Composite forming post-manufacture: reducing complexity and de-risking manufacture

PALUBISKI Dominic R.[1,a *], LONGANA Marco L.[2], DULIEU-BARTON Janice M.[1], HAMERTON Ian[1], and IVANOV Dmitry S.[1,b]

[1]Bristol Composites Institute, School of Civil, Aerospace, and Design Engineering, Faculty of Science and Engineering, University of Bristol, Queen's Building, University Walk, Bristol, BS8 1TR, U.K

[2]Department of Chemistry, Material, and Chemical Engineering, Politecnico di Milano, Milan, Italy

[a]dominic.palubiski@bristol.ac.uk, [b]dmitry.ivanov@bristol.ac.uk

Keywords: Composites, Modular Forming, Multi-Matrix Systems, Post-Manufacture Forming

Abstract. Forming is a high-risk operation as the deformation of precursors, such as preforms or prepregs, is difficult to control. Aiming at de-risking manufacturing and improving processing logistics, a new forming concept is presented involving pre-structuring, *i.e.* producing fully cured flat structure with integrated formable hinge regions, and assembly, where the part is given the targeted shape using localised forming in the hinge regions. Such a technique becomes feasible if (a) the hinges are produced with the aid of covalent adaptive networks (CANs, cross-linked polymers that can flow when heated above a certain temperature), (b) the excess fibre length (that can occur in the process of forming) is incorporated at the pre-structuring stage. Hence, we pursue an idea of multi-matrix continuously-reinforced composites (MMCRC) with embedded fibre path features, where the main body of composites structure is produced with a conventional epoxy matrix and the hinged areas are produced with reformable CANs. The current paper explores the potential and limitations of this technology in manufacturing trials. It is demonstrated that the presented concept can yield high quality solutions. It is highlighted that an improved manufacturing procedure using specially designed and portable machinery would enable application of the MMCRC technology in the field, facilitating repair and efficient transportation.

Introduction

Manufacturing composite components typically includes high-risk forming actions that result in morphological defects that typically occur when reinforcement materials are conformed to produce geometric features. The evolution of such defects is difficult to avoid and may lead to a high rate of part scrappage. It is imperative to reduce material usage and time lost at the manufacturing stage to enable the adoption of composite materials in broader market segments and to provide lower cost solutions. The defects are formed either during layup/deposition or occur as part of consolidation/forming processes and can take on a range of forms, from the presence of resin-rich regions, to misaligned fibres, and delaminations [1,2]. If the defects remain in the cured component they may result in reduced in-service performance and can lead to an early failure.

There are various mechanisms for the formation of fibre-path defects, mostly associated with compressive forces acting on compliant precursor, constrained ply-to-ply and/or ply-to-tool interaction, excessive shearing, stack bending, or a combination of these. The resultant precursor deformations are typically manifested through ply buckling, fibre crimp, in-plane waviness, ply separation, and thickness variations, *etc.* The probability of defects evolving are particularly high with large movement/rotations of preforms, conforming materials to complex shapes, particularly those involving double-curvature, and for forming operations that occur across a majority of the laminate. The concept presented here addresses the challenge of defect mitigation in cases involving prominent bending and deep drawing deformations over corner geometries.

The proposed concept, named Multi-Matrix Continuously-Reinforced Composites (MMCRC), is illustrated in Fig. 1. Separate composite precursors comprising formable and non-formable material are connected by continuous reinforcement. Such composites have been proven to yield benefits through added functionality [3], improved mechanical performance [4], and potential for composite repair [5]. In a forming context, the allocation of different domains to different matrices permits the production of a 'flat' pre-structure first, followed by folding the formable regions to the desired geometry using localised heat and pressure. As the formable material takes shape, the unconfigurable material outside the forming zone restricts any undesirable deformations. By enabling local forming operations by introducing pre-structures, it is expected that better control of the material state is achieved at relatively low heat and pressure demands. Limiting the allowable deformations in manufacturing is known to result in defect mitigation, as observed by Turk *et al.* [6], where matrix patches were integrated into dry preform at critical locations. Alongside defect mitigation, additional benefits include a reduction in lay-up time; improved manufacturing logistics (where the flat pre-structure parts could be easily transported to assembly locations); locality of forming regions (allows the use of reformable matrices with challenging processing characteristics that would be prohibitive for the overall construction); reinforcement continuity (ensuring efficient load transfer); and the allocation of formable matrix strictly where it is needed (minimizing the impact of new materials on overall cost and permits greater design flexibility).

