

Thick-walled Semi-finished Products. With a new and cost-effective method, thick-walled pipe profiles can be made of low-viscous PA66 without “sagging” on conventional extrusion production lines. The viscosity of the low-viscous PA66 can be increased by reactive compounding.

Reactive Compounding Reduces Sagging Effects

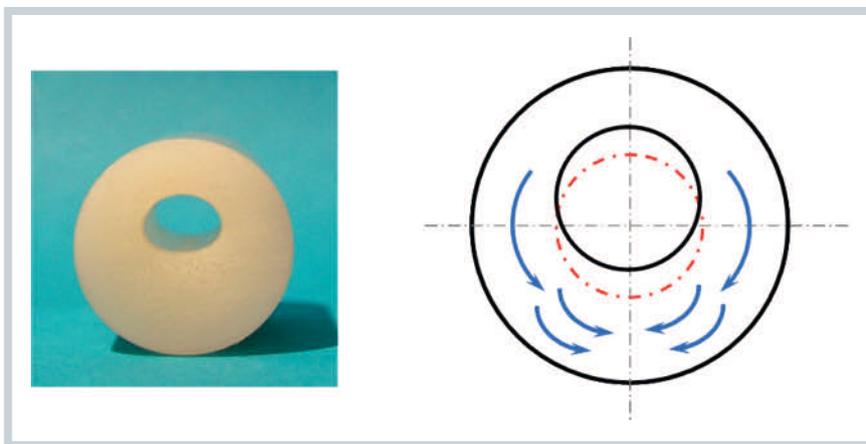


Fig. 1. Sagging behavior of a thick-walled tube due to gravitation

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In order to employ lightweight construction concepts, components made from technical plastics and high-performance polymers are used more than ever today in machine engineering and building construction. Typical materials for such applications are polyamides, semi-crystalline thermoplastic polycondensates. Such technical parts can be produced either by injection molding or by machining from extruded semi-finished products. These are frequently very thick-walled tubular strands requiring very long cooling times due to their geometry. During the product calibration and cooling process, undesirable changes frequently

occur in the circumferential wall thickness distribution due to the effect of gravity. The results are eccentric tubular elements, an effect referred to as “sagging” (Fig. 1). The semi-finished product manufacturer avoids this problem by using highly molecular, and hence highly viscous material grades which, however, are correspondingly expensive and furthermore have only a limited availability on the market. In order to improve the overall economy it would be desirable to be able to run production processes also with less expensive, low viscous standard material grades. This has now become possible through the development at the Institut für Kunststofftechnik (IKT) at the University of Stuttgart, Germany.

Reactive Compounding Step

The uppermost goal was the development and testing of a process concept for the

production of thick-walled tubular semi-finished products from low-molecular and hence low-viscous standard PA66. The original basic viscosity of these polycondensates was to be increased by between 10 and 100 times by means of a reactive compounding step. This was achieved by covalent coupling of the PA macromolecules with inexpensive function molecules such as styrene maleic anhydride (SMA) and epoxy (EP) which result in an extension of the chain and also a change in the chain structure. For this, questions of the formulation and the process control first have to be clarified. The resulting chain-extended PAs require a comprehensive characterization of their rheological and mechanical properties. The dimensional stability and concentricity of the tubular semi-finished products extruded from the basic material grades and the modified polymer grades had to be quantified and evaluated.

During the experimental investigations, a commercially available polyamide 66 (type: Zytel101 NCO010, manufacturer: DuPont) was used as standard material. Due to its number-average molecular weight of $\bar{M}_n = 28,000$ g/mol, this PA grade has a low melt viscosity.

The product type SMA EF-40 from Cray Valley was used as SMA functional molecule. The bisphenol A diglycidyl ether (EPA) epoxy resin was sourced from Sigma-Aldrich. Irganox 1098 from BASF was used as PA66 thermal stabilizer.

For the reactive compounding process, a co-rotating, closely intermeshing twin-screw extruder (type: ZSK26 MC, manufacturer: Coperion) was used at the IKT.

