Naturally Effective

Air Brake Pipes and Tank Breather Hose Made of Bio-Based Polyamide 6.10

Excellent performance properties combined with low environmental impact were the main requirements made on new polyamide 6.10 grades developed for usage in media resistant pipe system in the automotive industry. Current application examples are pneumatic brake lines for trucks and, developed by Fiat Chrysler Automobile, tank breather hoses for passenger vehicles.

Extruded heat and media-resistant car tank breather hose (blue) made of partially bio-based PA6.10, in assembled state (© RadiciGroup)

Carrying out research and development into polymers that have a lower impact on the environment presents a big opportunity for plastics producers. Demand for materials that are based on renewable resources and also meet the stringent demands on physical, chemical and mechanical properties is constantly growing. In numerous areas of application, such materials can already replace plastics based on fossil raw materials and thus contribute to the more sustainable handling of resources. RadiciGroup Performance Plastics, Chignolo d'Isola (BG), Italy, has commercialized a range of partially bio-based polyamide (PA) 6.10 types that are suitable for a wide variety of applications in many areas of industry. The examples selected here are an air brake pipe for trucks (**Fig. 1**) and a tank breather hose for passenger cars (**Title figure**) from Fiat Chrysler Automobile (FCA), Orbassano (TO), Italy. Both applications make particularly high demands on material testing and approval procedures.

Base Polymer from Renewable Raw Materials

PA6.10 is produced by polycondensation of hexamethylene diamine and sebacic acid (**Fig. 2**). Sebacic acid is obtained from the beans of the castor oil plant which is cultivated above all in India and China. Since it grows primarily on dry soil, it does not compete for the production of foodstuffs. During the polycondensation of PA6.10 sebacic acid represents the component of natural origin while hexamethylene diamine is the monomer of fossil origin. Hexamethylene diamine is also used for example in the polymerization of PA6.6.

The proportion of sebacic acid in PA6.10 is around 64 wt. % . Since the castor oil plant breaks down carbon dioxide during its entire life cycle, the environmental balance of this bio-based polymer is considerably better than that of a comparable type of fossil origin.

Consequently, the greenhouse potential of PA6.10 – a measure of the environmental influence through CO_2 emissions – is significantly lower than that of conventional engineering plastics.

Properties in Comparison

PA6.10 is a semi-crystalline polymer, available as both an injection molding grade and an extrusion grade. Furthermore, fillers, stabilizers and additives can be incorporated to fine-tune specific properties for a particular application. Among its outstanding characteristics are low water absorption, high heat resistance, very good chemical resistance and good mechanical properties. The water absorption

Fig. 1. Extruded air pipe made of Radilon D 40EP25ZW 333 BK for the pneumatic braking system of a truck (© RadiciGroup)

of test bars according to ISO 62 on exposure to a standard climate (23 °C, 50 % relative humidity) and on immersion in water is shown in **Figure 3**. The water absorption on immersion is around a third of the value obtained with PA6 and PA6.6. At 50 % relative humidity, the moisture absorption is somewhere between the values for PA6.6 and PA12. The bio-based PA6.10 is thus suitable for most applications that call for good dimensional stability in moist environments.

The melt and heat deflection temperature (HDT) are in the range of PA6, but significantly higher than PA11 and PA12 (**Fig. 4**). This is particularly important if the material is to be used as a substitute for PA11 and PA12, for example for applications in which the temperatures exceed those tolerated by PA12, as is the case with many diesel fuel lines in new cars. Furthermore, the polymer has very good chemical resistance (also in the presence of salts such as zinc chloride and calcium chloride), high hydrolysis resistance and, compared with PA6 and PA6.6, undergoes smaller changes in the mechanical properties after the absorption of moisture.

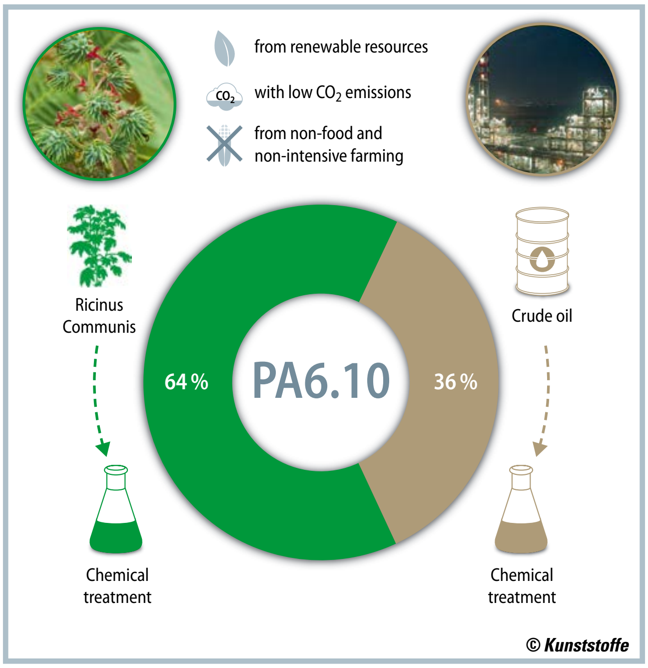

Fig. 2. Schematic representation of the polymerization of PA6.10. It comprises 64 wt. % sebacic acid, obtained from castor oil (source: RadiciGroup)

