Removing barriers for bio-based composite production with novel water-insensitive cure systems

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The use of bio-fibers in unsaturated polyester resins has to date been limited since the fibers need to be dried and processed immediately after to obtain a high quality composite. Curing systems that remove this costly and time-consuming barrier have now been developed. Roel Zuijderduin, Technical Development Manager, AkzoNobel Polymer Chemistry, and Ron Verleg, R&D Program manager, DSM Composite Resins, explain how manufacturers can replace their glass reinforcement with the right bio-fibers and produce light-weight composites with a much lower carbon footprint.

Bio-composites are defined as fiber reinforced polymeric composites based on natural (or bio) fibers and/or bio-renewable-based resin systems. Over the last decades, two main trends have driven the composite industry's interest in the use of bio-renewable-based raw materials in the production of fiber reinforced polymer components:

(1) the trend from fossil-derived resources to non-fossil based bio-renewable raw materials; and
(2) the weight reduction of structural and non-structural composite components.

The availability in bio-renewable resources in the last 20 years has resulted in the development of bio-based thermosetting resins with bio-content reaching up to 50 wt%. In 2010, DSM Composite Resins launched several grades of styrenated bio-based unsaturated polyester resins for application in automotive and infrastructure products. In 2014 the company's styrene-free bio-based vinyl ester resin was introduced under the Beyone (TM) brand for wind turbine blade applications.

The specific stiffness of natural fibers allows composite fabricators to increase the stiffness per kilogram of material resulting in lighter composite parts with comparable stiffness to glass fiber reinforced composite alternatives. This allows designers and engineers to develop lighter weight alternatives to current glass fiber reinforced composites.

Bio-fibers in unsaturated polyester resins

At the moment the use of bio-fibers is predominantly limited to the car industry where polypropylene is used as the matrix material. The use of bio-fibers in epoxy resins is also widespread. In unsaturated polyester (UP) resins the use of bio-fibers has so far been difficult because the water content in the fibers deteriorates the curing process. The fibers therefore need to be dried first. This, requires an expensive oven, which is also costly in daily operation consuming energy and having a negative impact on CO_2 emissions. In addition the dry fibers need to be stored under certain conditions to avoid re-uptake of moisture when exposed to air. For this reason the use of bio-fibers in UP resin composites was not successful thus far.

In 2012 AkzoNobel and NPSP, a Dutch manufacturer of sustainable, fiber reinforced plastics, introduced the Nouryact™ cobalt-free accelerators, which are not sensitive to the presence of water during the cure of an unsaturated polyester resin. This has led to new opportunities for working in moist conditions and using wet filler materials such as, for example, non-dried bio-fibers. AkzoNobel, in cooperation with Polymer Science Park (PSP) and DSM Composite Resins, has now proven that structural bio-composites based on non-dried flax fibers and different grades of unsaturated polyester resin can be produced in a vacuum infusion process.

Water insensitive

For a number of years AkzoNobel has been developing and promoting replacement products for cobalt carboxylates for curing UP resins. This is in anticipation of possible reclassification of cobalt carboxylates to CMR 1B in the near future. The products are marketed under the brand name Nouryact. Apart from being more user friendly the new curing technologies provide significant benefits over cobalt.

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One of the spin-off benefits of Nouryact is that these products are insensitive to water and can promote cure in water-rich environments. This is of particular interest for companies using large amount of fillers which could potentially be contaminated with water, and also for companies working in the monsoon season or using fillers which contain high amounts of water, such as natural fibers. Bio-fibers are known to contain up to 12% water. Curing such water-rich composite systems is challenging if not impossible when using standard cobalt-based cure systems. Cobalt carboxylate is prone to hydrolysis under the influence of water and then is unreactive for the curing process.

Table 1 shows the reactivity data for a styrene-based high reactive orthophthalic resin to which a certain amount of water is added. Nouryact CF12, a copper-based complex, is compared with a standard cobalt accelerator. Intake levels are in phr (parts per 100 resin parts).