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Barrel zone	1	2	3	4	5*	6	7	8	9**	10	11
Temperature [°C]	25	200	250	270	270	280	280	280	280	280	280

* Opening for vertical or side-flow metering ** Vacuum degassing

Table 1. Axial barrel temperature profile of the compounding line

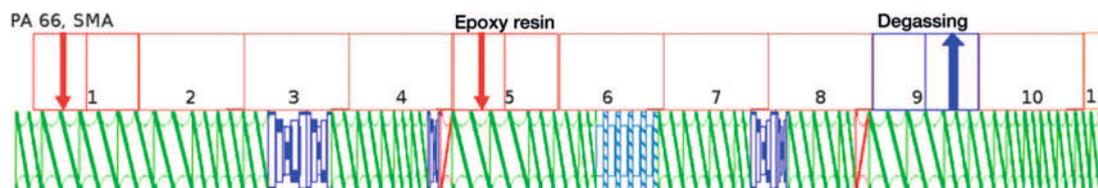


Fig. 2. Optimized screw concept

Its screw diameter is $D_a = 25.5$ mm, his L/D ratio 40.2. A cooling bath and strand pelletizer complete the compounding line.

This article presents as examples two PA66 grades modified with SMA and epoxy resin. **Figure 2** shows the optimized screw configuration that was used in the experiments, and the nominal temperature profile along the extruder barrel (**Table 1**). The melt throughput of the starting material and the screw speed of the extruder were held constant at $\dot{m}_{PA66} = 4.5$ kg/h and $n_s = 100$ rpm.

The standard PA66 predried at a temperature of $T_T = 80^\circ\text{C}$ for $t_T = 6$ h was metered gravimetrically into the first barrel zone of the twin-screw extruder. The SMA functional material and the thermal stabilizer were also metered gravimetrically into the first barrel zone. The epoxy resin functional material was injected into roughly the middle of the compounding unit using a medical injection pump. Decomposition products occurring during the coupling reactions were removed via a degassing opening in barrel zone 9.

Chemical Reactions

The amino end group $[-\text{NH}_2]$ of the PA66 macromolecules is highly reactive. If a small percentage of a functional molecule (SMA/epoxy resin) is added to the PA66, it can form covalent bonds with the functional groups of the PA66. The resulting extension of the chain and the change in the chain structure leads to an increase in

the molecular weight, and hence to a significant increase in viscosity as shown in equation 1 [1]:

$$\eta_0^*(T) = k(T) \cdot \overline{M}_w^{-3,5} \quad (1)$$

Figure 3 shows schematically the coupling reaction of PA66 with SMA/epoxy resin. The maleic anhydride group of the SMA can react with amino end groups of the PA66, giving off water, in order to create an extension of the chain and at the same time an increase in the basic viscosity of the PA66. By contrast with SMA, the epoxy resin ring is linked covalently with the amino end groups of pairs of PA66 molecules during a ring opening reaction, resulting in a drastic lengthening of the chain and a corresponding increase in the basic viscosity.

Rheological Characterization

The rheological material characteristics complex viscosity $\eta^*(\omega)$, memory modulus $G'(\omega)$ and loss modulus $G''(\omega)$ of the standard polyamide and the material modifications produced were determined using an oscillating plate/plate rotary rheometer (type: DSR 200, manufacturer: Rheometrics). The plate diameter was $D_p = 25$ mm and the frequency to be measured lay in the range $0.1 \leq \omega \leq 100$ rad/s.

Figure 4 shows the complex viscosities of the standard materials and of the modified PA66 grades as a function of the an-

gular frequency ω . The material characteristic $\eta^*(\omega)$ can be interpreted as the deformation rate-dependent shear viscosity $\eta(\dot{\gamma})$ using the Cox-Merz relationship. With very low deformation rates, the basic viscosity is the crucial factor for the

Specimen description	χ	\overline{M}_n	$\tan \delta$
	[-]	[g/mol]	[-]
PA66	1	28,000	22
PA_SMA	27	72,000	1.53
PA_SMA_EPA	129	112,000	1.1

Table 2. Rheological characteristics of standard PA66 and the generated copolymers

occurrence of sagging effects. The viscosity increase rate for $\omega = 0.1$ rad/s can be determined from the viscosity functions shown:

$$\chi (\omega = 0,1 \text{ rad/s}) = \frac{\eta_{\text{mod. PA66}}^*}{\eta_{\text{PA66}}^*} \quad (2)$$

η_{PA66}^* stands here for the viscosity of the standard material at $\omega = 0.1$ rad/s and for the viscosity of the modified $\eta_{\text{mod. PA66}}^*$ polyamide at the same deformation rate.

