They can also work with low wind speeds, which helps to bring them closer to urban areas. At the same time, wind turbines must have a service life of 25 years with minimal maintenance, particularly for offshore wind farms where this is especially difficult.

Structures must therefore respond to increasingly rigorous constraints; they are built in increasingly large batches under increasingly stringent standards. These requirements that are set out in terms of precision, dependability and quality control filter down to the entire value chain to reach the suppliers of the materials.

The wind turbines are made of a polyester or epoxy composite reinforced with glass or carbon fibres with a foam core made of PVC, PET, SAN or balsa, glued bonds, a polyurethane coating and metallic conductors.

For every kW installed, 10kg of materials are needed for the blades, that is, 75 tonnes for a 7.5MW turbine.

This sector consumed 15,000 tonnes of carbon fibres in 2012 and could reach 23,000 tonnes in 2016 and 37,000 tonnes in 2020. These figures are however less optimistic than those that were forecast by the specialists in previous years. Indeed, even if the pressure to use renewable energies is high and if legislation is increasingly restrictive, the policies of the public authorities in terms of subsidies and development strategies (offshore wind farms, etc.) can have a decisive influence on the market for composites.

Reduction in the costs of carbon fibres.

Until recently, it was only possible for the high-tech markets or certain niche markets to take advantage of the excellent properties of carbon fibre composites given the

high prices practised in these markets. Technical advances in the manufacturing of fibres and the development of new precursors should have an effect on costs in the years to come.

The following four key domains are being looked at:

- Carbon fibres are now made by the carbonisation of an acrylic fibre precursor (PAN). These PAN fibres are what govern 50% of the cost price of the carbon fibre and their cost is linked to the price of petrol. The cost of producing carbon fibres is therefore on the rise. Alternatives must therefore be found. Consequently, a fibre made from lignin would be 30 - 50% cheaper than a fibre made from PAN. A development conducted at the Oak Ridge National Laboratory on carbon fibres using a new precursor, polyethylene, could cause a major transformation in the markets. Using a multi-component extrusion process and suitable threading devices, researchers can make filaments from 0.5 to 20 μm . The bundles of filaments are then subjected to a sulphonation treatment that combines them into fibres, rendering them infusible and giving them certain functional features. A high-temperature carbonisation treatment then eliminates certain components that are transformed to the gaseous state, leaving a carbon matrix.
- Other research is being focused on alternative treatment technologies: the conversion of PAN fibres by diffusional thermal stabilisation and oxidation takes time, consumes lots of energy and is costly. A "simple" acceleration of the oxidation process could reduce the price of the carbon fibre.
- The plasma and microwave technology (Microwave Assisted Plasma, MAP) must ultimately replace the carbonisation ovens used in conventional processes. This technology should speed up the conversion.
- Although the surface treatments and adaptations for the end use have very little impact on costs, they do have a significant impact on performance. Suitable 'formatting' techniques must be developed to be able to use inexpensive carbon fibres.

Finally, the polyolefin precursor combined with new thermal treatments (oxidation by atmospheric plasma, carbonisation by microwave plasma) could reduce the cost of the carbon fibre from 21.2 \$/kg in 2012 to 10.5 \$/kg at the level of the pilot scheme in 2017.

Conclusion

Carbon fibre composites have a great future ahead of them, even if some uncertainties make it impossible to accurately foresee how the market will develop.

Whether it is in the fibres themselves and the reinforcements, the thermoplastic or thermosetting matrices, the implementation processes or the design tools, there are a vast array of innovations.

The task of reducing the cost of the fibres, which has already begun, will open up new promising areas.

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This article forms part of a series of technical articles aimed at industrial manufacturers wishing to increase their knowledge of the field of composite materials. It was produced within the Composites project (www.pluscomposites.eu).

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