

Sustainable reinforcement

Research shows that bio-based polyamide polymers offer a sustainable option

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The requirement to reduce the CO₂ emissions of cars motivated the automotive industry to develop lighter, more efficient cars and to reduce their rolling resistance. These aspects are important during the use phase of cars. For complete evaluation of CO₂ emissions however, car production and the raw materials used – including those in tires – have to be considered as well.

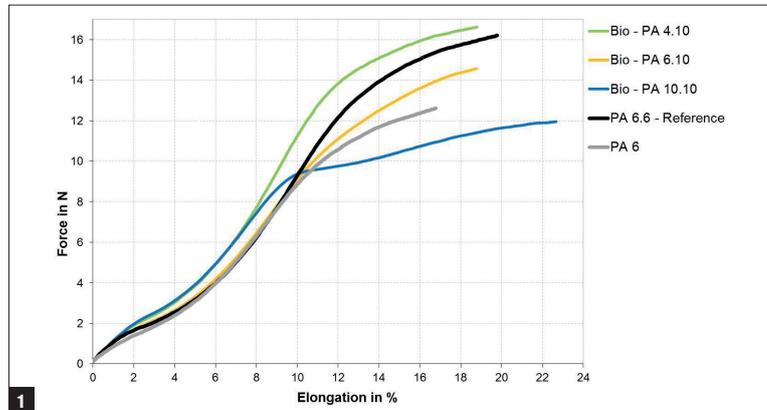
In modern passenger car tires, polyamide 6.6 tire cords are a widely used reinforcement material. Polyamide 6.6 tire cords are derived from 100% fossil resources. Suitable and sustainable reinforcement alternatives would support a reduction in the CO₂ emissions of tire raw materials.

PHP Fibers started a research project and looked for polymer materials that could make tire reinforcements more sustainable. A suitable reinforcement material has to comply with all requirements of a modern passenger car tire. Regarding tire manufacturing, the reinforcement material should be able to be processed in the existing production lines. Just as important is the ability of the polymer to be converted into reinforcement fibers, i.e. yarn spinning, twisting and dipping.

For this study, fiber materials based on fossil PA 6 and PA 6.6 were used to benchmark possible alternatives.

PHP identified bio-based polyamide polymers PA 4.10, PA 6.10 and PA 10.10 as promising

Figure 1: Force-elongation curves of yarns



candidates. All three polymer types contain sebacic acid as a sustainable building block in their molecular structure. Sebacic acid is a dicarboxylic acid produced from castor oil, a vegetable oil obtained from the seeds of the castor oil plant. Whereas PA 10.10 is 100% bio-based, PA 4.10 and 6.10 still contain the fossil-based building blocks tetramethylenediamine and hexamethylenediamine.

In Table 1, polymer properties of the three bio-based polymers and of the reference polymers are listed. The melting temperatures of the bio-based polyamides are within the benchmark range of PA 6 and PA 6.6. Regarding glass transition temperature, only PA 4.10 reaches PA 6.6. An advantage of these bio-based polyamides is that they all show reduced moisture pick-up and that they have a lower density compared with the reference polymers. It is remarkable that for the manufacturing of PA 4.10 polymer the total CO₂ emission balance is even negative.

All three bio-based polyamides were subjected to a comparative yarn spinning trial with polyamide 6 and polyamide 6.6 polymers from PHP Fibers as reference. The polymers were spun and drawn in a two-step research spinning device. All spinning and drawing conditions were set to comparative levels, where possible.