The formulation-specific χ values determined in this way are listed in **Table 2**. It is quite possible to strive for increases in viscosity in the range $30 \leq \chi \leq 130$ with the technology applied, depending on the formulation; some results already achieved are presented in [2]. In the range →

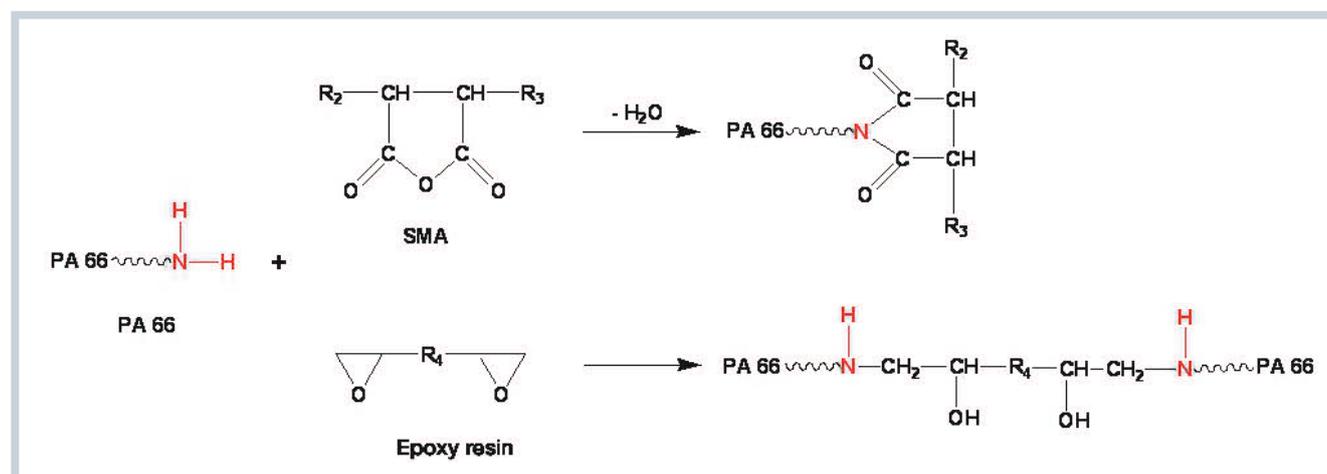


Fig. 3. Chemical reaction during the coupling of SMA/epoxy resin and PA66 [6]

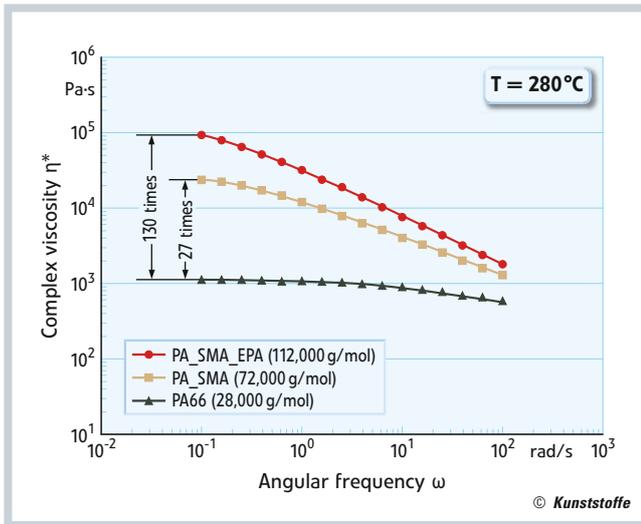


Fig. 4. Rheological material characteristics $\eta^*(\omega)$ of the standard PA66 and the grafted PA66

