APPLICATION INFORMATION

MODIFIERS FOR GLASS FIBER REINFORCED POLYPROPYLENE

Content

Introduction

Polypropylene (PP) is among the most significant thermoplastic materials in terms of quantity. This is due, firstly, to the diverse application possibilities and secondly, to the extremely attractive manufacturing costs. In the past, polypropylene was mainly used for inexpensive tasks which were not particularly demanding. But for some time now this interesting material has tapped into more and more fields of application which were previously reserved for the so-called technical thermoplastics, such as polyamides (PA), acrylonitrile butadiene styrene (ABS), etc. This has been made possible by factors including the use of functional fillers and fibers such as talc and glass fibers. Now that glass fibers are being used, we also see more and more coupling agents being used today, enabling the chemical bonding of the sized glass fibers to the polymer matrix. This has given rise to a substantial improvement in the mechanical property profile of the resulting compounds, which have been able to replace technical thermoplastics in the most diverse applications as a result of their continuously increasing level of properties.

For additional information on additives and technical topics, please contact us:
Thermoplastics.BYK@altana.com

Note

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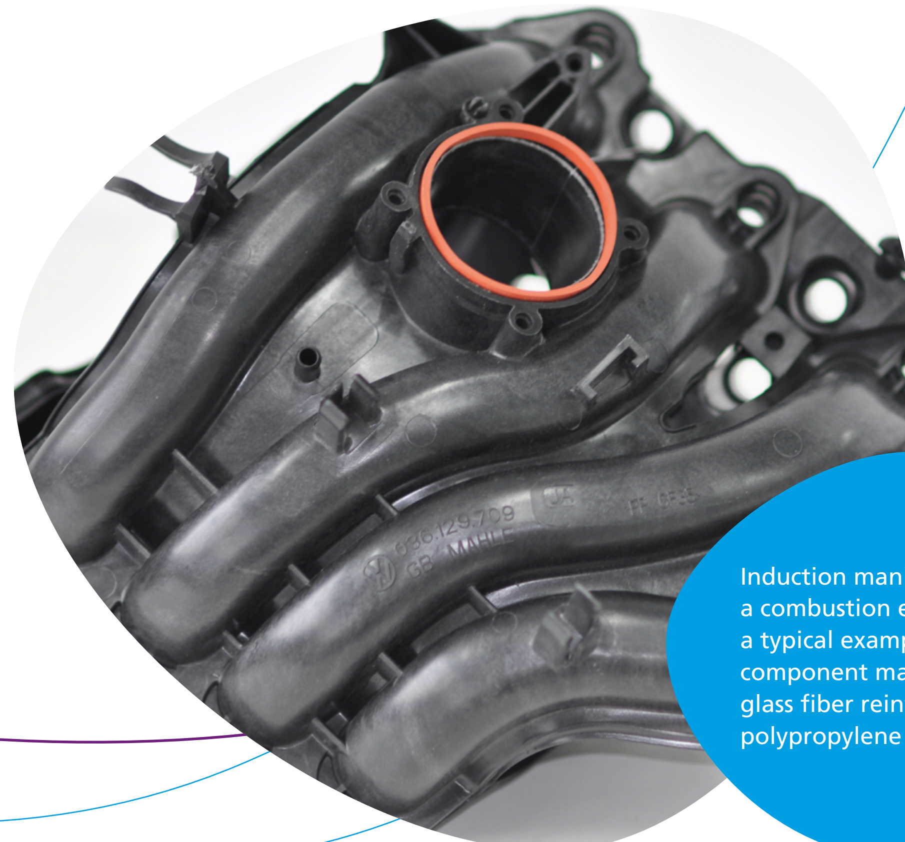
Application fields

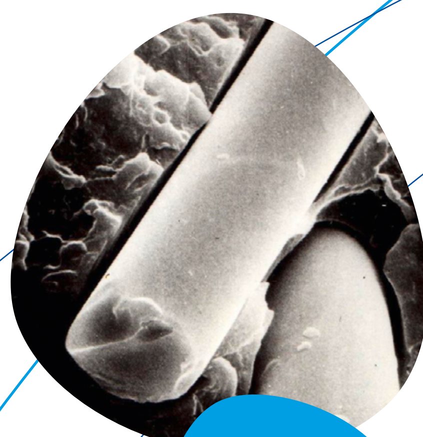
A key field of application for glass fiber reinforced polypropylene is automotive engineering. The picture shows a typical example of the induction manifold of a combustion engine which was previously manufactured out of metal. Later, technical thermoplastics (polyamide/GF) were used. Due to the ongoing trend towards lightweighting (e.g. in transportation applications), such parts are nowadays made from the considerably cheaper and, equally important, lighter polypropylene glass fiber (PP/GF) solution.