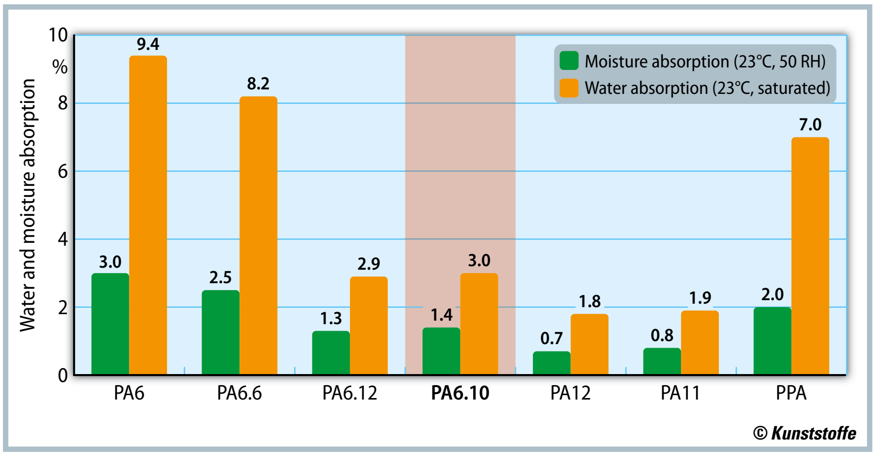

Fig. 3. PA6.10 has, at 50 % relative humidity, a much lower water absorption than PA6 and PA6.6 and is approximately the same as PA12 following water immersion (source: RadiciGroup)

Air Pipes for Pneumatic Brake Systems

For pneumatic brake systems air pipes, RadiciGroup has developed the extrusion grade Radilon D 40EP25ZW 333 BK (**Fig. 1**). The material has particularly high flexibility in order to facilitate installation of the pipes, which, especially with trucks, can reach a considerable length. Furthermore, it is heat-stabilized, which means that components made from it can be exposed to high temperatures even over a prolonged period.

To gain approval for application in air pipes for pneumatic brake systems, the materials have to comply among other things with the requirements of standards DIN 74324 and ISO 7628. The data given here stem from tests carried out in line with these standards. The subject of the tests were pipes with a nominal diameter of 8X1, manufactured with the tolerances defined in the standards on conventional industrial machines. The values calculated according to DIN 74324 for the basic stress are above the given minimum of 20 N/mm². After thermal aging in air (70 h at 150 °C), the basic stress increases. Below are the results of other tests carried out on the air pipes according to ISO 7628, before and after heat and UV aging. Furthermore, the behavior of the part after contact with liquids, including aggressive chemicals, was also examined.

Based on the burst pressure curve up to a temperature of 125 °C, the material is suitable according to ISO 7628 for lines at a nominal pressure of up to 10 bar and up to 12.5 bar. **Figure 5** shows the burst pressure after the contact with media that trigger stress cracking, and after aging in artificial light. To examine the stress cracking resistance, the installed pipes were first exposed at 60 °C to an increased air humidity of 85 %, then bent by a given diameter and dipped at regular intervals into a corrosive solution. No cracks are allowed to develop and the value for the burst pressure must be at least 80 % of the original value. The corrosive solution is made up of 50 % water, copper chloride, sodium chloride, potassium chloride and zinc chloride. For aging in artificial light, the pipe was irradiated with xenon lamps for 750 h at 65 °C. In this case, too, the burst pressure must be at least 80 % of the original value.

Tank Breather Hose for Passenger Vehicles

As part of a joint project with FCA, RadiciGroup has developed a material that has similar properties to the material described above. At the request of the customer, the material is colored blue and is used for the production of tank breather hoses for cars (**Title figure**). Such parts »