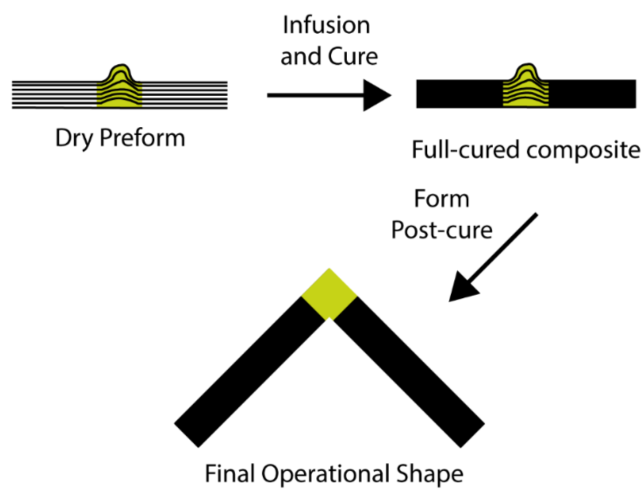

Figure 1. The post-manufacture forming concept, utilizing the MMCRC design concept.

Among the candidates for formable regions, covalent adaptive networks (CANs), also known as vitrimers [7], present a particular interest. These are a modern class of plastics that are similar to thermosets mechanically and in their structural chemistry, while (through the addition of reversible chemical side chains) are able to be reformed at temperatures in a similar manner to thermoplastics. What is particularly attractive about vitrimers is that (a) processing temperatures to form and reverse the cross-linking are relatively low (50-200 °C), (b) their viscosity is much lower compared to thermoplastics, (c) they are compatible with host thermosetting resins in non-reformable domains. Vitrimer resins can use typical thermoset chemistry for cure, such as epoxy ring-opening, allowing for improved chemical integration into the bulk thermoset structure. This

Materials Research Proceedings 41 (2024) 440-448 https://doi.org/10.21741/9781644903131-49

is an important feature for MMCRCs, although the major contribution to the strength of the vitrimer-thermoset interface is mechanical bridging of continuous reinforcement.

The main challenge of the presented concept is that the fibres are constrained within non-formable regions and cannot slide with respect to each other during forming. This creates a danger of trapping excess length and generating defects at the stage of folding pre-structures, as the fibre paths in upper and lower plies must be different when formed. Some of the forming challenges for MMCRCs were previously reported by Palubiski *et al.* [5]. Even though the laminate was not produced by bending the pre-structure, the high viscosity and long working times of the vitrimer led to fibre winkling and poor geometrical compliance. The study also revealed a high sensitivity of the forming operation to defect morphology and consistency of sample quality. In the context of pre-structuring, there is a particular need to incorporate the excess length at the stage of making the flat pre-structure. The current paper examines the feasibility of incorporating such features and examines the forming operations required to handling such pre-structures.

Concept Implementation: Materials, Feature Design and Manufacture

A L-shaped corner geometry was chosen for the demonstrator due to its frequent use within composite parts. In addition, this simple shape does not involve shear deformations, which needs to be addressed separately, and allows only pure bending to be examined. The shape of the excess feature must be designed in a way that respects the different fibre lengths after forming on the inner side of the corner, on the mid-plane, and at the outer surface. For simplicity, the inner side of the corner in the pre-structure was chosen to be flat, then each subsequent ply increases in length, thus creating an embossed region resembling a non-buckled wrinkle. The embossed region can be mathematically represented by hyperbolic secant, (Equation 1) [8],

$$w = A\ \mathrm{sech}(Bx) \tag{1}$$

where A is the highest point of the feature, and B is the shape parameter and can be roughly estimated as 1/8th of the embossed region span. The excess length, Δ, can then be calculated using Equation 2.

$$\Delta = A^2B/3 \tag{2}$$

To capture the correct excess length, the final target geometry was determined, with a calculated 3.5 mm final sample thickness, with a 6.4 mm inner corner radius. These values were chosen to align with standards on testing through-thickness strength of composites, ASTM D6145 [9].

Manufacturing samples for post-manufacture forming began with Vitrimax™ T100, a proprietary imine-linked vitrimer (*ex* Mallinda, Inc.) [10], which was mixed in accordance with the manufacturer's standard directions, 1:2.5 (epoxy:imine hardener), at 80 °C and left to cool and cure for 24 hours at room temperature. The cured vitrimer was broken into small pieces no larger than 5 mm^3 and evenly spread into a flat thin film mould, which was heated to 140 °C and then pressed at 6 bar for 2 hours to produce a 0.3 mm thick vitrimer film of width 20 mm and length 150 mm.

Dry carbon fibre (3K, 2x2 twill with a cloth weight of 210 g.m^{-2}, Pyrofil HT TR 30S 3L *ex* Easy Composites Ltd) [11] was used as the reinforcement. To produce the vitrimer region with the feature in the form of an 'embossed region', a bespoke tool was designed as shown in Fig. 2. The geometry of the recess was determined using the procedure described above so that the embossed region shape accommodated the excess length required for the outer ply of the final L-shaped panel. A $[0/90]_{15}$ laminate was laid up, with a single film of vitrimer between each ply and one on the top of the stack, placed so the 20 mm width straddled the recess. The fibres in the plies were orientated so that they were either aligned with the recess, or transverse to the recess in the bespoke tool. A laminate size of over 150 mm width and 100 mm length was used to ensure the final composite was large enough for forming. This lay-up was then sealed into a vacuum bag and the tooling placed externally on top of the bag.

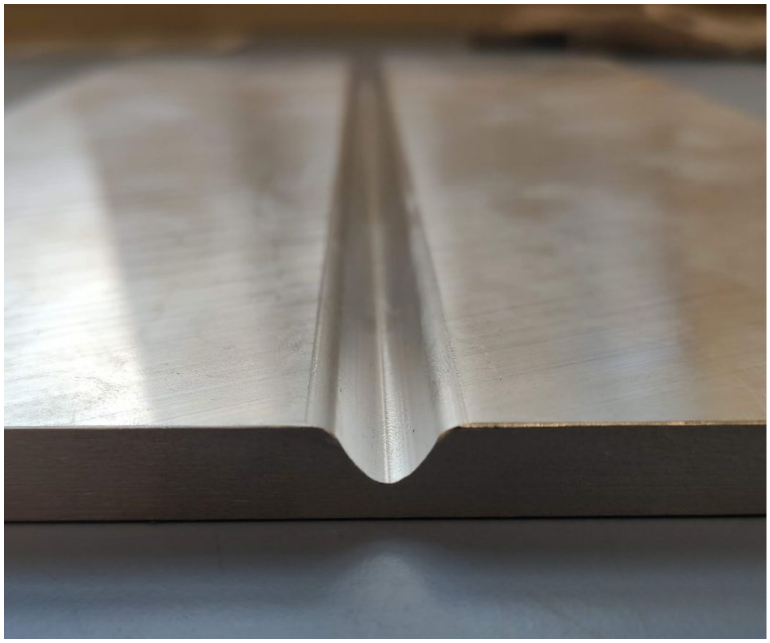

Figure 2. Mould for manufacturing pre-structures with the excess length feature. The width of the feature is 13.91 mm, with an embossment height of 5.95 mm. The mould surface is the outer surface of the corner in final shape.