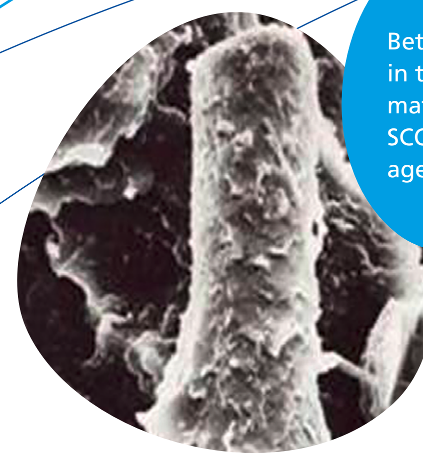
Induction manifold of a combustion engine as a typical example of a component made from glass fiber reinforced polypropylene

SCONA modifiers in glass fiber reinforced polypropylene

Coupling agents are used in glass fiber reinforced compounds to increase the adhesion of the fibers to the polymer matrix, thereby significantly improving the compound's mechanical properties. The improved fiber-matrix adhesion results in a particularly significant increase of the charpy (notched) impact strength of the material. Consequently, the coupling agent ensures an efficient load transfer from the matrix to the reinforcing fiber. A modifier concentration as low as 1 wt% or even less already ensures such a significant improvement.



Glass fibers in polypropylene



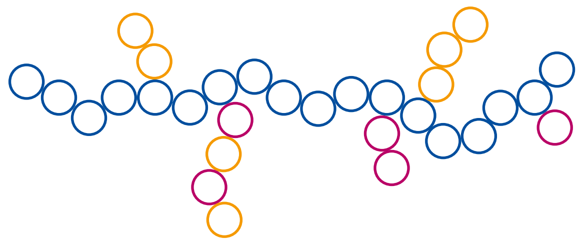
Better incorporation in the polypropylene matrix when using SCONA coupling agents

Chemistry of the modifiers

BYK offers a broad portfolio of polymeric modifiers under its SCONA brand for different applications to the market. The SCONA modifier consists in general of a base polymer – a polymer backbone. These base polymers are functionalized with different monomers in a grafting process. By doing so, reactive moieties can be attached to the polymer backbone. Typical examples of the grafting moieties are monomers like maleic anhydride (MAH), acrylic acid (AA), glycidyl methacrylate (GMA) but are not limited to those (see G. 01). There is also a broad selection of base polymers suitable for the grafting process – from polyolefins (PP, PE), elastomers (POE, SEBS, ...), acrylic copolymers (EBA, EVA, ...) to polyester (PLA, ...). The modifiers employed as coupling agents in glass fiber reinforced polypropylene are usually based on polypropylene co- or homopolymers functionalized with maleic anhydride.

