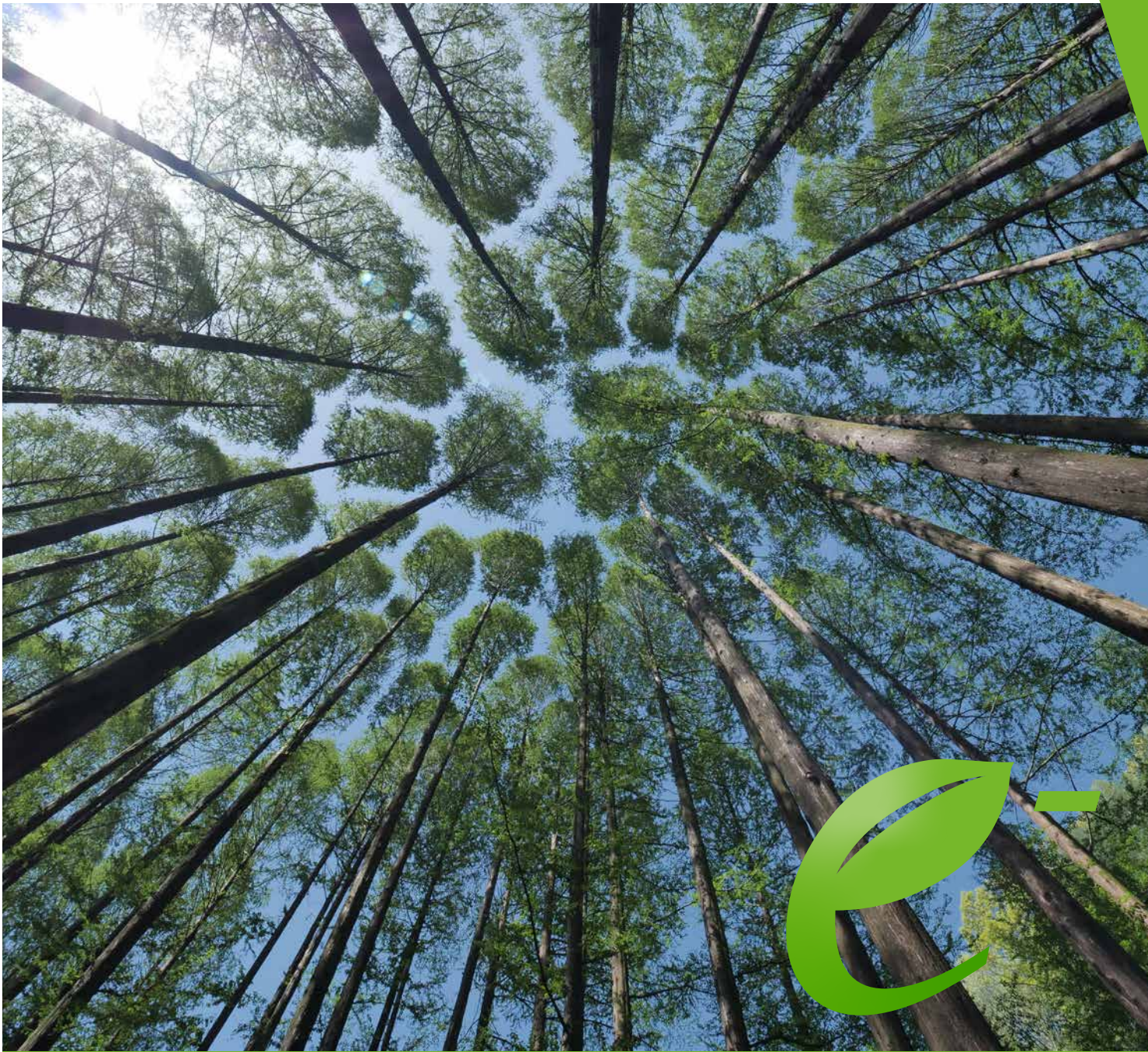


Paint Preparation of SMC Form Parts

Robot-controlled surface functionalisation and post-curing by electron treatment



Abstract

The robot-controlled edge layer treatment of defect-free three-dimensional SMC form parts before the industrial coating process completely cures their edge layer. This reduces or prevents the escape of gas inclusions from the SMC through this cured edge layer and the generation of surface defects in the industrial coating process. For the user, this leads to an improved coating quality of SMC form parts, low and inline-capable cycle times as well as the saving of previously necessary cost- and time-consuming reworking or additional processes.

