Towards a Fully Circular Aramid Yarn

Stan Maassen[1]**,** B. Gebben[1], V. Srinivas[1] and R. Hartert[2]

[1]*Teijin Aramid Tivolilaan 50 6802 ED, Arnhem The Netherlands*
stan.maassen@teijinaramid.com
[2]*Teijin Aramid Kasinostraße 19-21, Wuppertal Nordrhein-Westfalen 42103 Germany*
ruediger.hartert@teijinaramid.com
+49 173 9448751

Abstract. When it comes to armour systems, ballistic and protective performance is the key parameter. However, in today's world, also the topic of sustainability increasingly gains attention. Not only to reduce the waste of end-of-life armour materials, but also by lowering the eco-footprint of these materials at the production side. Key future developments will therefore be in the combined effects of circularity and reduction of greenhouse gas emissions in scope 1, 2 and 3. Aramids are one of the main materials used in personal protection, for example in vests, shields, and helmets. As one of the main aramid producers, Teijin Aramid wants to accommodate both topics by producing yarns with excellent performance in a sustainable way. To reach this goal, we are developing various new recycling routes: 1. Mechanical recycling: a route that we are already operating in the production of pulp and want to extend to other products. 2. Physical recycling: a completely new recycling route that allows production of aramid yarn using aramid from a recycle source as input. 3. Chemical recycling: by using a depolymerization process, we aim to convert end-of-life aramids to resources that can be used in our polymer factory for the production of new polymer that will be used to produce aramid yarn.
Besides these recycling routes, Teijin Aramid puts significant effort on gaining access to sustainable resources for the production of our yarn. By joining research consortia and by collaboration with business partners, we study the possibilities of sourcing our raw materials from a renewable source, such as bio-based or plastic waste-based sources, to move away from fossil resources. With these and other developments, Teijin Aramid aims to lower its carbon footprint to net zero, thus making a significant impact on the sustainability of aramid-based products such as armour systems. And while doing this, Teijin Aramid ensures thatv the high quality and performance of the aramid materials stay intact. Here, the latest developments with regards to sustainability and circular economy in the personal protection market are discussed, covering the steps Teijin Aramid has made, and is making, to lower our eco footprint and invite all value chain partners to join the discussion on how we can collaborate in becoming fully circular over the whole market.

1. INTRODUCTION

Ballistic and protective performance is the key parameter in the design and production of armour systems such as vests, shields, helmets, and panels. A lot of effort goes into improving the design of these products and the optimization of the material(s) that are used aiming to further increase their performance, and comfort in use.
However, in contrast to only a few years ago, sustainability and recycling of armour systems is increasingly gaining attention. First and foremost, solutions are sought for reusing or recycling End-of-Life (EoL) products. At the moment, most are still landfilled or incinerated at the end of their lifetime. Only a small fraction of the EoL products, primarily 100% aramid and clean, such as aramid ballistic vests, are currently recycled.
But also in the production phase changes need to be made to lower the eco-footprint of the various armour systems. This can be achieved by moving from non-renewable, fossil resources to renewable raw materials. These can, for example, be bio-based sources but they may also derive from plastic waste recycling or include recycling of EoL aramid yarn back into new aramid yarn. Furthermore, by increasing the efficiency of the production processes involved the footprint is reduced further.
Aramids are one of the main materials used in personal protection, for example in vests, shields, and helmets. As one of the main aramid producers, Teijin Aramid wants to accommodate both topics by producing yarns with excellent performance in a sustainable way. Figure 1 presents the fully sustainable and circular value chain for aramid products that Teijin Aramid envisions for the future.

https://doi.org/10.52202/080042-0002

Figure 1. A fully sustainable and circular value chain for aramid products [1]

As described in Figure 1, the chain starts with renewable carbon resources, for example from biobased or EoL plastic sources. From these, aramid polymer (Poly-(para-phenylene-terephthalamide), PPTA) and yarn are produced which are used in applications, *e.g.* in armour systems. To lower the eco-footprint in the production phase, all processes involved need to be operated as efficient as possible and using 100% renewable and clean energy. After the use phase, all applications are given a new life. For this, EoL products need to be collected and different materials need to be separated, think for example of separating the inner aramid layers from the outer fabric of a protective ballistic vest. After separation, various pretreatment steps, *e.g.* washing and cutting, are required to prepare the materials for the three recycling routes that Teijin Aramid has or is developing:

1. Mechanical recycling: a route that we have already been operating for over 20 years in the production of pulp and which we want to extend to other products.
2. Physical recycling: a completely new recycling route that allows production of aramid yarn using aramid from a recycle source as input.
3. Chemical recycling: by using a depolymerization process, we aim to convert EoL aramids to resources that can be used in our polymer factory for the production of new polymer that will be used to produce aramid yarn.

With these three recycling routes, aramid from different production left-over and EoL sources can be reintroduced in the production chain to produce new aramid products.

2. RECYCLING ROUTES

2.1. Mechanical recycling

The first route to recycle aramid materials is to reprocess into new products using mechanical processes. In general, such processes involve cutting, milling, or refining of the fiber to yield a short fiber product. This can be a cut or milled fiber of a specific length, or aramid pulp. At the moment, ballistic fabrics are the main source for recycling through this route.

At Teijin Aramid, this mechanical recycling route has already been in place for over 20 years, yielding Twaron pulp (Figure 2). Due to its chemical and physical properties, *e.g.* high abrasion and temperature resistance, aramid pulp can be used as a replacement for asbestos in applications such as brake pads, gaskets, and clutch plates. Although this is a very relevant recycling route for various applications, due to the fact that it does not yield new aramid fiber it can be considered a downcycling route.

https://doi.org/10.52202/080042-0002

Figure 2. Twaron pulp [2]

2.2. Physical recycling

To become fully circular, there is a need for recycling of aramid fiber not only to a different product, *i.e.* pulp as described in section 2.1, but also back into new aramid fiber. One way to achieve this is through the physical recycling route that is currently being developed at Teijin Aramid.
The physical recycling process involves obtaining aramid yarn, *e.g.* from EoL or production left-over sources, and processing it such that it can be dissolved and reintroduced into the aramid yarn spinning process. This technology has already been proven at a pilot stage at Teijin Aramid's research centre in Arnhem, The Netherlands and a patent on this technology is pending [3]. Here, a process has been developed to recycle aramid yarn by dissolving the yarn in sulphuric acid and using the obtained spinning solution in Teijin Aramid's wet-spinning process to produce new aramid yarn. As input, aramid yarn from various sources and having different morphologies have been recycled. Furthermore, different recycle contents have been obtained producing yarn from a combination of the recycle feedstock and virgin PPTA, mixed at different ratios. Interestingly, the dissolution behaviour of aramid yarn differs from the dissolution of PPTA polymer powder. This means that the dissolution conditions, such as time and temperature, need to be tuned to the recycle content. Figure 3 shows mechanical properties of yarn produced under similar conditions with varying recycle content.