The data clearly show that with cobalt the curing collapses completely when water is present, whereas with Nouryact CF12 the cure remains good, even with up to 6 wt% water in the resin.

TABLE 1

Reactivity data for a styrene-based high reactive orthophthalic resin containing different percentages of (added) water

Resin intake (parts)	100	100	100	100	100	100
Water intake (wt%)	0	2	0	2	4	6
Butanox M-50 (medium reactive MEKP) (phr)	2	2	2	2	2	2
Cobalt-1% solution (phr)	1	1				
Nouryact CF12 (phr)			1	1	1	1
Gel time (min)	6	69	8	13	39	61
Time to peak (min)	15	72	12	22	54	82
Peak exotherm (°C)	170	27	167	140	126	121

Curing non-dried bio-fibers

The findings above indicate that curing of UP resin with non-dried bio-fibers should be possible using Nouryact. In 2012 NPSP generated further proof for this approach. The company cured standard UP resin in a resin transfer molding (RTM) process using wet and dried fibers and noticed that curing with Nouryact worked very well whereas the cobalt-based cure system failed.

Figure 1 shows panels manufactured with dry and wet flax fibers and cobalt and Nouryact CF32 (a metal mix accelerator). The wet fibers in combination with cobalt (panel 2) did not cure at all, whereas Nouryact CF32 in combination with the same wet fibers (panel 4) showed excellent cure. In addition, the mechanical properties did not deteriorate due to the presence of water.

It has always been assumed that it is essential to dry bio-fibers to achieve good mechanical properties. This might be true for a cobalt-based cure system but not when using a Nouryact system. The experiments discussed below demonstrate that drying of the fibers is not necessary and that the mechanical properties obtained using wet fibers are good, provided the proper cure system and resin are used.

Mechanical properties

In the past 12 months two students at the Polymer Science Park (PSP) in Zwolle, The Netherlands, have been working under guidance from DSM Composite Resins and AkzoNobel Polymer Chemistry to develop a bio-composite demonstrator using non-dried flax fibers as reinforcement and a series of UP resins from DSM cured with a Nouryact system. Unidirectional (UD) laminates were manufactured using a vacuum injection molding process at room temperature (Fig. 2) and evaluated on tensile and flexural properties.

The raw materials used are shown in the tables below:

AkzoNobel Polymer Chemistry provided the cure systems:

Nouryact CF12	Copper-based accelerator
Nouryact CF13	Copper-based accelerator
Inhibitor NLC-10	tert-Butyl catechol
Butanox M-50	Medium reactive methyl ethyl ketone peroxide

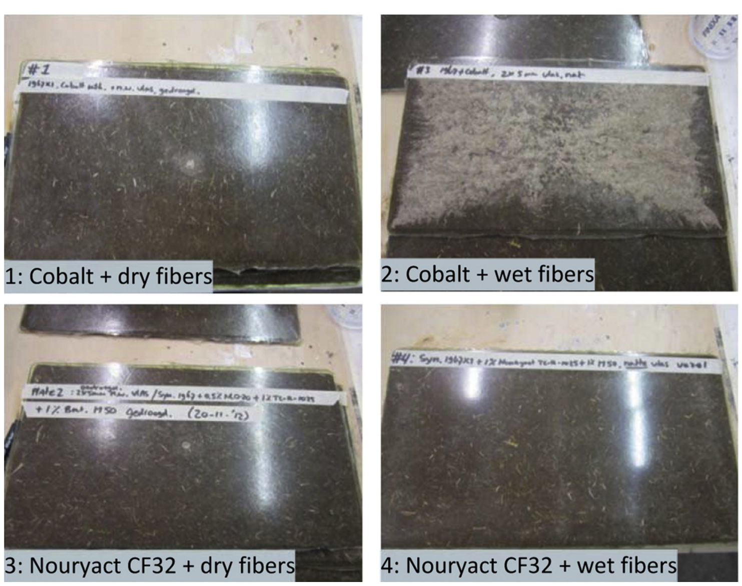

FIGURE 1

Laminates produced using wet and dry fibers. Picture courtesy NPSP.