SMC form parts with a slight three-dimensional structure, such as tailgates and bonnets, can be modified with a high-power area emitter. The additional running costs amount to about 0.10 €/m².

Very complex SMC form parts require the development of a more powerful emitter with a higher acceleration voltage in order to enable an economic mode of operation.

Content

1. Standardised plants that are not standard	3
2. Physical process for chemical modification.....	4
3. Precise process control	6
4. Compact facility design	7
5. Novel pre-coating method for Sheet-Moulding Compounds	8
6. Summary	11
7. Contact.....	11
8. Literature.....	12

1. Standardised plants that are not standard

The ASIS GmbH, headquartered in Landshut near Munich, is a system provider for automated systems in surface technology. The internationally positioned company exports from four locations in Germany and a subsidiary near Shanghai to over 30 countries worldwide.

The range of services includes turnkey systems for wet paint or enamel coating, systems for quality control, surface treatment and electron treatment, wet paint application technology and process automation technology.

A dedicated digital simulation site develops material flow simulations, offline robot programming and feasibility studies.

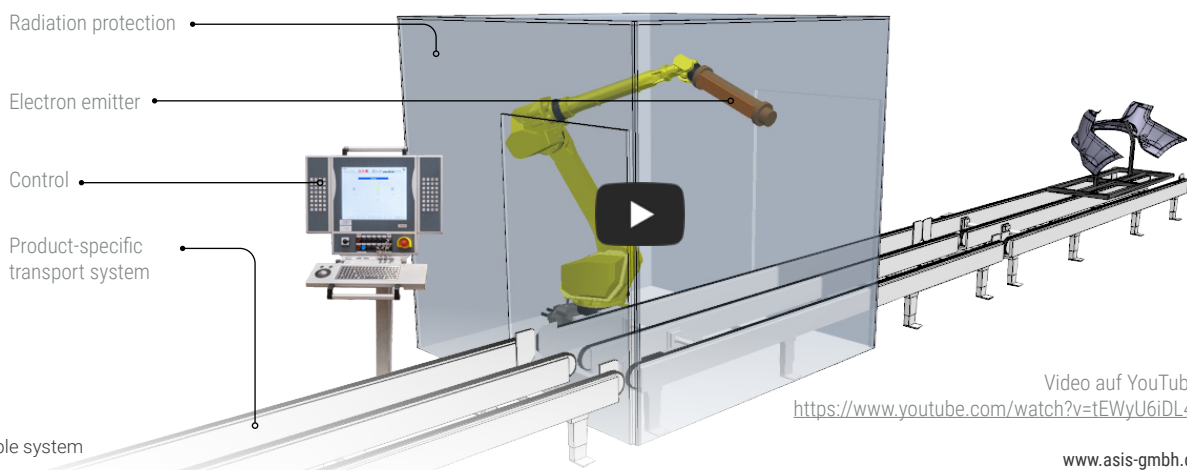


ASIS in numbers

- Founded: 01.05.1998
- CEO: Hans-Jürgen Multhammer
- Quality assurance: ISO 9001
- Inform. assurance: TISAX
- Export countries: > 30 worldwide



Complete solutions in the area of inline electron beam technology for surface and edge layer modification of plastic parts are the newest business field. These industrial systems consist of compact electron emitters connected to an industrial robot as well as a product-specific transport, control and radiation protection system (see Fig. 1).



Video auf YouTube:
<https://www.youtube.com/watch?v=tEWyU6iDL4k>



2. Physical process for chemical modification

Edge layer modification using low-energy electrons is a physical process for the chemical modification of plastic parts and uses the temporally and spatially precise energy input via accelerated electrons. The first industrial applications were established in the 1970s, e.g. at FORD Motors Corporation for the curing of liquid coatings on plastic interior parts [1].