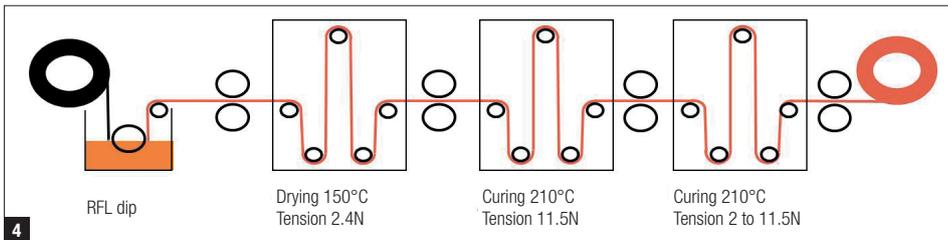
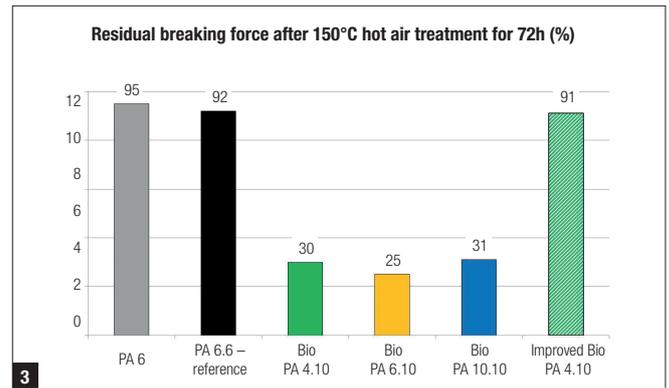
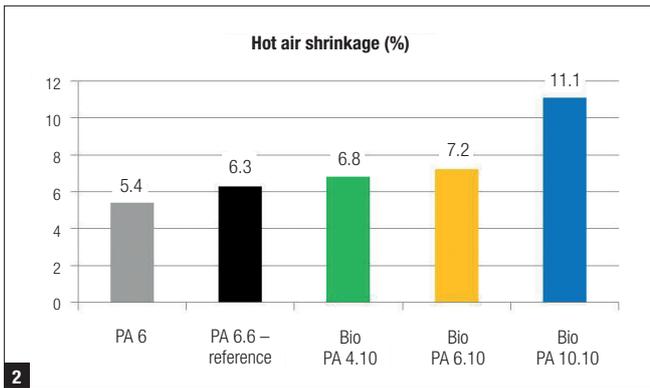
Results and discussion

In Figure 1 the force-elongation curves from the obtained yarns are displayed. All yarns from bio-based polymers produce graphs similar to reference PA 6.6 for low elongations to 8%. In this area, it is remarkable that PA 4.10 and PA 10.10 have a higher modulus than the reference yarn made of PA 6.6. For higher elongations until yarn break, the curves differ significantly: PA 4.10 is permanently steeper than the reference PA 6.6 and outperforms slightly the breaking force level of PA 6.6. PA 6.10 is at first on PA 6.6 level, but decays and ends below break force level of PA 6.6. The PA 10.10 curve changes remarkably from steep growth toward poor increase resulting in the lowest breaking force.

Besides the tensile characteristics it is important to know the thermal stability that can be assessed with the hot air shrinkage of yarns. It indicates the relative change in length when a pre-tensioned yarn is exposed for two minutes in 180°C hot air. The higher the shrinkage, the more the yarns would contract

Table 1: Polymer properties (source: DSM)

Property	PA 6	PA 6.6	Bio PA 4.10	Bio PA 6.10	Bio PA 10.10
Melting temp. T _m (°C)	215	255	250	223	203
Glass transition temp. T _g (°C)	60	74	70	48	37
Density g/cm ³	1.13	1.14	1.09	1.04	1.02
Moisture uptake @ 50%RH* (%)	3.1	2.7	1.9	1.6	0.9
Bio-base (%)	0	0	70	63	100
CO ₂ emission* (kg CO ₂ eq / kg polymer)	9	8	<0	4	2



and possibly change its properties, e. g during tire vulcanization.

Figure 2 shows that bio-based polymers PA 4.10 and PA 6.10 are in the area of PA 6.6 even if they are slightly elevated. PA 10.10, however, produces the highest shrinkage result with 11.1%.

Besides the hot air shrinkage behavior, the thermo-oxidative resistance of the yarn polymers is an important criterion for the stability of the reinforcement fiber. For that reason, PA 6.6 and PA 6 tire yarn polymers are equipped

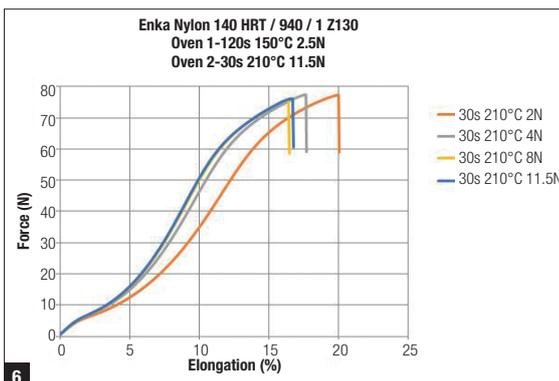
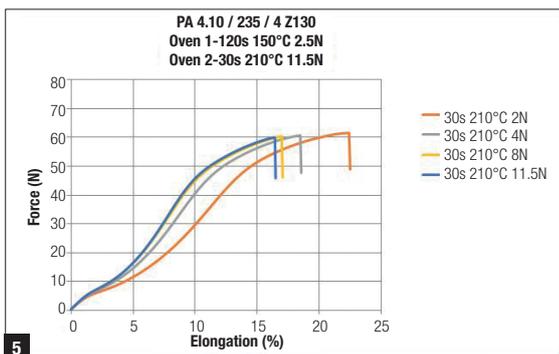
Figure 2: Hot air shrinkage