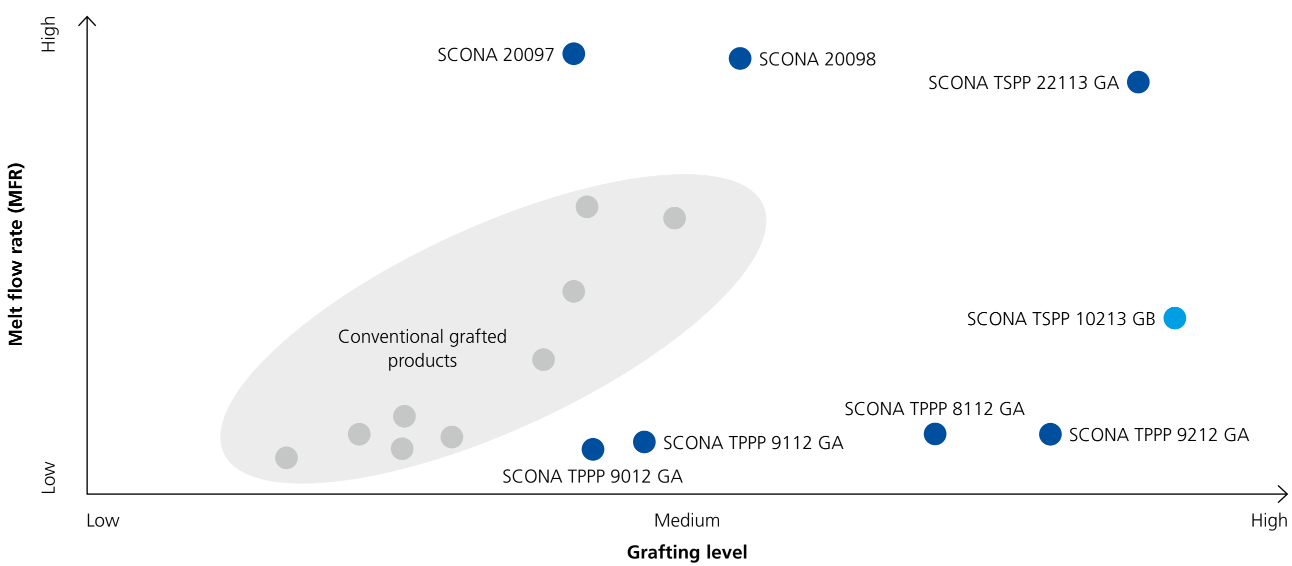
BYK´s product portfolio of SCONA modifiers covers a broad spectrum of products for reinforced polypropylene composites. One feature that all the products have in common is that they exhibit a substantially higher degree of functionalization compared to most conventional modifiers. A high degree of functionalization will result in a better overall performance and/or in cost advantage as less modifier is needed to achieve the same level of properties. Due to the unique design of BYK´s grafting processes, a broad range of melt flow rates can be covered to ensure extensive fiber wetting in the different processes. At the same time, a broad range of grafting levels can be achieved as illustrated in G. 02.

Chemistry of the SCONA coupling agents



Polymer backbone (multiple: e.g. PE, POE, PP, SEBS, EBA, EVA, PLA, ...) Grafted monomers (multiple: e.g. MAH, GMA , AA, ...) **G. 01**

SCONA coupling agents for reinforced polypropylene: Melt flow rate versus grafting level

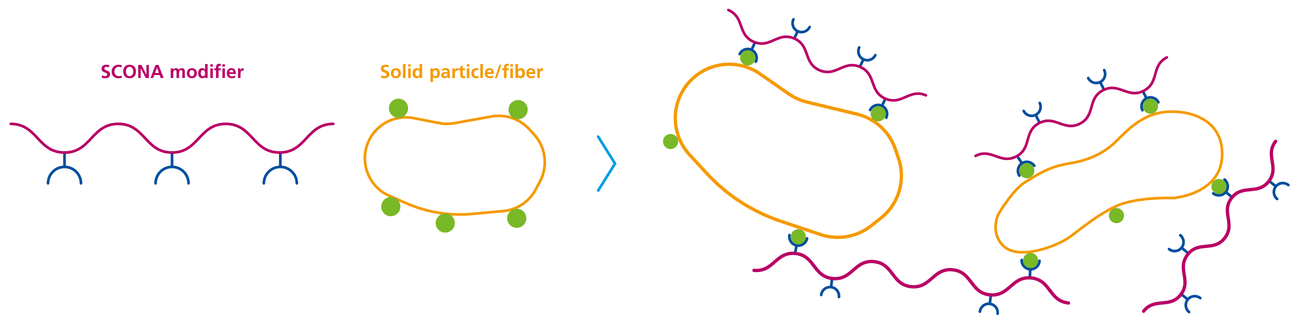


Polypropylene homopolymer (hPP) Polypropylene copolymer (cPP) **G. 02**

Mode of action

As already mentioned, the coupling agent brings about a stronger adhesion of the glass fibers to the polymer matrix. To achieve this, it must interact with the glass fibers. In fact, this interaction does not take place directly with the glass surface, but rather with the surface treatment of the glass fibers – called sizing. Specifically in the present case, this means a reaction of the maleic anhydride groups of the coupling agent with the amino groups of the silane of the sizing. The reaction results in an extremely stable imide. As illustrated in G. 04, multiple reaction sites on the surface of the glass fiber as well as on the polymeric backbone of the SCONA modifier result in strong adhesion of the glass fiber to the polypropylene matrix.

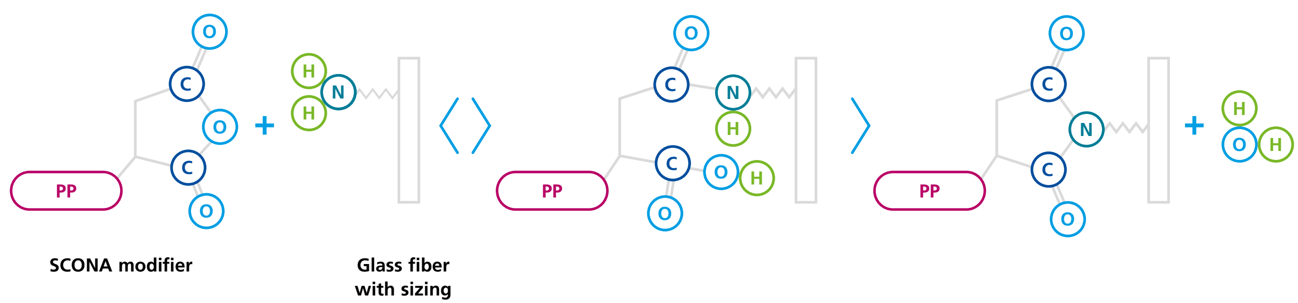
Schematic coupling mechanism of grafted SCONA modifier to solid particles/fibers



Reactive group (e.g. hydroxy, amine) Reactive group (e.g. anhydride, acidic)

G. 03

Reaction of the coupling agent with the glass fiber sizing



G. 04

Advantages of SCONA modifiers

One of the most important fields of application for PP/GF is automotive structural parts. For years now, it has been increasingly important to reduce volatile organic compound (VOC) emissions.

A significant contribution to reducing these emissions is made by PP/GF compounds and, in particular, the coupling agents used. Coupling agents can contain large quantities of low-molecular by-products resulting from chain-scissioning and decomposition of the base polymer at the elevated process temperature. Furthermore, the degradation products of the initiator system are another source of organic volatiles. The initiator system is needed for the grafting reaction. As a result of BYK´s sophisticated grafting technologies and the underlying process design, the SCONA modifiers have a significantly reduced VOC content in comparison to competitive materials (T. 01).

Comparsion of VOC content of coupling agents

Polymer	VOC (mean value) µg/g*[1]
SCONA TPPP 9012	88
SCONA TPPP 8112 GA	127
Competitive MAH-g-PP	158
Polypropylene (non-grafted)	34

*[1] based on VDA 277

T. 01

T. 02 shows a comparison of SCONA TPPP 9012 FA with different competitive products. All products are used as coupling agents for the manufacture of PP/GF compounds. The high effectiveness of the SCONA product results from the high content of bound MAH.

Comparison of different coupling agents for glass fiber reinforced polypropylene

Modifier	MFR g/10 min (190 °C/2.16 kg)	MAH content %			Yellowness index
		total	free	bound	
Competitive sample 1	260	0.95	0.24	0.71	32.0
Competitive sample 2	280	0.90	0.30	0.60	22.0
Competitive sample 3	380	0.80	0.20	0.69	28.1
SCONA TPPP 9012 FA	123	0.98	0.02	0.96	6.8

T. 02

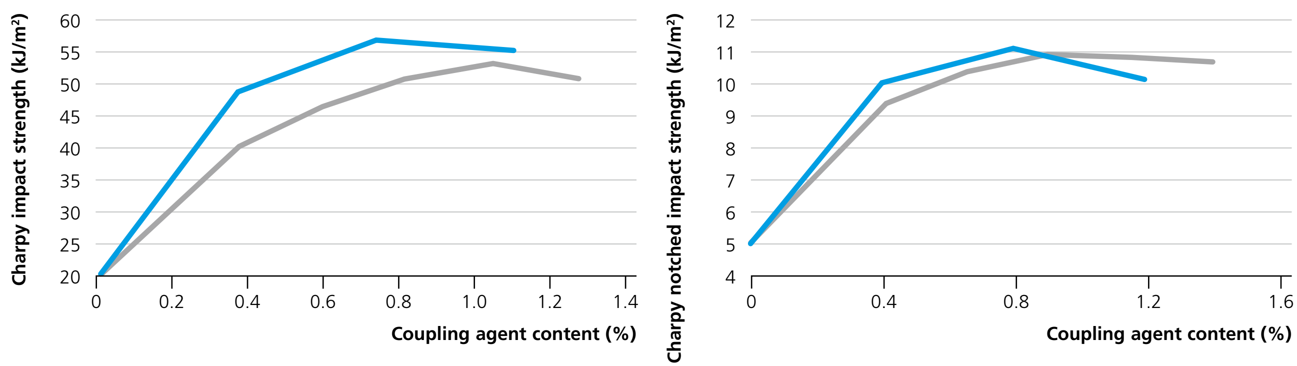
G. 05 illustrates this once again by means of the impact strength and notched impact strength in a 30 % glass fiber polypropylene composite. The high content of free MAH in the competitive product is responsible for the high VOC emissions of these products. Furthermore, the free MAH also naturally reacts with the sizing of the glass fiber, thereby coating the surface of the glass fiber without contributing to the adhesion between the glass and the polymer matrix.