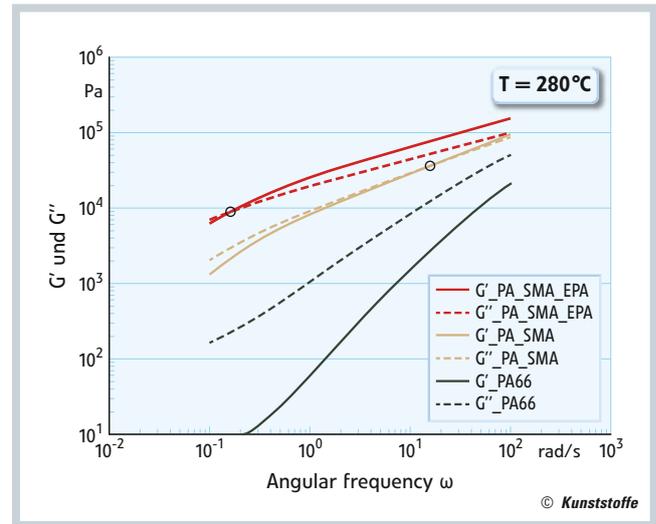


Fig. 5. Rheological material characteristics $G'(\omega)$ und $G''(\omega)$ of the standard PA66 and the grafted PA66

of the processing-relevant deformation rates, the increases in viscosity are far smaller due to the pseudoplasticity, thus simplifying processing. The processor can therefore set the optimum viscosity range for his application via the formulation.

[2] contains the detailed description for calculation of the number-average molecular weight \bar{M}_n for the various modified PA66. Compared with the original value $\bar{M}_{n,PA66} = 28,000 \text{ g/mol}$, they are 2.5 to 4 times higher as a result of the reactive compounding process (Table 2).

The storage modulus (G') and loss modulus (G'') are used to describe the viscous and elastic behavior. The relationship of loss modulus (G'') to storage modulus (G') is referred to as the loss factor $\tan \delta$ and is a measure of the ability of a material to store mechanical energy. Table 3 lists the loss factor of the generated copolymers and of the standard PA66 for $\omega = 0.1 \text{ rad/s}$. The loss factor $\tan \delta (\omega = 0,1 \text{ rad/s}) = G''/G'$ decreases with increasing molecular weight, i.e. the elastic material properties become more predominant.

For comparison, Figure 5 shows the rheological characteristics $G'(\omega)$ and $G''(\omega)$ of the modified PA66 and the standard PA66. It can be clearly seen for the standard PA66 that the loss modulus G'' is above the memory modulus G' over the whole frequency range $0.1 \leq \omega \leq 100 \text{ rad/s}$. The polymer melt exhibits sol character [3], i.e. the viscous properties dominate over the elastic properties. For the modified PA66 specimens the intersection point $G' = G''$ shifts to a very small angular frequency, i.e. the modified PA66 have a higher molecular weight [3], far more pronounced elastic

properties and a higher rigidity than the standard PA66.

The representation for the standard PA66 and the modified PA66 independently of the molecular weight according to the Boltzmann time/temperature superposition principle in [2] confirms that the molecular weight distribution MWD has not changed as a result of the compounding step, and that the increase in molecular weight results from a lengthening of the chain.

Mechanical Characterization

The pellets resulting from the compounding step are dried again before they are molded to form standard test specimens on an injection molding machine (type: Allrounder 220M, manufacturer: Arburg) for the mechanical characterization.

The mechanical material characteristics were determined using a tensile test machine (type: 1455, manufacturer: Zwick) and a pendulum impact tester from the same manufacturer. Tensile tests in accordance with DIN EN ISO 527-1 and Charpy tests in accordance with DIN EN ISO 179-1 were performed on the injection molded standard test specimens in

both freshly molded and in conditioned state. The accelerated conditioning for polyamides was performed in accordance with DIN EN ISO 1110, determining the water absorption up to the equilibrium state. The tensile and pendulum impact test were performed to determine the E modulus, tensile strength R_m , tear strength R_B , elongation at break ϵ_B and the notched impact strength a_{cN} . The mechanical characteristics are shown graphically in Figs. 6 and 7. The plasticizing effect of the water absorbed during the conditioning process can be very clearly recognized.

The E modulus of the modified PA66 remains practically unchanged from that of standard PA66 in both freshly molded and conditioned state (Fig. 6). In freshly molded state, the modified PA66 exhibit a slightly lower notched impact strength, whereas the water absorbed by the modified test specimens results in a significant increase in the notched impact strength, but with a larger standard deviation.

The elongation at break value for the standard PA66 increases from approx. 50 % in the freshly molded state to almost 500 % in conditioned stated. By contrast, the modified PA66 exhibit an increase to

PA66	PA_SMA	PA_SMA_EPA
Offset of the center point: Y = 2.76 mm	Offset of the center point: Y = 0.465 mm	Offset of the center point: Y = 0.407 mm

Table 3. Eccentricity of the extruded pipe profiles

approx. 260 % for specimen PA_SMA and an increase to 100 % for specimen PA_SMA_EPA (Fig. 7). For the most important technical applications of PA66, an elongation at break of 100 % is quite sufficient.