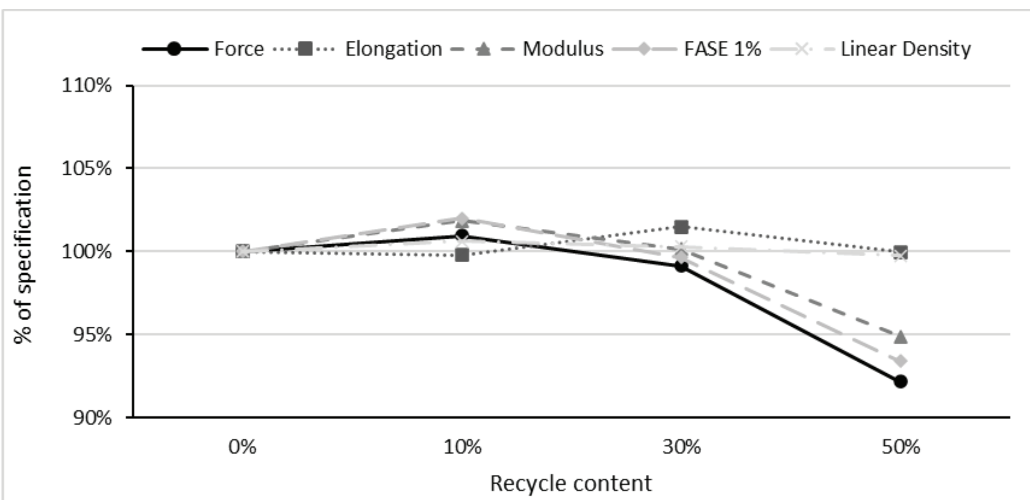

Figure 3. Mechanical properties for Twaron yarn with 0-50% recycle content, introduced using physical recycling and produced under the same conditions. Dots show the force at break (Force), squares show the elongation at break (Elongation), Triangles show the modulus of the yarns (Modulus), Diamonds show the force at 1% elongation (FASE 1%), and Crosses show the linear density (Linear Density). All data is normalized relative to the virgin (0% recycle content) yarn.

As observed from Figure 3, at recycle contents ≤ 30% no significant changes in mechanical properties are measured. At 50% recycle content, the linear density and elongation at break of the yarn remain unaffected, while the Force, Modulus, and FASE 1% show a significant reduction. The cause of this, and

 https://doi.org/10.52202/080042-0002

how to avoid it, is still under investigation. Further development and optimization of this recycling route, especially for high recycle contents, is currently under investigation.

Although the mechanical properties presented in Figure 3 already give a good impression on the quality of the yarn, further evaluation was performed to understand the yarn's performance in applications. As an example of this, Figure 4 shows "Time-to-Failure" (TTF) results for yarns with varying recycle contents.

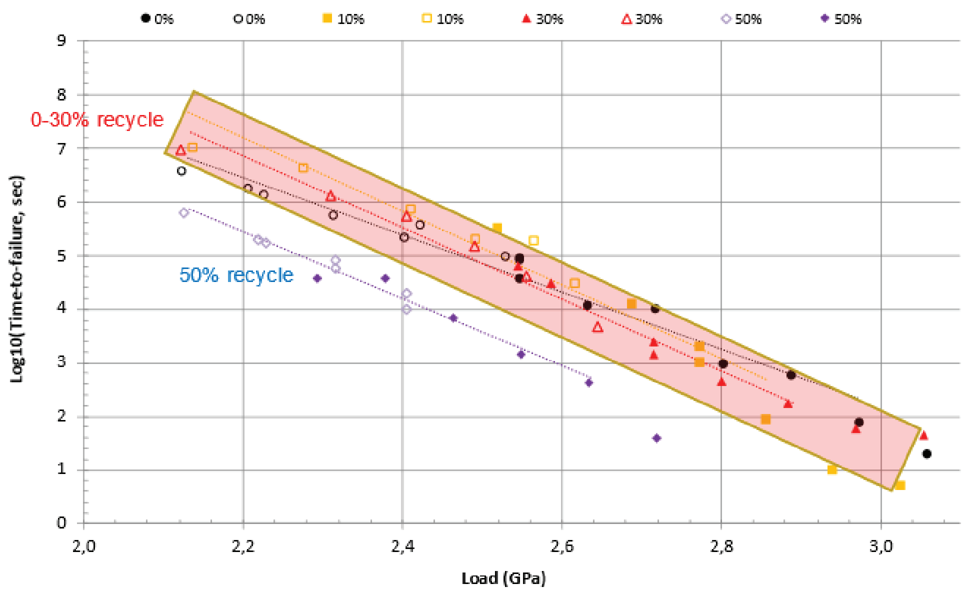

Figure 4. Time-to-Failure data of aramid yarn containing 0% (circles), 10% (squares), 30% (triangles), and 50% (diamonds) recycle content, introduced using physical recycling under the same process conditions.

TTF data gives information on the performance over longer times and the lifetime of synthetic fibers [4]. Similar to the data presented in Figure 3, from Figure 4 can be seen that no significant changes in performance are observed between aramid yarns with a recycle content of 0%, 10%, and 30% that were produced under the same process conditions. Similar yarns with a recycle content of 50% clearly show poorer TTF performance, as can be observed by the shift down of the data set for this yarn (blue diamonds) indicating shorter time to failure at a given load as compared to the other samples.

To evaluate the performance of these yarns with recycle content in high-demanding, real-life applications, Teijin Aramid collaborated with the companies FibreMax, located in The Netherlands, and Hampidjan, based in Iceland. First results have shown that also in these applications, no difference in performance is observed between virgin yarn and yarn with 30% recycle content [5-8].

Also for ballistic applications further research towards the performance of these aramid yarns with recycle content has been performed.

A theoretical estimate of the ballistic potential of a yarn can be provided by the characteristic velocity reported by Cunniff [9]. This parameter is a function of the primary yarn properties in the longitudinal direction. A physical interpretation can be best thought of as the product of the yarn specific toughness and the longitudinal wave speed or simply the energy absorption rate of a yarn. Based on the mechanical properties measured, Twaron containing 30% recycled content shows a comparable characteristic velocity. Furthermore, ballistic evaluations reveal the energy absorption due to addition of recycled content also does not vary, so does the speed of sound though the yarn/fabric. These results, shown in Figure 5, indicate that a yarn with 30% recycle content shows the same ballistic performance as a virgin aramid yarn.

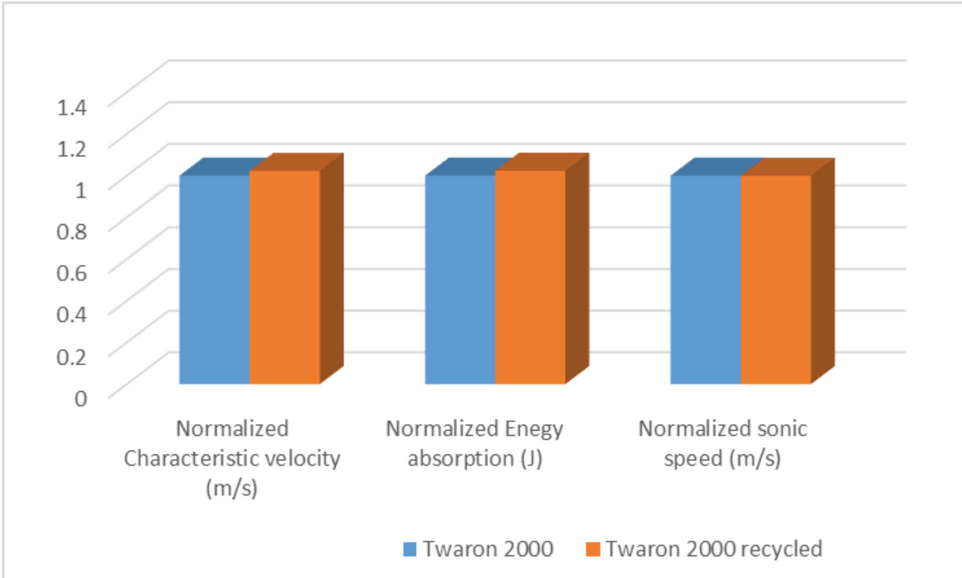

Figure 5. Normalized ballistic performance characteristics comparing standard Twaron 2000 yarn with a similar yarn containing 30% recycle content.

Currently, Teijin Aramid is working on moving this development from a R&D to a production scale. If successful, a Twaron yarn with recycle content can be produced commercially in the near future.

2.3. Chemical recycling

The third recycling route that is currently being studied and developed by Teijin Aramid involves chemical recycling of aramid products. This process comprises depolymerization of the PPTA polymer into its monomers that can, after isolation, be reused to produce new, virgin-grade PPTA that can be spun into aramid fiber.

Similar to the physical recycling route described in section 2.2, this route also allows for the production of a yarn with a recycle content. However, in contrast to introducing the recycle material in polymer form during the fiber spinning process as is done in the physical recycling route, in the chemical recycling process the recycle content is introduced even further back in the value chain, replacing part of the raw materials required for the production of PPTA polymer.

Going further back in the production chain is inevitably associated with a higher footprint since more subsequent process steps are required. However, an advantage of this recycling approach is that it allows for the production of PPTA polymer that is of the same quality as virgin-based polymer while replacing fossil-based feedstock with recycle-based raw materials, and thus does not affect the aramid yarn that is produced from this recycle-based PPTA polymer.

3. PRETREATMENT

To facilitate the recycling routes discussed in sections 2.1, 2.2, and 2.3 various pretreatments of the production left-over and EoL products are required. In general, recycling of any material is easier the purer a material is. Separating the various different components of a product, *e.g.* metals, fibers, coatings, resins etc., before recycling the materials improves the quality of products that can be obtained through recycling. For this reason, for recycling of aramid fiber Teijin Aramids includes separation and cleaning steps to improve the quality of the input for recycling. Further research towards these separation technologies is done to enable recycling of heavily contaminated aramid products to high quality aramid products. An example of such a development is the mechanical process to remove resin from helmets, to recover aramid fiber with a lower contamination level [9].

To reduce the required amount of pretreatment required before recycling, designing our products beforehand with recycling in mind is crucial. An example of such a development is our proprietary fluor-free coating that can replace persistent and potentially harmful PFAS (per- and polyfluoralkyl substances) being current industrial standard as a water-repellent treatment for ballistic fabrics. We were able to maintain fragment and bullet resistance in wet and dry testing on similar level at reduced overall shoot-pack water take-up.

 https://doi.org/10.52202/080042-0002

4. RENEWABLE RESOURCES

The last aspect discussed here is the switch that Teijin Aramid aims to make from non-renewable, fossil-based resources to sustainable alternatives. For this, Teijin Aramid is looking into alternative sources of raw materials obtained from bio-based resources or produced in the recycling of plastic waste. Already in 2019, Teijin Aramid partnered with the Dutch company BioBTX to produce a completely bio-based aramid fiber. In this project, an 92% bio-based aramid fiber was produced at a lab scale which had similar performance as conventional yarns.
Furthermore, Teijin Aramid is actively involved in research consortia, for example the "InREP"-project, to convert plastic waste into resources for the production of aramid yarn [1]. These, however, are long term developments and will require more time before being applicable at a large scale.

5. CONCLUSIONS

Besides ballistic and protective performance, also sustainability is gaining importance for amour systems. This paper discusses the opportunities for aramid-based products to contribute to producing more sustainable armour systems without compromising on performance. With the developments discussed here, Teijin Aramid works to lower the eco-footprint of aramid products and reaches out to all value chain partners to collaborate on activities to become fully sustainable over the entire market.

References

[1] Teijin Aramid, Scaling for Impact, Sustainability Report 2021, 2021
[2] Teijin Aramid, Twaron Product Brochure
[3] Boerstoel, H., Nijenhuis, W., La Faille, R., Günes, R., Boudebah, S., Gebben, B., Maassen, S., Komiya, N., Continuous process for recycling, WO 2021/123210 A1, 2021
[4] Knoester, H., Den Decker, P., Van den Heuvel, J., Tops, N., Elkink, F., Creep and Failure Time of Aramid Yarns Subjected to Constant Load, Macromol. Mater. Eng., 2012, 297: 559-575
[5] Mary Bailey, Teijin Aramid demonstrates fiber-recycling breakthrough, Chemical Engineering, 2021
[6] FibreMax, FibreMax and Teijin A Sustainable Long-term Relation, https://fibremax.nl/projects/fibremax-teijin/
[7] Hampidjan, Terra Slings The Environmental Solution, 2021
[8] Teijin Aramid, Teijin Aramid demonstrates potential of circular high-performance fibers, 2021
[9] Cunniff, P. Dimensionless Parameters for Optimization of Textile-Based Body Armor Systems. In Proceedings of the 18th International Symposium on Ballistics, San Antonio, TX, USA, 15–19 November 1999; Volume 2, pp. 1303–1310.
[10] Korte, H., Process for recycling material containing high-tenacity fibers impregnated with a resin matrix, US 20010023903 A1, 2000

https://doi.org/10.52202/080042-0002