The bagged lay-up and excess length tooling were hot pressed, following the cycle in Table 1, using a Hare 50TUP4C hydraulic press. After cooling to room temperature, the pressure was removed and the partially infused preform is then bagged flat for resin infusion of the dry preform arms. Gurit PRIME™ 37 and Ampreg™ 3X extra-slow hardener [12] (100:29 weight ratio respectively) was mixed and then degassed for 30 minutes before infusion. Once infused, the part was cured at 25 °C for 13 hours, followed by a post cure at 50 °C for 16 hours. Then 100 mm lengths were cut for the final manufacturing procedure of forming into the L-shape for the demonstrator.

Table 1. Manufacturing parameters for vitrimer hot press infusion.

Step	Pressure [bar]	Temperature [°C]	Time [minutes]
1	0	140	120
2	0.1	140	10
3	0.2	140	10
4	0.4	140	10
5	8	140	120

A polished edge of the produced panel was optically imaged prior to forming into the L-shape using a Zeiss Axio Imager.M2 microscope and the proprietary software. The epoxy thermoset arms showed good infusion with minimal voids or defects. The 'flat' formed panel embossed region shows a very resin rich structure with evenly spaced plies (Fig. 3). The fibres conform well to the excess length shape change with minimal observed defects. Due to the reduced

Materials Research Proceedings 41 (2024) 440-448 https://doi.org/10.21741/9781644903131-49

consolidation pressure within the embossed region, along with the viscous nature of the vitrimer, there is consistent sporadic dry fibre sections within the core of the tows. These were expected due to the forming conditions to create the embossed region. During final forming to the L-shape and consolidation, it was expected that the embossed vitrimer region would experience higher impregnation forces and so the vitrimer would infiltrating the inner fibres of the final formed component.

Figure 3. Pre-formed vitrimer embossed region.

Final Forming

To form the final L-shaped panel a ‘flat’ panel, as produced above, was heated locally in the embossed vitrimer region to above the vitrimer disassociation temperature and mechanically formed when the vitrimer is in this softened state. The initial forming was undertaken using a Shimadzu Autograph AGS-X electromechanical test machine with the panel and tooling placed within a heated chamber held at 140 °C, as shown in Fig. 4a. The support for the tooling consisted of a fixed bottom mount, an extender support, and a flat plate for the lower female tool. For the upper male tool, a fixed top mount, two extender supports, and a fixture attachment mount were used. Both sets of extenders were necessary to allow the placement of the tooling within the oven. For forming, a crosshead speed of 0.5 $mm.min^{-1}$ was used, which took roughly 2 hours. An average 50 N force was required throughout the forming process.

Final consolidation was undertaken using a hot press, as the extended tool supports required to produce the L-shape in a controlled manner in the oven mounted on the test machine, risked buckling. Instead, the male and female tools, with the panel between, were heated to 140 °C and then pressed at 6 bar for 60 minutes. The panel was allowed to cool to room temperature before pressure was removed.

Materials Research Proceedings 41 (2024) 440-448 https://doi.org/10.21741/9781644903131-49

Panel Manufacture and Forming Results

Despite successful realisation of the concept the suggested technique was sensitive to variation in manufacturing procedures. These included asymmetries resulting from uneven heating making the panels susceptible to unintended forming scenarios. As can be seen in the Fig. 4b some forming operations produced samples with significant wrinkling and defects. The multiple support linkages required resulted in multiple points with small degrees of movement as indicated in Fig. 4a. When the panel was being formed, an inaccuracy in positioning of material with respect to the forming rig or asymmetry in heating could result in asymmetrical forming that accumulates the excess length as it progresses. Additionally, the vitrimer extended beyond the embossed region by roughly 5-15 mm either side on all samples, and in this case the entire hinge region became soft and started to sag under its own weight. As the panel sagged, the resultant movement could unpredictably shift the centre of the embossment to misalign with the tooling.

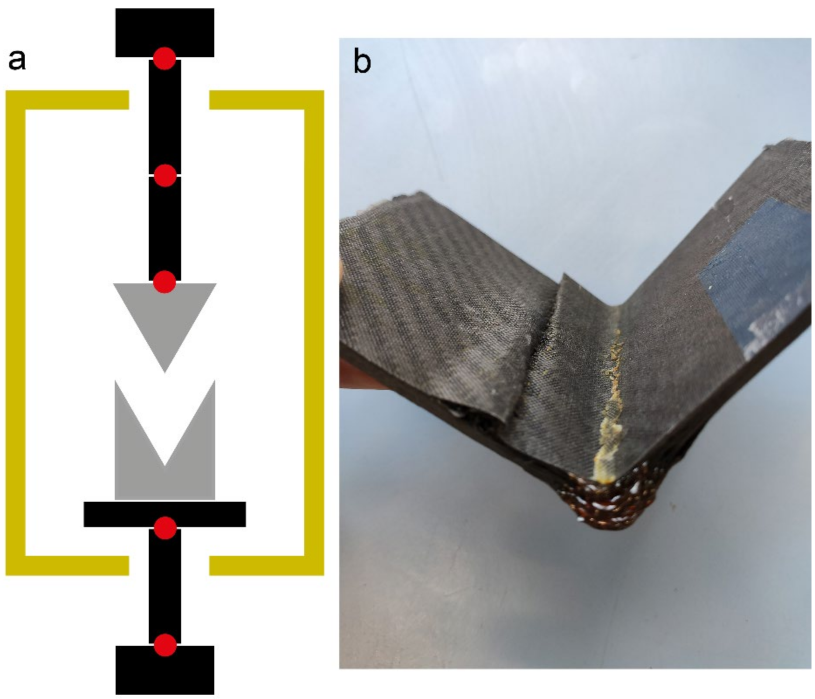

Figure 4. ‘a’ shows the forming set up with the tooling (grey), connected to the supports (black) within the oven (yellow). The points of linkage movement are highlighted with red circles. The second image, b, showcasing wrinkles produced during initial forming trials due to poor tooling alignment.

A primary conclusion is that a more highly controlled forming procedure is required for producing the pre-structure that utilises specifically designed machinery, rather than the set-up in the test machine. Such machinery would not only allow for more secure positioning of the panel, but also implement targeting heating of only the formable region. In addition, the current forming tooling applies forming forces (via the female tool) to the epoxy arms. Applying the force directly to the vitrimer region would allow for the final shape to be ‘pinched’ into form, and aid in reducing defect formation.

Even with the limitations of the apparatus used in the initial trials, successful forming operations were achieved, with Fig. 5 showing the three stages in the procedure to produce the final panel. At each stage a strip of material was cut from the panel to provide a coupon for further investigation. The top image in Fig. 5 shows a coupon from the 'flat' panel with the embossed MMCRC region before forming. The middle image in Fig. 5 shows a coupon after the first forming to the L-shape. There are observable delaminations occurring in this stage of the forming process, as the vitrimer cannot flow through the thermoset epoxy matrix and is also unable to flow fast enough through individual plies. This results in the vitrimer at the centre of the panel pushing the laminates apart, resulting in the delaminations. The slow forming time (2 hours with a 0.5 $mm.min^{-1}$ head speed) was decided upon to best minimize any delamination damage in the unrepairable epoxy regions. In the next consolidation step (not shown in Fig. 5), the delaminations were removed, with excess vitrimer resin squeezed out the ends of the corner region of the panel. The bottom image shows a coupon from the final formed panel after consolidation. The process was successfully able to form the composite panel with minimal defects observed. It is worth emphasizing that the manufacturing sequence de-risks not only forming but also infusions. Manufacturing the 'flat' panel is less susceptible to uncontrolled race-tracking typical for complex features [5] and minimises the risks of dry regions or excessive porosity.

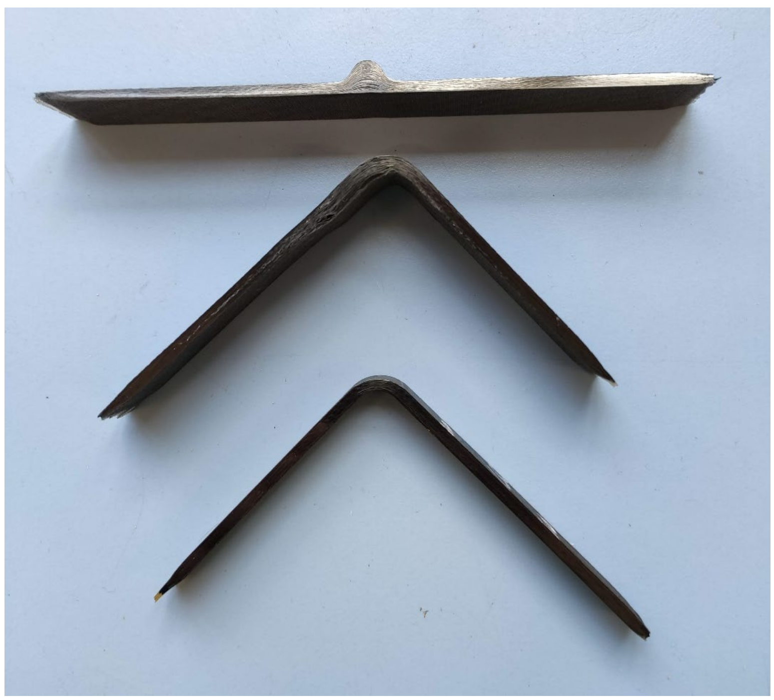

Figure 5. The three stages of manufacture outlined in this paper. Top is the initial MMCRC 'flat' panel, with a vitrimer excess length region and typical epoxy arms. The middle is the panel after forming, with ply separation present due to vitrimer flow. The bottom section is the final panel after consolidation.

A micrograph of the coupon after the final consolidation is shown in Fig. 6. It can be seen that the delaminations have been consolidated and repaired with no obvious fibre damage or wrinkling is present in the entire corner region. The confidence in the delamination repair has been shown in previous work [5] with multiple reprocessing stages not significantly effecting the properties of the system [13,14]. However, the process has not been perfected yet, with some vitrimer rich regions still extant and some dry spots still present. It considered that an improved forming regime using bespoke machinery, as mentioned above, would reduce the defects.

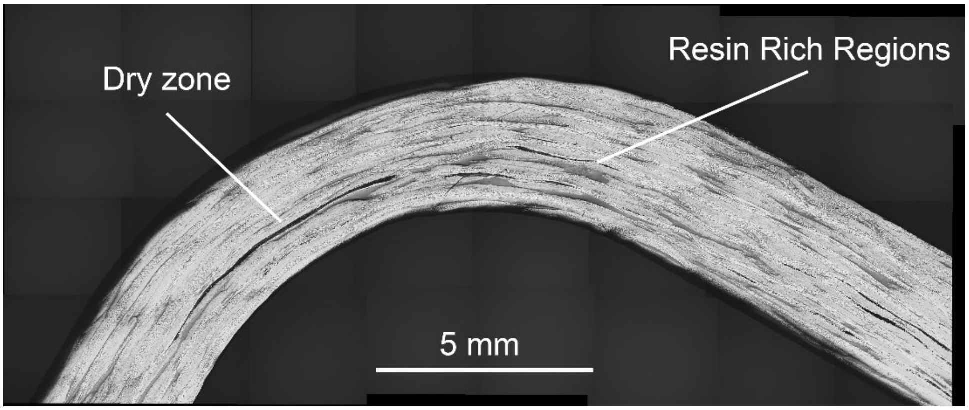

Figure 6. The vitrimer corner region after forming. While some dry zones and resin rich zones still exist, the fibres have been formed to the correct geometry with minimal wrinkling observed.

Conclusions

The concept of utilizing vitrimers in the form of additional features to ease the forming of composites parts to reduce fibre wrinkling and damage has been successfully achieved. The rudimentary manufacturing procedure used to form the part, based on utilising a standard test machine and testing oven resulted in variation that led to defects forming due to uneven heating and small variations in the rig/tool/material positioning. To eliminate the anomalies caused in the forming process specially designed machinery is being developed that provides a more uniform introduction of bending accuracy and localised heating targeted at the vitrimer embossed corner region. The machinery gradually encourages the vitrimer to form in the corner region and reduce the build-up of excess resin. The outcome of the work will be included in a future publication. Importantly, the work in the present paper has demonstrated the concept and manufacturing feasibility of a procedure for producing pre-structured Multi-Matrix Continuously-Reinforced Composite flat panels. The concept is a promising route for future composite design where handling and forming on site both improves transportability and reduces geometry defects.

References

[1] Hassan MH, Othman AR, Kamaruddin S. A review on the manufacturing defects of complex-shaped laminate in aircraft composite structures. The International Journal of Advanced Manufacturing Technology 2017;91:4081–94. https://doi.org/10.1007/s00170-017-0096-5

[2] Lukaszewicz DH-JA, Ward C, Potter KD. The engineering aspects of automated prepreg layup: History, present and future. Compos B Eng 2012;43:997–1009. https://doi.org/10.1016/j.compositesb.2011.12.003

[3] Radhakrishnan A, Georgillas I, Hamerton I, Shaffer MSP, Ivanov DS. Manufacturing Multi-Matrix Composites: Out-of-Vacuum Bag Consolidation. J Manuf Sci Eng 2023;145. https://doi.org/10.1115/1.4063091

[4] Stanier D, Gent I, Roy SS, Hamerton I, Potluri P, Ivanov DS. Mechanical Behaviour of Patterned Multi-Matrix Composites with Gradient Properties. 2016.

[5] Palubiski DR, Longana ML, Dulieu-Barton JM, Hamerton I, Ivanov DS. Multi-matrix continuously-reinforced composites: A novel route to sustainable repair of composite structures. Mater Des 2023;235:112446. https://doi.org/10.1016/J.MATDES.2023.112446

Materials Research Proceedings 41 (2024) 440-448 https://doi.org/10.21741/9781644903131-49

[6] Turk MA, Vermes B, Thompson AJ, Belnoue JP-H, Hallett SR, Ivanov DS. Mitigating forming defects by local modification of dry preforms. Compos Part A Appl Sci Manuf 2020;128:105643. https://doi.org/10.1016/j.compositesa.2019.105643

[7] Leibler L, Tournilhac F, Capelot M, Montarnal D. Silica-Like Malleable Materials from Permanent Organic Networks. Science (1979) 2011;334:965–8. https://doi.org/10.1126/science.1211649

[8] Ivanov DS, Volatier J, Rosli A, Nixon-Pearson O, Belnoue JP-H, Potter K, et al. Novel Methods of Assessing Inter-Ply Properties of Toughened Prepregs in Application to the Analysis of Fibre Path Defects. 20th International Conference on Composite Materials, Copenhagen: 2015.

[9] ASTM. D6415/D6415M 2013. https://doi.org/10.1520/D6415_D6415M-06AR13

[10] Mallinda n.d. https://mallinda.com/product/ (accessed August 16, 2022).

[11] Easy Composites n.d. https://www.easycomposites.co.uk/ (accessed August 16, 2022).

[12] Gurit Prime Resin Systems n.d. https://www.gurit.com/en/our-business/composite-materials/liquids/infusion (accessed August 16, 2022).

[13] Taynton P, Yu K, Shoemaker RK, Jin Y, Qi HJ, Zhang W. Heat- or water-driven malleability in a highly recyclable covalent network polymer. Advanced Materials 2014;26:3938–42. https://doi.org/10.1002/ADMA.201400317

[14] Kissounko DA, Taynton P, Kaffer C. New material: vitrimers promise to impact composites. Reinforced Plastics 2018;62:162–6. https://doi.org/10.1016/j.repl.2017.06.084