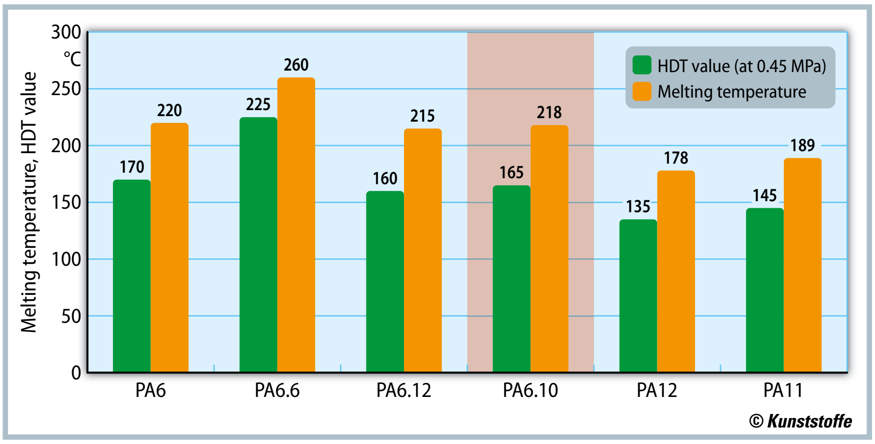

Fig. 4. With PA6.10, the heat deflection temperature and melt temperature are in the range of PA6 and significantly higher than PA11 and PA12 (source: RadiciGroup)

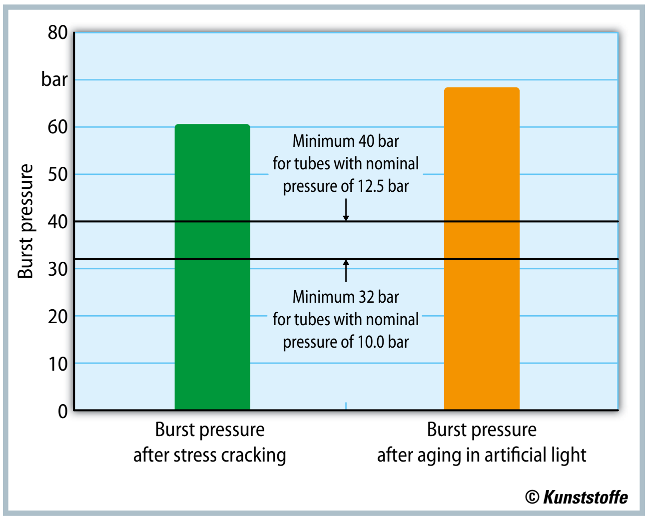

Fig. 5. Burst pressure after exposure to media that trigger stress cracking, and after aging in artificial light (source: RadiciGroup)

are conventionally made of an impact-modified PA12 incorporating a plasticizer. To gain approval, a number of technical requirements had to be met, as specified in the Fiat Chrysler guidelines FCA 9.02137/04 (plastic hose with connections for dissipating fuel vapors) and FCA 9.02144/01. During development of the material, particular attention was placed on the ease of processing via extrusion. Here, low part tolerances are essential – something which is very difficult to achieve with materials having poorer processing properties. The corrugated tubes must, especially in the corrugated areas, comply with strict measuring tolerances as too thin areas in the wall can lead to failure of the component during operation.

The part was subjected to a number of tests to determine its suitability for practical application. Among the most important were the tests to determine the mechanical properties before and after exposure to aggressive chemicals, after heat aging, and in contact with gasoline and diesel fuel vapors.

The following summarizes some of the details. The component passed the pressure test with the introduction of air of 2.5 bar before and after thermal aging at 90 °C for 168 h. The specimen also successfully passed the cold impact strength test using a free falling dart (2 kg weight, diameter of the hemispherical ended portion of the dart: 10 mm) when dropped from a height of 400 mm and 500 mm after storage at -40 °C for 4 h. These tests were performed both on fresh new parts and on others that had been aged in hot air at 90 °C for 168 h. Furthermore, a pull-off test was carried out on the hose and/or connections both when new and after aging in fuel vapors at 60 °C over a period of 168 h. For these tests, gasoline TF1 (unleaded gasoline, low benzene content + 10 % ethanol) and diesel fuel EN 590 + 10 % FAME (B100) were used. To test the resistance to zinc chloride, the specimen was first immersed for 200 h in an aqueous solution with 50 wt. % zinc chloride. Subsequently, it was bent by 180 °C in a radius corresponding to five times the outer diameter of the hose. After this, there was no visible damage, not even at the fixing points for the connections. After immersion for 200 h at 60 °C in an aqueous solution with 50 wt. % calcium chloride and subsequent bending as described above, there were no visible signs of damage either, not even at the fixing points of the connections.

Conclusions

The example of PA6.10 shows that engineering plastics based to a large extent on renewable raw materials can replace materials of fossil origin even in technical parts. Specific formulations geared to the respective application help to meet or even exceed the requirements for the approval of critical components such as pneumatic brake pipes and tank breather hoses. Potential new applications are currently emerging through the demand for ever higher operating temperatures. Because of its high thermal resistance compared with materials used until now, additional possible applications in vehicle fuel systems could thus emerge for PA6.10. ■

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