Low-energy electron emitters in the energy range from 100 keV to 300 keV are used.

This mostly unknown physical process offers enormous potential for sustainable and environmentally friendly chemical modification of raw materials, semi-finished products and end products.

Compared to thermal processes, the energy consumption can be significantly reduced, resulting in cost reductions for the user.

In the case of sustainable and highly productive electron beam technology, the use of chemical reaction initiators (e.g. peroxides, photo-initiators) is not required, as the accelerated electrons transfer their kinetic energy to the atoms and molecules of the plastics to be modified in several interactions.

At the end of the energy transfer process, covalent bonds are broken and radicals are formed (see Fig. 2).

The main applications are:

- curing of coatings and paints [2]
- curing of pressure-sensitive adhesives [2]
- cross-linking of shrinking films [3]
- partial cross-linking of tyre components [4]
- cross-linking of green fibres prior to solid state pyrolysis [5]
- grafting of separators for lithium secondary batteries [6]
- grafting of proton exchange membranes for fuel cells [7] and vanadium redox flow batteries [7]

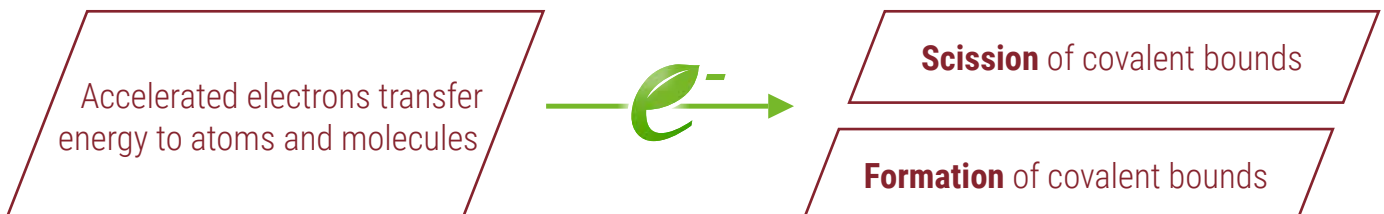


Fig. 2: Basic mechanisms of the interaction of accelerated electrons

The radicals are the starting point of complex chemical reactions leading to a change in the chemical structure and altered chemical (e.g. oil resistance), mechanical (e.g. strength) and thermal (e.g. heat resistance) properties of the treated plastics.

A tailor-made chemical modification of plastics requires the specific selection of the process parameters acceleration voltage, beam current, dose, and dose rate.

Furthermore, the process parameters depend on the properties of the plastics to be modified (constitution and configuration of the polymers [8], cross-linking additives [9], and antioxidants [10]) and the chemical environment during electron treatment.