Figure 3: Residual breaking force after 150°C hot air treatment for 72 hours

Figure 4: Dip setup

Figure 5: PA 4.10 force-elongation

Figure 6: PA 6.6 – Enka Nylon 140HRT – force-elongation



with heat-resistant additives. In an exposure test, the yarns were stored in 150°C hot air for 72 hours. Figure 3 expresses this resistance by showing the residual breaking force after heat treatment. All bio-based polyamide yarns show low resistance, i.e. they must be protected when they are used as rubber reinforcements.

Based on the above yarn results, bio-based PA 4.10 not only reaches the properties of reference PA 6.6. It is even better regarding modulus and breaking force. Bio-based PA 6.10 does not reach the reference regarding breaking force, but is clearly stronger than PA 10.10. However, the latter two have lower melting temperatures and significantly lower glass transition temperatures than reference PA 6.6 or PA 6.

Good tensile properties and thermal resistance of yarn are the first criteria to assess a reinforcement fiber for tire or mechanical rubber good applications. The next step is to assess the yarn toward rubber reinforcement. Typically tire reinforcements have to be prepared for use in rubber goods. At first, the yarns are twisted and if necessary plied to cords. These constructions are then coated with an adhesion promotor containing resorcinol formaldehyde resin and latex, known as RFL dip. The application of the aqueous dip is done by impregnation of the cord followed by drying at 150°C and by curing the dip resin at temperatures of above 200°C. During the latter

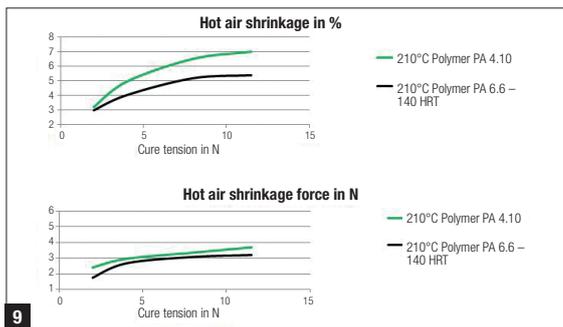
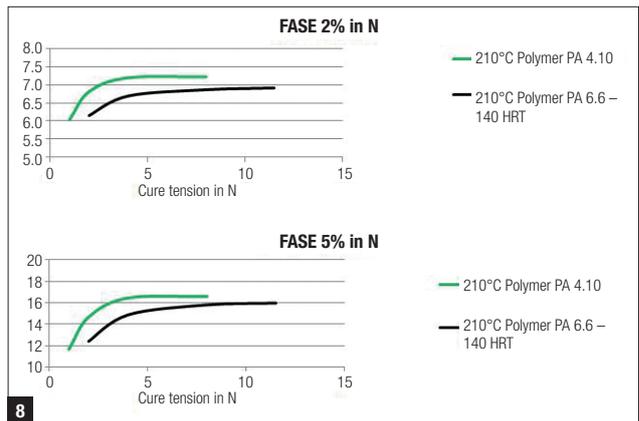
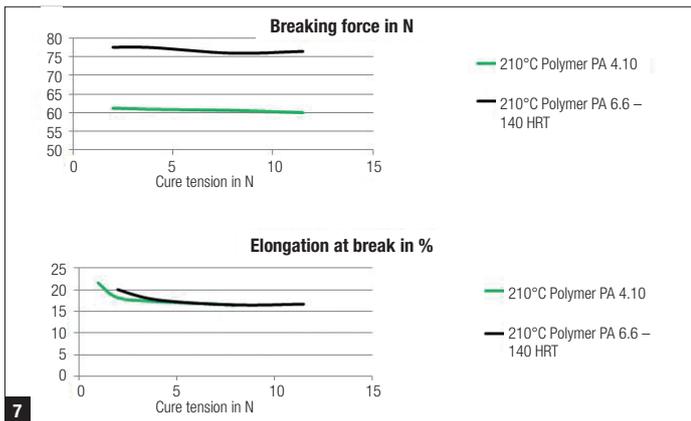
treatment step, thermoplastic cords (e.g. based on polyamide or polyester polymer) are subjected to elevated tensions in order to set the requested parameters for modulus and hot air shrinkage. After this converting step, the dipped cords are prepared for further processing in mechanical rubber goods.

Due to the good results obtained from bio-based PA 4.10 yarn, it was decided to continue only with PA 4.10 for further assessment. This time a bio-based PA 4.10 polymer with improved heat resistance was used for the adjacent spinning trial. Again yarns with 235dtex were produced on the research spinning machine. Figure 3 shows that at this time, heat resistance could be improved significantly. The improved yarn reached the resistance level of reference PA 6.6 yarn.

For the conversion to dipped cords, this PA 4.10 yarn was plied and twisted. As reference a typical PA 6.6 yarn for tire reinforcement, Enka Nylon 140HRT, was used. The yarn material for PA 4.10 was 235dtex and for the reference PA 6.6, 940dtex with Enka Nylon 140HRT. Cord construction for the PA 4.10 was 235dtex x 4 Z130; for the reference PA 6.6 sample it was 940dtex x 1 Z130.

The yarn constructions were dipped in an I+H dipping process (Figure 4). Different cure tensions were applied, to find out to what extent modulus and hot air shrinkage can be modified.

Figures 5 and 6 show the force-elongation curves of PA 4.10 and PA 6.6 dipped cords. Similar to PA 6.6 dipped cords, the PA 4.10 dipped cords can be influenced by the tension during the curing process: the higher the tension, the steeper the graph. However, the cure tension does not influence the breaking force while elongation at break decreases.



For better comparison, the tensile properties and hot air shrinkage of dipped PA 4.10 and PA 6.6 are shown in Figures 7 to 9; the breaking force of the referential dipped PA 6.6 cord is clearly higher than the dipped cord based on PA 4.10 yarn (Figure 7). The following aspects help to explain the difference: for the PA 4.10 yarn with improved polymer, only a small polymer quantity was available for the spinning trial and a reduced draw ration was applied during spinning. Here, further spinning trials are necessary to find the ideal spinning conditions.

Looking at the modulus expressed by force at specified elongation

Figure 7: Breaking force and elongation at break

Figure 8: Force at specified elongation (FASE) 2% and 5%

Figure 9: Hot air shrinkage and hot air shrinkage force

Figure 10: Strap peel adhesion force test according to ASTM 4393

Figure 11: Results from strap peel adhesion force test

(FASE) 2% and respectively 5%, the PA 4.10 dipped cords always showed bigger values than PA 6.6 – similar to the results obtained from yarns. Both moduli of PA 4.10 and of PA 6.6 dipped cords can be influenced when low cure tensions are applied. At high cure tensions the impact decays (Figure 8).

Besides the modulus, the hot air shrinkage can be influenced by increasing the cure tension, as well: PA 4.10 is always higher than PA 6.6 (Figure 9). The same applies to the hot air shrinkage force (Figure 9).

Finally, this dip evaluation was made to assess whether the adhesive activation is also suitable for cords based on PA 4.10 bio-based polymer.

Therefore, the dipped cords were subjected to a strap peel adhesion force test according to ASTM standard 4393 (Figure 10). For this test, straps consisting of two layers of parallel aligned cords embedded between three rubber plates were manufactured and vulcanized. The force to peel off the cord layers from each other was determined. The test reveals that the PA 4.10 dipped cords produced slightly higher peel forces than the PA 6.6 reference cord does (Figure 11).

Conclusion

The investigated polyamide polymers based on renewable resources have certain advantages over fossil-based polyamides such as PA 6 and 6.6: all have lower density, less moisture pick-up, and the CO₂ emission is clearly lower or even negative.

All bio-based polyamide polymers could be spun into multifilament yarns. The achieved tensile properties reveal that only bio-based PA 4.10 yarn meets the breaking force and modulus demands compared with reference polyamide 6.6. Bio-based PA 4.10 yarn had even higher modulus and breaking tenacity. The thermo-oxidative resistance of the bio-based polyamide yarn types must be improved when applications in mechanical rubber goods are considered. Yarn produced from improved bio-based PA 4.10 polymer achieved the same heat resistance as the reference yarn.

In a comparative twisting and dipping trial, cords based on PA 4.10 polymer again showed higher modulus. The adhesion to rubber of dipped PA 4.10 is comparative to reference PA 6.6.

In all presented tests, bio-based PA 4.10 yarn showed at least the performance of PA 6.6 tire yarn. This, and the reduced moisture pick-up, makes bio-based PA 4.10 polymer a promising candidate for further evaluation.

In the next step, a heat-resistant bio-based PA 4.10 yarn will be produced in typical tire yarn counts and under industrial spinning conditions. With this new bio-based yarn material, further evaluation such as fatigue tests and evaluations in tires or MRG will be made. Once this is successfully done, bio-based PA 4.10 yarns can be considered as a sustainable and equivalent alternative for PA 6.6 yarns. **tire**