The line marked with circles in Figure 7 shows that in freshly molded state, all three PA66 types have the same tensile strength R_m as they all have the same E modulus value. The line marked with triangles in Figure 7 describes the value of the tear strength R_B . In freshly molded state: The higher the basic viscosity of the PA66, the higher its tear resistance. This is due to the modification step which extends the molecule chains of the PA66 and hence changes its chain structure. After conditioning, the water in between the molecule chains in the PA66 test speci-

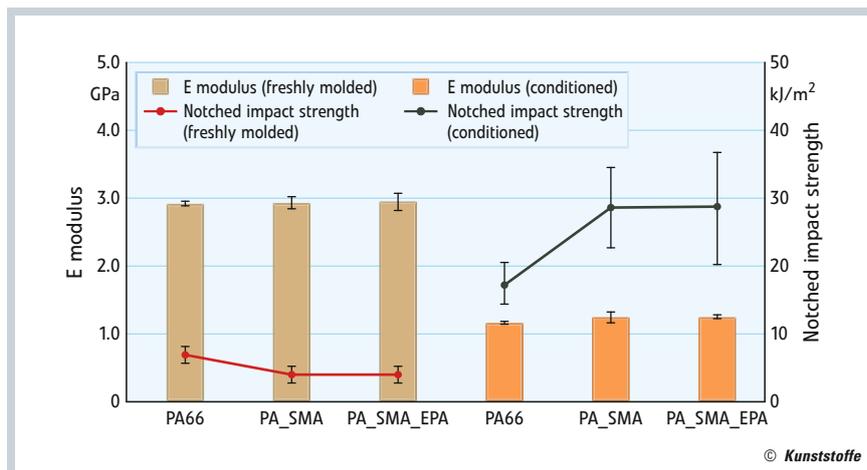


Fig. 6. E modulus and notched impact strength of the PA66 specimens

mens acts as a plasticizer and hence results in a decrease in R_m and R_B . It can be

seen here that the absorbed water has a comparatively stronger effect on the modified PA66 as the chains of the modified PA66 are significantly longer than those of the standard PA6.

Extrusion of Thick-walled Pipe Profiles

In a forming step thick-walled pipe sections were produced from the standard material and two modified PA66 grades (PA_SMA and PA_SMA_EPA). A grooved-barrel extruder with a screw diameter of $D = 60$ mm and an L/D ratio of 25 was used. The die used was a spider-type die with ring dimensions of $D_a = 28$ mm and $D_i = 10$ mm. The pipe profiles were calibrated by vacuum calibration and cooled in a downline quench bath. The die temperature was 240–255 °C for standard PA66, 275–280 °C for the PA_SMA specimen and 285–290 °C for the PA_SMA_EPA specimen.

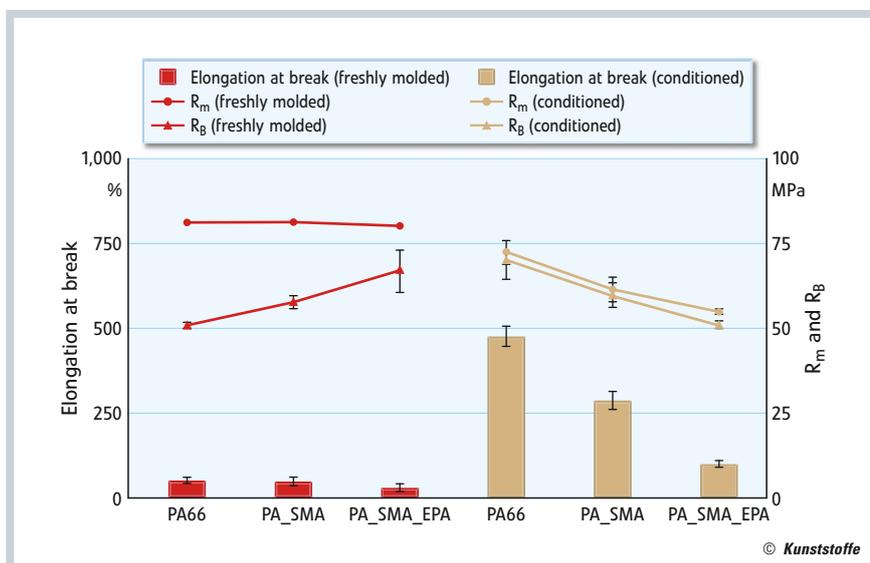


Fig. 7. Elongation at break, tensile strength and tear resistance (R_m , R_B) of the PA66 specimens



Table 3 shows the dimensional stability and concentricity or eccentricity of the extruded specimens. The sagging behavior of the pipes made from standard polyamide can be clearly seen as a pronounced offset of the center point by $Y = 2.76$ mm in gravity direction. The deviation in the wall thickness distribution of this pipe section is more than 25 %. The modified PA66 grades processed on the same production line show a greatly improved result. The offset is only $Y = 0.465$ mm for the PA_SMA specimen and only $Y = 0.407$ mm for the PA_SMA_EPA specimen. The deviation in the wall thickness distribution of the two specimen products is ≤ 5 % and thus satisfies industrial production criteria.

Conclusion

During this project, high-viscosity PA66 was produced by reactive compounding. A pipe section of modified PA66 was successfully produced using the conventional processing technology (1st possibility in Fig. 8). As not every extrusion shop has both process steps on the premises, either investment can be made in a single-stage process or concentrates can be used.

The single-stage process (2nd possibility in Fig. 8) also increases the profitability. This can be achieved e.g. by the use of a gear pump as pressure generator which enables the material modification and the forming step to be combined. This type of single-stage process offers advantages such as lower raw material prices compared with high-molecular polyamide grades, lower operating costs (electricity, water, personnel), improved material properties thanks to lower mechanical and thermal material load and high flexibility in the production of application-special special formulations and products [4]. A disadvantage of the single-stage process is that

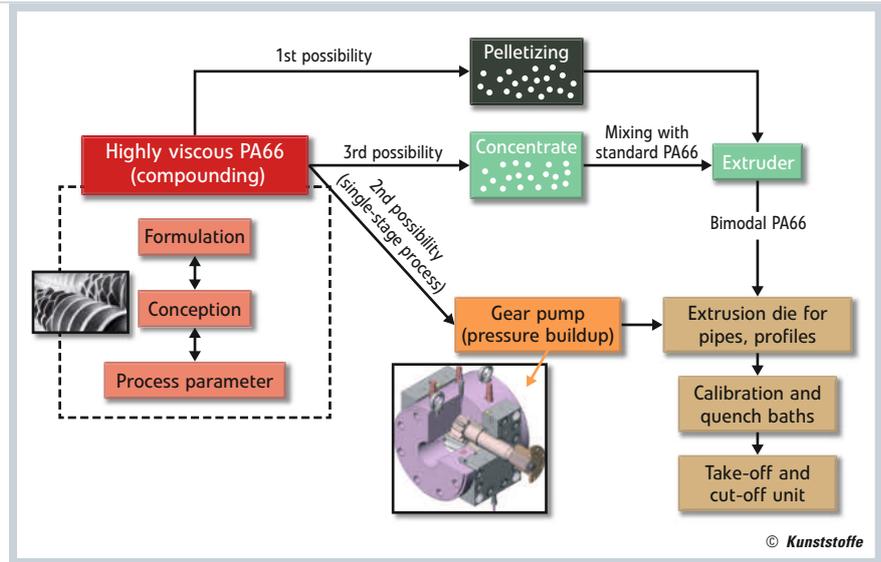


Bild 8. Process flow chart of the practical application possibilities for production of the pipes [7, 8]

the replacement of the extruder with a twin-screw extruder and gear pump represents an investment that is only viable above a given volume demand.

The high-molecular PA66 produced here has such long chains that it can also be used as a concentrate (3rd possibility in Fig. 8). Dry mixing of standard PA66 with 10 or 20 % of high-molecular concentrate and processing on a conventional extruder produces a bimodal PA66 that has a sufficiently high viscosity to prevent sagging. Other bimodal materials are also known to have higher strengths and better long-term properties [5]. The test series on these materials are currently being carried out at the IKT. ■

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- 8 Photographic material from Coperion GmbH, Stuttgart, Germany

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