The lower yellowness index is also a consequence of the gentle process conditions of BYK's grafting processes. Harsh process conditions (e.g. high temperature, short dwell times, etc.) can generally give fluctuating results in terms of the MAH content and the molecular weight.

Thanks to BYK's unique process design, it can be assured that the SCONA modifiers have very high grafting levels for maximum performance and efficiency in conjunction with a reliable and constant product quality.

G. 05 also shows that there is an optimum for the mechanical properties. Higher coupling agent dosages do not lead to any improvement, or a slight deterioration is even observed. Nevertheless, it may sometimes be necessary to use a higher modifier dosage in certain applications, such as suds containers in washing machines, in order to achieve the required alkaline resistance (G. 06).

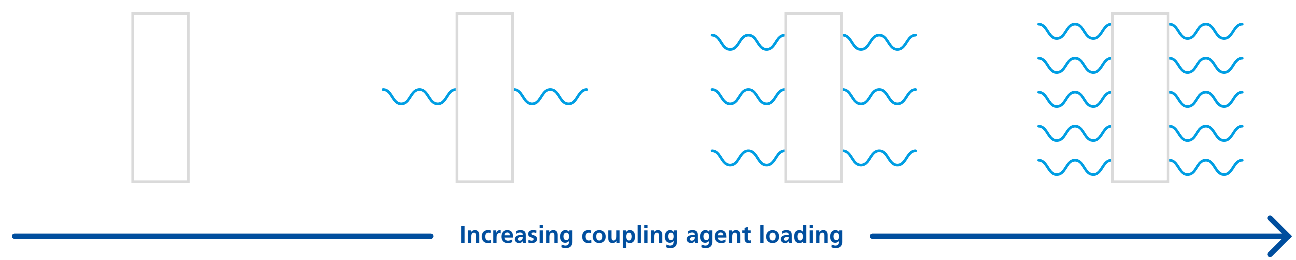
Better impact strength as a result of the coupling agent having a higher MAH content



SCONA TPPP 9012 FA   Competitive sample 2

G. 05

Effect of coupling agent dosage on the properties of the PP/GF compound



No coating	Partial coating	Virtually total coverage	Total coverage
Poor mechanical properties	Significantly improved mechanical properties	Maximum mechanical properties	Possible slight decline in the mechanical properties, but excellent alkaline resistance

G. 06

Labeling-free coupling agents

Changing environmental regulations are a continuous driver for new innovative products. The 13th Adaptation to Technical Progress (ATP) to the regulation on classification, labeling and packaging of substances and mixtures (CLP) was published by the European Union at the end of 2018. Compounders and processors of thermoplastic materials of such glass fiber reinforced polypropylene are now impacted by changes in the product classification for maleic anhydride (MAH). Products containing a free residual MAH content of as low as 10 ppm (0.001 %) now need to be classified as skin sensitizing (T. 03). This is currently a topic with relevance in Europe but might become also of relevance in other regions in the course of changing regulations.

As outlined up to now, maleic anhydride is the most frequently used functional group of grafted polyolefin polymers. BYK has developed a labeling-free alternative to meet the changing market requirements. Such an innovative product is SCONA TSPP 8219 GA, using alternative monomers. The functionality remains very similar and compared to state-of-the-art MAH-grafted products, such as SCONA TPPP 9112 GA, there is no drawback in terms of mechanical performance when using the labeling-free alternative SCONA TSPP 8219 GA at the same dosage level (G. 07). While there is no loss in physical properties there is a significant benefit in regulatory and environmental “friendliness” as the new product requires no special labeling, which results in the key benefit for the customer, that no precautionary measures need to be taken to meet the hazardous potential of the coupling agent. At the same time there is no drawback in terms of efficiency and performance.