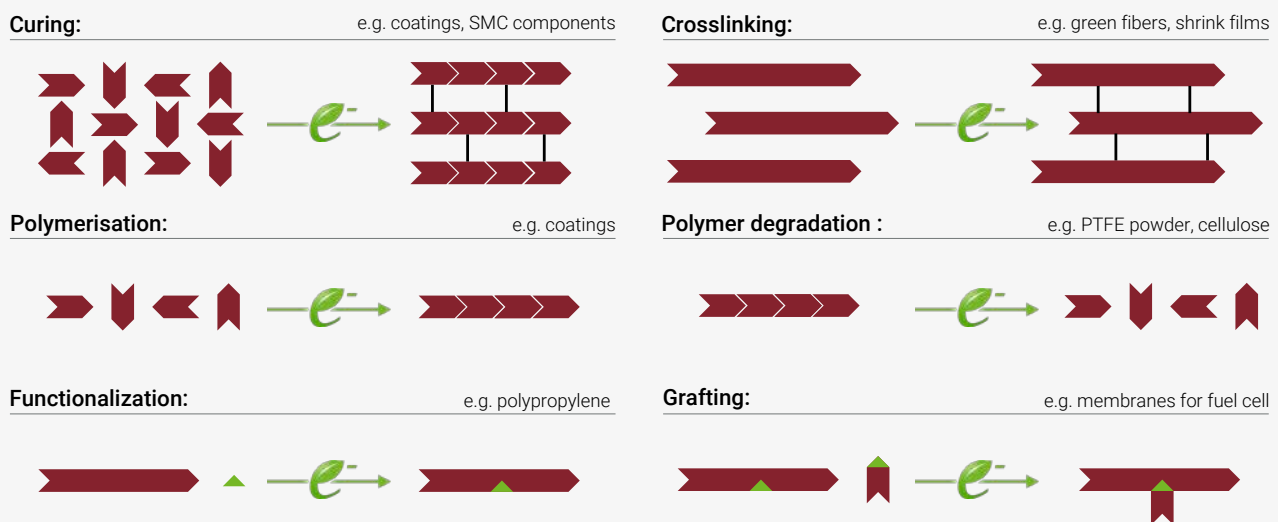


Fig. 3: Overview of electron-induced chemical reactions

The chemical environment includes the gas atmosphere [11], water [12], pH-value [13], and temperature during electron treatment [14].

An overview of the electron-induced chemical reactions is shown in Figure 3.

3. Precise process control

The dose characterises the energy absorbed per mass and controls the number of radicals produced per polymer molecule and thus the intensity of the desired chemical reaction. The unit of the dose is Gray (abbreviation: Gy).

The dose rate during electron treatment describes the dose absorbed per time and controls the radical generation rate.

Consequently, it influences all time-dependent processes during the chemical modification of the plastic parts.

These are, for example, the reaction kinetic, secondary reactions in an aqueous environment, the influence of atmospheric oxygen as well as the temperature increase in the plastic part.

The acceleration voltage controls the spatial energy input in the plastic part to be modified (see Fig. 4).

The beam current controls the temporal energy input into the edge layer of the plastic part and thus the surface rate (see Fig. 5).

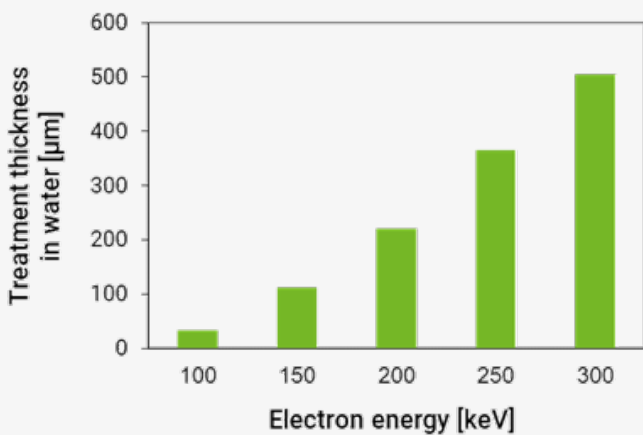


Fig. 4: Treatment thickness as function of electron energy

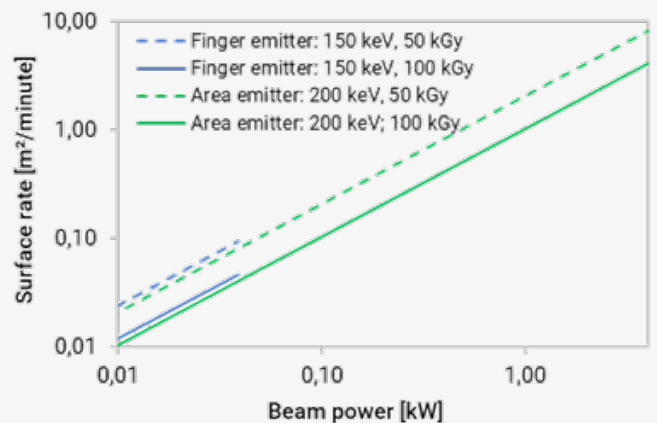


Fig. 5: Surface rate as function of beam power

4. Compact facility design

The availability of maintenance-free, compact, low-energy electron emitters allows the construction of facilities for surface layer modification that can be integrated into the production line.

These facilities are characterised by low costs, short service times as well as high energy efficiency, high surface rate and long service life (see Fig. 6).

Furthermore, these compact electron emitters can be coupled with a robot so that, for example, lacquers on three-dimensional components can be cured or surfaces of three-dimensional plastic parts can be pre-treated before a coating or bonding process.

For outdoor applications, high UV protection is usually required. Here, the curing with low-energy electrons offers an energy-efficient solution approach.

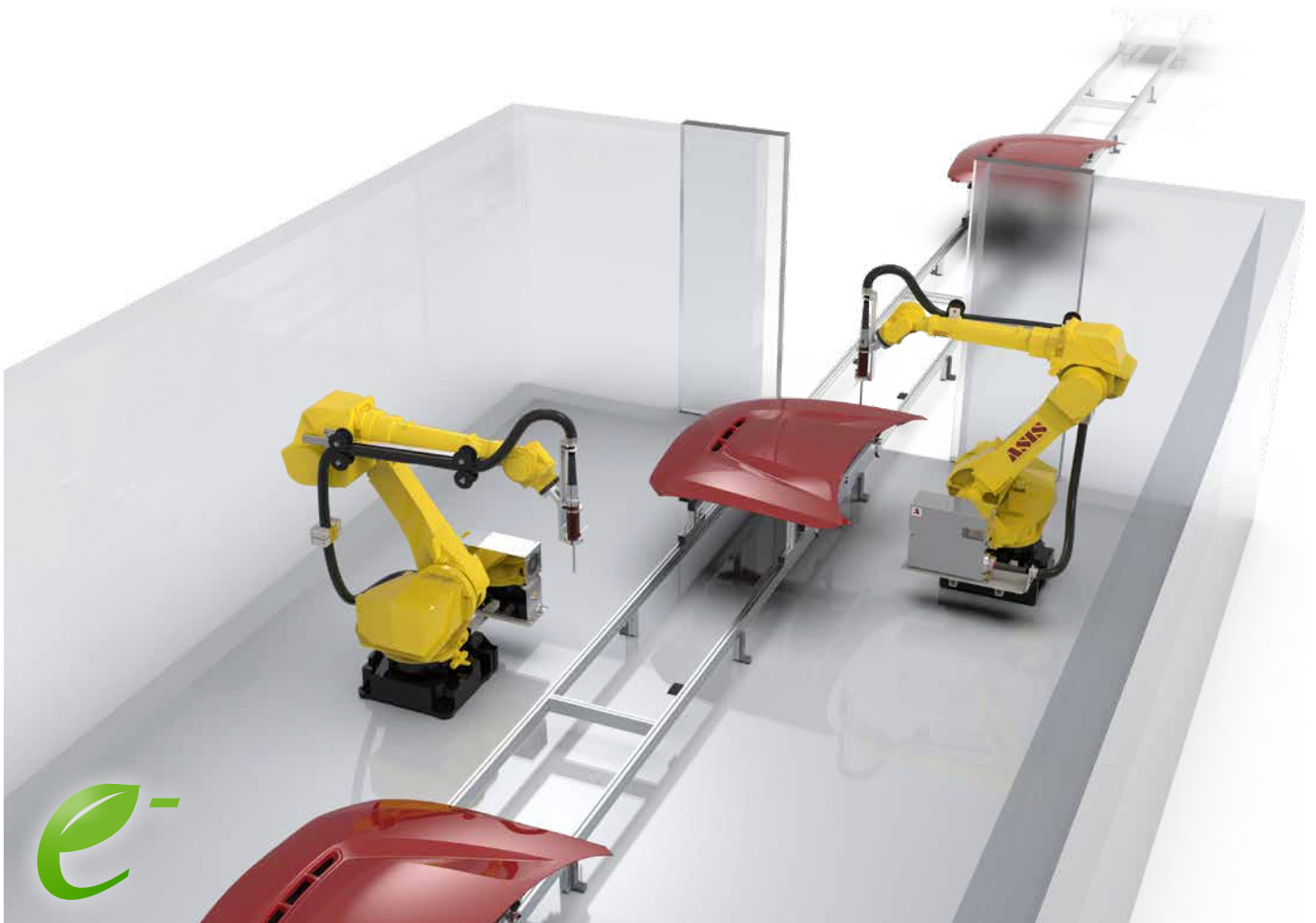


Fig. 6: Robot coupling of a finger emitter for the purpose of edge layer modification of three-dimensional form parts

5. Novel pre-coating method for Sheet-Moulding Compounds

Sheet-moulding compounds (SMC) are increasingly used and coated. The production of SMC components with defect-free surfaces requires the careful adjustment of insert size, production viscosity, pressure and temperature depending on the filler and fibre content as well as the component geometry.

Sufficient degassing of the gases caused by the curing reaction, especially nearby of edges and ribs, is of central importance in the SMC pressing process.

Despite defect-free SMC surfaces, surface defects (Fig. 7) are observed after the industrial coating process. The reasons are trapped air bubbles in the SMC component under the closed form part surface and in the edge layer area as well as the incomplete thermal curing of the SMC components in the industrial pressing process.

Subsequent temperature treatment in the industrial coating process increases the pressure in the enclosed bubbles. Due to not fully cured SMC material, the surface cannot resist and the bubbles burst. The remove or avoidance of these surface defects requires additional cost- and time-intensive process steps (e.g. in-mould coating or sanding, filling).

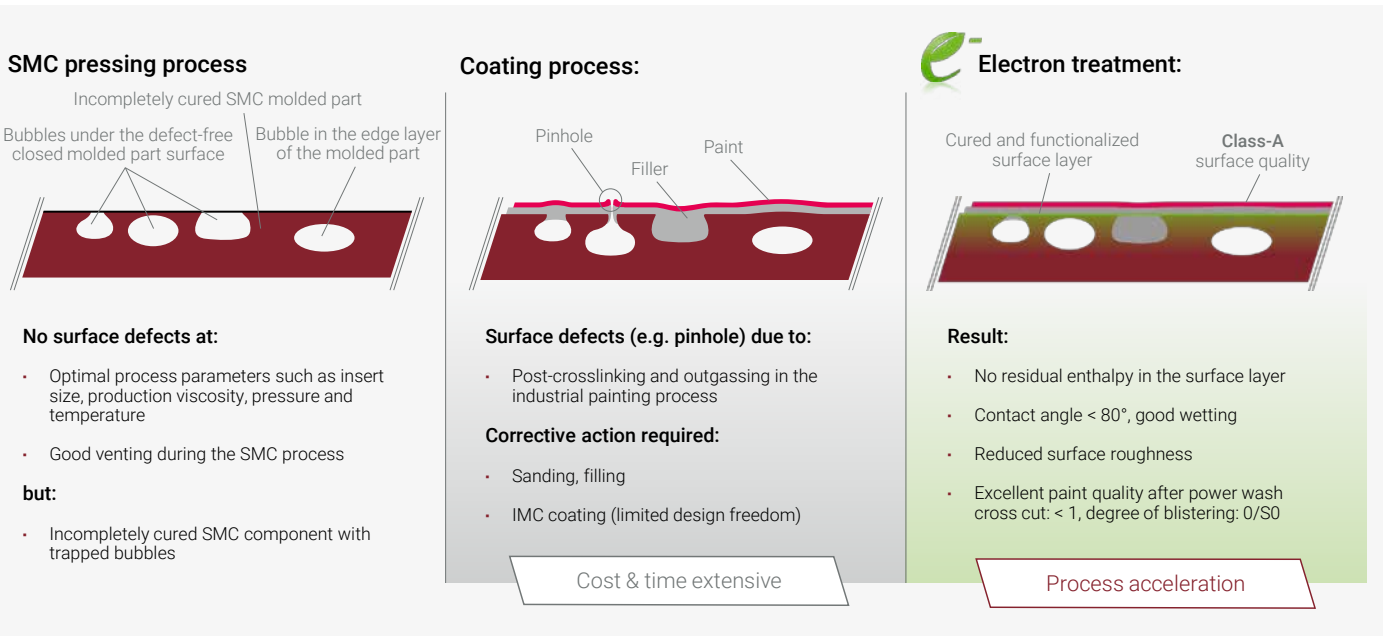


Fig. 7: Novel pre-coating method for Sheet-Moulding Compounds

This is where the new concept comes in. It uses electron beam curing to completely cure the incompletely cured SMC moulded part in the edge layer.

Maintenance-free compact low-energy electron emitters can be coupled with a robot to, for example, cure coatings on three-dimensional components or to pre-treat surfaces of three-dimensional plastic parts before a coating or bonding process.

A robot-controlled electron treatment of defect-free SMC edge layers cures them completely ($\geq 130 \mu\text{m}$) and simultaneously functionalises the SMC surface.

This completely cured SMC edge layer reduces or avoids the escape of gas inclusions from the SMC and thus the generation of additional surface defects after the industrial coating process (Fig. 7).

Based on the component-specific CAD data, the calibration parameters of the electron emitter to be used and a programming tool, the modification paths for complex three-dimensional moulded parts are calculated.

The new method leads to an improved coating quality of SMC moulded parts in the industrial coating process, low and inline capable cycle times as well as the saving of previously required cost- and time-intensive rework.

Modern compact low-energy electron accelerators use linear cathodes (area emitters) and point cathodes (finger emitters) as well as a single-stage acceleration, so that no scanner is needed for the out fanning of beam.

The vacuum system required to generate free electrons is sealed off in the beam exit direction by a thin electron beam exit window (usually titanium foil).

When leaving the vacuum system, the low-energy electrons release a part of their kinetic energy in the electron beam exit window and heat it up.

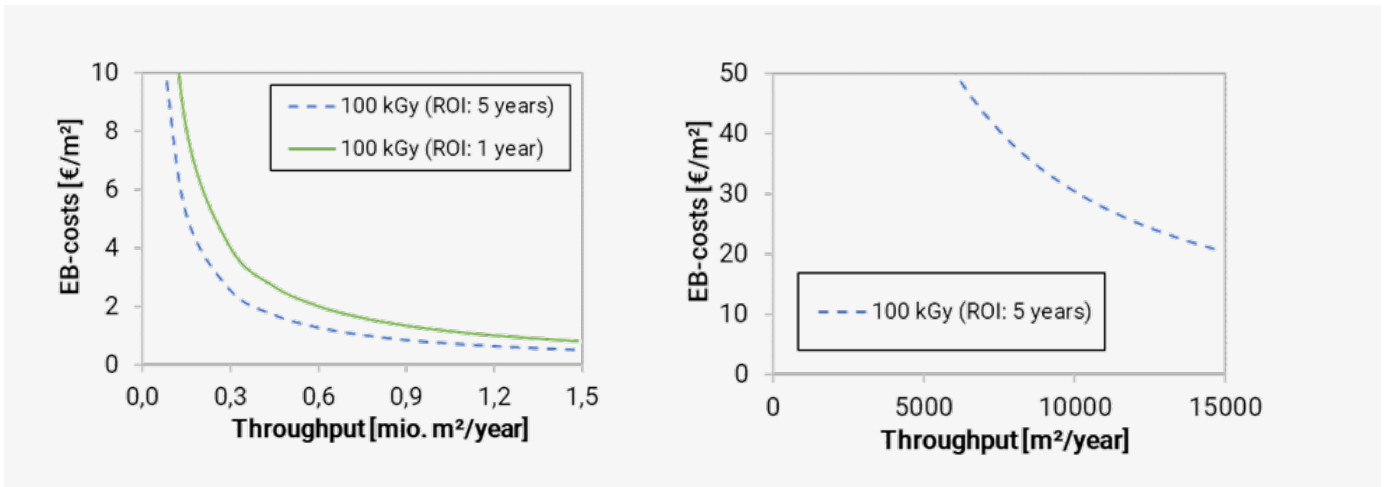


Fig. 8: Additional total costs of electron beam (EB) modification with an area emitter (left) or finger emitter (right)

Excessive operating temperatures of the electron beam exit window lead to fatigue and later to mechanical failure. In the interest of long lifetimes, the area-specific beam power is limited.

Thus, the maximum beam power of compact electron emitters is also dependent on the area of the electron beam exit window.

The required 3D capability of a compact electron emitter decreases with increasing area of the electron beam exit window and beam power of the electron emitter.

Thus, an economic modification of three-dimensional moulded parts requires the use of efficient area emitters in combination with a 3D-capable finger emitter (see Fig. 8).

6. Summary

The coupling of compact low-energy electron emitters with an industrial robot enables a surface functionalisation and a complete edge layer curing of SMC components in a single process step. This leads to an improved coating quality in the industrial coating process.

SMC components with a slightly pronounced three-dimensional structure (e.g. tailgates, bonnets) can be modified with an area emitter. The additional total costs including investment and maintenance are less than 1 € per m² if the total surface area of SMC components to be modified annually amounts at least 1.2 million m² (see Fig. 8).

The surface modification of complex three-dimensional SMC components requires the development of a more powerful finger emitter with an acceleration voltage of at least 200 kV (so far only 150 kV is available on the market). This increase in power is associated with an increase in the area of the electron exit window and a reduction in the 3D capability of the finger emitter. Consequently, an economic modification of three-dimensional moulded parts requires the use of efficient area emitters in combination with a 3D-capable finger emitter (see Fig. 8).

7. Contact

For further information on electron treatment, please contact:



Dr. rer.-nat. Uwe Gohs

u.gohs@asis-gmbh.de

ASIS GmbH
Kiem-Pauli-Straße 3
84036 Landshut, GERMANY

www.asis-gmbh.de



Otto Pritscher

o.pritscher@asis-gmbh.de

ASIS GmbH
Kiem-Pauli-Straße 3
84036 Landshut, GERMANY

www.asis-gmbh.de

8. Literature

- [1] Glöckner, P.; Jung, T.; Struck, S.; Studer, K.: Radiation curing for coatings and printing inks, Vincents Network, Hannover, Germany, 2008, ISBN 978-3-86630-904-4.
- [2] Holl, P.: Two ideal applications for the low energy electron-beam accelerator: Vulcanization of pressure-sensitive adhesives and controlled through-curing of coatings on parquet. In: Radiation Physics and Chemistry 1995, 46(4-6), S. 953-958.
- [3] Günthard, C.; Lee, D. W.: New applications of 10 MeV electrons for reeled goods. In: Radiation Physics and Chemistry 2000, 57, S. 641-645.
- [4] Hunt, J. D.; Alliger, G.: Rubber – application of radiation to tire manufacture. In: Radiation Physics and Chemistry 1979, 14(1-2), S. 39-53.
- [5] S. Machi: Radiation technology for sustainable development. Radiat. Phys. Chem. 1995, 46(4-6), 399-410
- [6] Gwon, S.-J.; Choi, J.-H., Sohn, J.-Y.; An, S.-J.; Ihm, Y.-E.; Nho, Y.-C.: Radiation grafting of methyl methacrylate onto polyethylene separators for lithium secondary batteries. In: Nuclear Instruments and Methods in Physics Research B 2008, 266(15), S. 3387-3391.
- [7] Ke, X., Drache, M., Gohs, U., Kunz, U., Beuermann, S.: Preparation of polymer electrolyte membranes via radiation-induced graft copolymerization on poly(ethylene-alt-tetrafluoroethylene) (ETFE) using the crosslinker N,N0-methylenebis(acrylamide). In: Membranes 2018, 8, ID102, doi:10.3390/membranes8040102.
- [8] K. Naskar, U. Gohs, G. Heinrich; Influence of molecular structure of blend components on the performance of thermoplastic vulcanisates prepared by electron induced reactive processing. Polymer 91 (2016) 203-210
- [9] D. H. Han, S.-H. Shin, S. Petrov, Crosslinking and degradation of polypropylene by electron beam irradiation in the presence of trifunctional mono-mers. Radiat. