New Material: Vitrimers Promise to Impact Composites

Denis A. Kissounko, Philip Taynton, Chris Kaffer

Strong and durable like thermosets, yet moldable and recyclable like thermoplastics, *vitrimers* are "malleable thermosets" which are challenging the status quo in the composites industry. Mallinda, a startup company founded by some of the pioneering inventors of the technology, is developing malleable CFRP's for rapid (~30 second) production cycle times.

Background

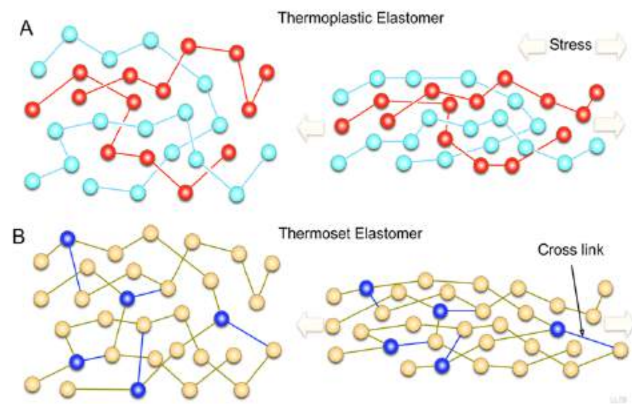

Figure 1. Thermoplastics vs. Thermosets

For over 50 years, synthetic polymers have been divided into two general categories: thermosets which have excellent mechanical properties, but must be irreversibly cured; and thermoplastics, which can be melted down and reprocessed, but have inferior thermal and mechanical properties (Figure 1)[†]. This characteristic allows thermoplastics to be molded relatively quickly for high volume manufacturing, using techniques such as injection molding. Futhermore, these materials can be recycled by melt-processing. On the down side however, the majority of thermoplastics are susceptible to mechanical deformations and creep at elevated temperatures; therefore, they don't have a sufficiently robust dimensional stability at high temperature. In addition, commercial thermoplastics are typically of higher cost in comparison to analogous thermoset resins. Thermosets are the resins of choice for structural composites applications, such as aerospace composite part fabrication where stiffness and durability are critical. While thermoset resins offer significant performance benefits compared to their thermoplastic counterparts, significant cure times for thermoset resins make them unsuitable for high volume applications such as automotive. Furthermore, due to the inability to reprocess thermoset resins after they've been cured, these materials are refractory to repair and remolding. Recently, this paradigm has been challenged by the arrival of malleable thermoset materials, also known as vitrimers.

Vitrimers are covalently-bonded crosslinked network polymers, like thermosets, but with the distinguishing feature that the chemical bonds in the network are exchangeable. Typically, a catalyst is included in the resin formulation, which enables bond exchange reactions when the material is heated above the vitrimeric transition temperature[‡]. When vitrimers are heated to the

[*] chris@mallinda.com; denis@mallinda.com; philip@mallinda.com

[†] Alkonis, J. & MacKnight, W. *Introduction to polymer viscoelasticity 2nd ed.* Wiley, New York, 1983

[‡] T_v Montarnal, D.; Capelot, M.; Tournilhac, F. & Leibler, L. Silica-like malleable materials from permanent organic networks. *Science* **334,** 965-968 (2011)

malleable state, their total crosslink density remains constant, but the rate of bond exchange increases with temperature (see Figure 2), since all chemical reactions run faster at higher temperatures. This leads to a gradual decrease in viscosity with temperature, which differs from the relatively abrupt drop in viscosity associated with the melting transition of thermoplastic materials. The reversible nature of vitrimers enables welding, molding, reshaping, and recycling of fully cured materials.

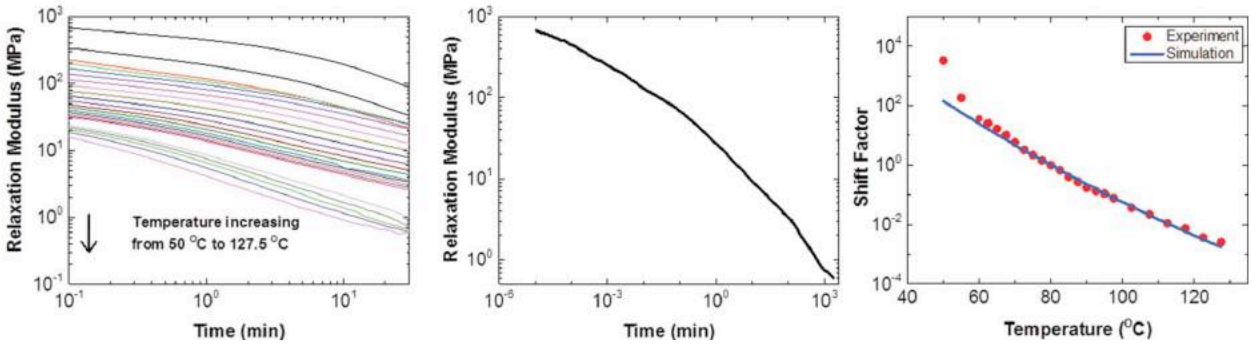

Figure 2. Temperature-dependent stress relaxation behavior of vitrimers shows that malleable flow of vitrimers correlates with reaction-rate of bond exchange.

Mallinda co-founders invented the first known vitrimeric materials which do not require a catalyst, and behave like traditional thermosets under ambient conditions. Mallinda's catalyst-free vitrimers exhibit malleable behavior only when heated above the glass transition temperature (T_g) of a given formulation. This means that below the glass transition, the polymer network is frozen, and is thus indistinguishable from a traditional thermoset. Mallinda's vitrimeric polyimine platform is also quite tractable. T_g, for example, can be tuned with formulation from below room temperature to upwards of 200º C.

What does this mean for composites?

The Mallinda team has shown that when structural composite materials, like carbon fiber reinforced plastics (CFRPs), are made using vitrimeric resins, several distinct advantages arise. First, unlike traditional thermosets, vitrimeric composite materials can be reprocessed after being cured. Fully cured materials can be heated, remolded, and reshaped without losing their original strength. Second, these composite materials can be heat-welded together to form monolithic cured multilayer laminates. Finally, CFRPs made with vitrimeric resins can be easily recycled in a solution-based process in which the fiber and resin can be separated, recovered and reused to their original strength[§].

Mallinda is using vitrimer technology to develop a new class of "pre-cured pre-impregnated laminates (prepreg)" which will impact current prepreg users as well as high throughput producers who currently rely on Resin Transfer Molding (RTM) processes with quick-cure resins. The envisioned pre-cured prepreg malleable composite materials can be cured upstream in the manufacturing process as individual laminates in a roll-to-roll process, and stored indefinitely at

[§] Taynton, P.; Ni, H.; Zhu, C.; Yu, K.; Loob, S.; Jin, Y.; Qi, J.; Zhang, W. "Repairable Woven Carbon Fiber Composites with Full Recyclability Enabled by Malleable Polyimine Networks" **Adv. Mater. 2016**, **28**, 2904–2909 room temperature. To manufacture composite parts, any number of plies can be heated to the material's specifically-formulated T_g, laid up in a mold to the desired thickness, and both consolidated and formed into a final part through compression forming** (in a video demonstration, a 20 second compression forming step is used: https://youtu.be/o97q-2oDPfQ). Within 1-minute the formed part can be demolded and handled immediately, with full rigidity occurring upon cooling. Scrap material can be further repurposed to form other parts, or can be recycled in the solution-based process wherein the fiber and resin materials are recovered and reused (see demonstration video at https://youtu.be/FNd2bBt8CMU).

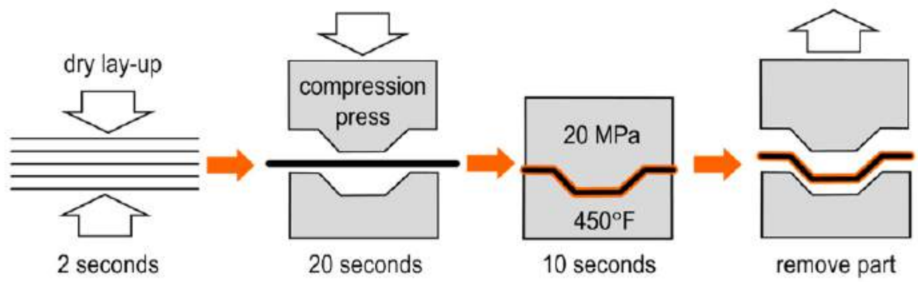

Figure 3. High speed consolidation and molding for Mallinda's malleable materials

At present, prepreg materials offer several advantages over other CFRP manufacturing approaches such as resin transfer molding (RTM) processes. Prepreg materials offer guaranteed (rather than estimated) fiber/resin ratios, and consistent mechanical properties. They are more reliable than RTM materials, as void space, and trapped bubbles are common problems for RTM materials. They offer a simpler, cleaner, and safer lay-up process, since there is no need to handle wet chemicals on site, as opposed to RTM. The drawbacks of traditional thermoset prepreg materials are related to shelf-life, refrigeration logistics, cost, and a higher scrap rate.

Due to the irreversible nature of traditional thermoset curing, prepreg materials, are partially cured in the roll-to-roll fiber impregnation process (called B-staging), and immediately frozen to prevent completion of the curing process until the material is used to manufacture a composite part. The manufacturing step typically involves vacuum bagging the lay-up over a mold, followed by autoclave treatment for up to several hours to cure the resin. Compared with current prepreg materials, pre-cured prepregs offer the advantages of extended shelf-life stability, ambient shipping and storage (no refrigeration), faster cycle time (no waiting for cure during layup/consolidation), and recyclability of cured scrap and end of life material. If the pre-cured prepreg materials are made at sufficient scales, these materials will become available at a fraction of the price of present prepreg materials.

How is it made?

While there are many features which are unique to malleable thermosets, one feature which is shared with traditional thermoset materials is the initial curing step. Similar to traditional thermoset

** Taynton, P.; Ni, H.; Zhu, C.; Yu, K.; Loob, S.; Jin, Y.; Qi, J.; Zhang, W. "Repairable Woven Carbon Fiber Composites with Full Recyclability Enabled by Malleable Polyimine Networks" **Adv. Mater. 2016**, **28**, 2904–2909 materials, malleable thermosets must be formed in a polymerization reaction in which a liquid precursor solution is cured into a polymeric solid. As with traditional materials, this initial curing step is the optimal step for combining the polymer with reinforcing fibers, since the low viscosity of the uncured resin enables consistent and even flow into, and impregnation of, the fine reinforcing fibers. This means that vitrimeric resins can be infused into reinforcing fibers using existing prepregging equipment. A key differentiation in processing vitrimeric prepreg materials is that the resins are cured in-line immediately after resin infusion. Mallinda has partnered with an existing prepreg supplier to pilot the infusion process with initial success, and the company is moving to scale-up its industrial processing for its introductory product offering.

Why are vitrimer composites easier to recycle?

Due to the same dynamic covalent bond exchange phenomenon described above, polyimine resins are intrinsically recyclable in a solution of some of the resin's precursors. The precursors in solution undergo bond exchange reactions with the vitrimeric resin at room temperature, leading to gradual dissolution of the polymer.
At this point, the solubilized resin solution can be separated from the fabric. Upon the addition of complementary precursor, the resin can polymerize again and can be reused in a new cycle (**Error! Reference source not found.**). Mallinda has incorporated up to 30% recycled resin onto new materials with no loss in mechanical performance.

Figure 2. New recycling paradigm of the polyimine-based composites

As the recycling process does not stress the fiber in any way, virgin-like fiber materials are recovered, with no loss in mechanical performance.

What is the expected cost of vitrimer resins?

Mallinda's resins are prepared from high-volume commercially-available precursors, which makes scaling, and supply chain manageable. It is expected that malleable resins will be cost competitive with epoxy resins when developed to similar scales. Due to other efficiencies, Mallinda expects its prepregs to be less expensive than competitive materials at launch.

What are Mallinda's near-term and long-term plans?

Currently, Mallinda is exploring the following markets as the entry points for precured prepregs: sporting goods, aerospace, automotive, wind energy, and gas storage pressure vessels.

Due to the relatively low barriers to entry, Mallinda's first market is within the sporting goods segment. As such, Mallinda has been developing its first product line of moldable protective sports gear with an OEM serving a branded sporting goods company. The company's initial product offering enables an end-user to heat Mallinda's protective materials to "activate" malleability to fit the fit the specific contours of the end-user's body and extremities. Mallinda's enabling technology is both fully malleable passes the impact test qualification required by National Operating Committee on Standards for Athletic Equipment (NOCSAE). Mallinda's partners will undergo an initial product rollout in 2018.

While the sporting goods vertical market represents the company's beach head market, Mallinda's vitrimeric composite maerials are poised to make a significant impact within the transportation segment.

CFRPs offer the most efficient means of reducing the mass of traditionally manufactured legacy metal parts/products without sacrificing mechanical performance (Table 1). However, despite the promise of CFRCs in vehicle lightweighting, their adoption has remained limited due to manufacturing challenges resulting in high costs, and challenging end-of-life material management. These challenges must be overcome, as lightweighting targets – and thus vehicle efficiency targets – cannot be met without carbon fiber composites.†† Vitrimer composites address both of these challenges and improves the economics of CFRP part production by improving manufacturing cycle times by enabling consolidation and compression forming of prepreg materials in a single step for sub 1-minute cycles times.

Table 1. Lightweighting potential of materials

Material	Density (g/cm^3)	Comparison to steel			
		Strength/density	Modulus/density	Cost	Mass reduction potential
Mild steel	7.87	1	1	1	0%
High-strength steel	7.87	1.86	1	0.9–1.2	10%
Adv high-strength steel	7.87	3	1	0.8–1.5	10%–28%
Gen 3 high-strength steel	7.87	7	1	1.0–2.0	15%–30%
Ceramics	3.9	0.7	3.05	1.5–3.0	10%–30%
Sheet molding compound	1.3–1.9	4.39	1.16	0.5–1.5	20%–30%
Glass fiber composites	1.4–2.4	4.74	5.75	0.9–1.5	25%–35%
Plastics	0.9–1.5	0.82	0.08	0.7–3.0	20%–50%
Aluminum	2.7	3.95	1.02	1.3–2.0	30%–60%
Titanium	4.51	4.73	0.98	1.5–10	40%–55%
Metal matrix composites	1.9–2.7	5.41	35.28	1.5–3.0	50%–65%
Magnesium	1.74	3.66	1.02	1.5–2.5	30%–70%
Carbon fiber composites	1.0–1.6	20.9	5.41	1.5–5.0	50%–70%

While the benefits of vitrimer technology will benefit the thermoset composite industry in general, the automotive segment will be significantly impacted should Mallinda's technology be adopted. Decreasing vehicle weight is one of the primary methods for improving vehicle fuel efficiency, and the integration of carbon fiber composites represents the most promising pathway to vehicle lightweighting. By improving the cost effectiveness of CFRPs through improved cycle times etc, vitrimers will be catalytic in the lightweighting of light, medium, and heavy duty vehicles. By enabling the recycling of carbon fiber composites, this technology will not only divert waste from landfill, but will also reduce the embodied energy in carbon fiber carbon fiber from end-of-life products.

In addition, based on the cost of Vitrimer materials, and the scale of the process, the company estimates that it can produce prepreg CFRP materials in the range of $11 to $16 per pound, which is only a fraction higher than the cost of bare fiber. As a result, Mallinda will enable greater adoption of lightweight composites in adjacent industries such as wind power.‡‡

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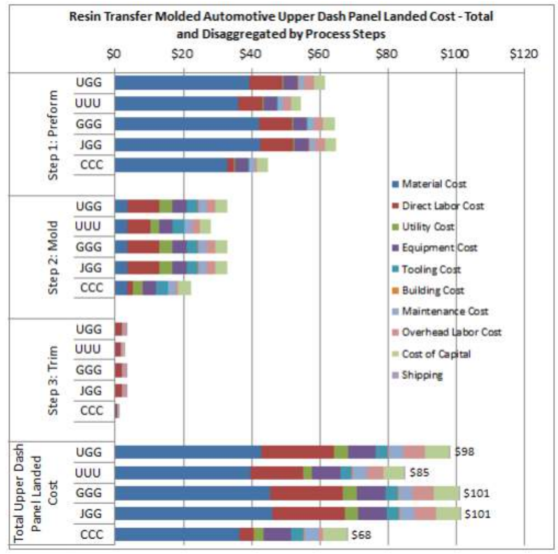
†† U.S. DOE, 2015. Quadrennial Technology Review: An Assessment of Energy Technologies and Research Opportunities. Available online: http://energy.gov/sites/prod/files/2015/09/f26/Quadrennial-Technology-Review-2015_0.pdf

‡‡ Alan Wheatley et al., 2014. Low-Cost Carbon Fibre: Applications, Performance and Cost Models. *Advanced Composite Materials for Automotive Applications: Structural Integrity and Crashworthiness.* John Wiley & Sons, Ltd.

Figure 5[§§] provides a window into the cost savings potential of vitrimer technology. By eliminating the need for a pre-forming step, all non-materials costs are removed from the "preform" step (Step 1 in Figure 5). Furthermore, by eliminating the need for resin transfer molds and autoclaves, Mallinda's customers can eliminate most of the capital, utility, and labor costs of the "molding" step (Step 2 in Figure 5). Mallinda expects an all-in production process cost reduction of roughly 25% to 30%.

Figure 5. CFRP Mfg Costs



Finally, it is well known that the overall process for making carbon fiber is an energy intensive process contributing to the high cost of carbon fiber. Thus the key energy benefit of Mallinda's pre-cured malleable thermoset prepreg materials is in the manufacturing energy savings related to part production and ambient solution-based recycling of scrap and end-of-life products for the recovery of full length and woven fibers.

§§ Figure source: Sujit Das et al., 2016. Global Carbon Fiber Composites Supply Chain Competitiveness Analysis. Clean Energy Manufacturing Analysis Center. National Renewable Energy Laboratory. ORNL/SR-2016/100 | NREL/TP-6A50-66071. Available online: http://www.nrel.gov/docs/fy16osti/66071.pdf