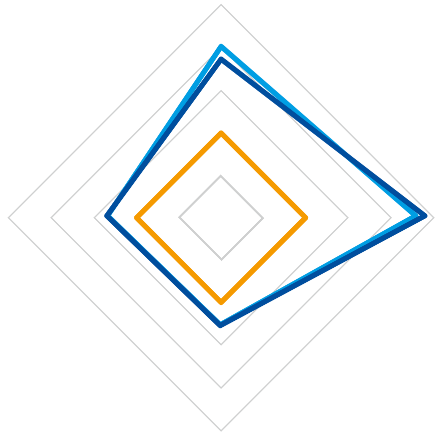
Comparison of standard coupling agents and innovative labeling-free coupling agents according to European legislation

	Standard coupling agent	Labeling-free coupling agent
Grafted monomer	Maleic anhydride	Labeling-free alternative
Hazard pictograms	 H317: May cause an allergic skin reaction*[2]	None

*[2] Labeling necessary if free residual MAH content is larger than 10 ppm

T. 03

Mechanical performance of labeling-free SCONA modifier in glass fiber reinforced (30 %) polypropylene compounds in comparison to state-of-the-art modifier



Control 0.8 % SCONA TPPP 9112 GA 0.8 % SCONA TSPP 8219 GA

G. 07

Product overview

Product	Base polymer	Delivery form	MFR/MVR	Grafting functionalization	Grafting level (%)	Grafting level	Dosage	Application/benefit
SCONA TPPP 8112 GA*3	hPP	Pellet	80–140 g/10 min (190 °C/2.16 kg)	Maleic anhydride	1.4 %*4	high	0.8 %–3.0 %	Very suitable for long glass fiber reinforced polypropylene compounds
SCONA TPPP 9012 GA*3	hPP	Pellet	50–110 g/10 min (190 °C/2.16 kg)	Maleic anhydride	> 0.9 %*4	medium	0.5 %–2.0 %	Standard grade for short glass fiber reinforced polypropylene compounds
SCONA TPPP 9112 GA*3	hPP	Pellet	70–120 g/10 min (190 °C/2.16 kg)	Maleic anhydride	> 1.0 %*4	medium	0.5%–2.0 %	Standard grade for lowest impact on discoloration
SCONA TPPP 9212 GA*3	hPP	Pellet	80–140 g/10 min (190 °C/2.16 kg)	Maleic anhydride	> 1.8 %*4	very high	0.5 %–2.0 %	Very highly functionalized grade for maximum efficiency and performance
SCONA TSPP 8219 GA	hPP	Pellet	100 g/10 min (190 °C/2.16 kg)	Proprietary	2.0 %*4	very high	0.5 %–3.0 %	Free of maleic anhydride
SCONA TSPP 10213 GB	cPP	Pellet	40–100 cm^3/10 min (170 °C/1.2 kg)	Maleic anhydride	2.0 %*4	very high	0.5 %–5.0 %	Especially suitable for polypropylene composites based on recycled carbon fiber reinforced polypropylene due to its extraordinary high grafting level
SCONA TSPP 22113 GA	hPP	Pellet	130–220 cm^3/10 min (170 °C/1.2 kg)	Maleic anhydride	> 1.8 %*4	very high	0.5 %–2.0 %	Very high flow and highly functionalized grade for extensive fiber wetting and maximum efficiency; especially suitable for processes with low dwell time
SCONA 20097	hPP	Pellet	25–30 g/10 min (190 °C/1.2 kg)*5	Maleic anhydride	(> 0.9 %*4) > 0.4 %*6	medium	1.0 %–4.0 %	Very high flow grade for extensive fiber wetting; especially suitable for processes with low dwell time
SCONA 20098	hPP	Pellet	15–35 g/10 min (190 °C/1.2 kg)*5	Maleic anhydride	(> 1.3 %*4) > 0.5 %*6	high	1.0 %–4.0 %	Very high flow grade for extensive fiber wetting; especially suitable for processes with low dwell time

*3 also available as a powder (FA-version) *4 according to BYK titration method *5 measured with a die 8/1 *6 according to BYK FT-IR method

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BYK-Chemie GmbH
Abelstraße 45
46483 Wesel
Germany
Tel +49 281 670-0
Fax +49 281 65735

info@byk.com
www.byk.com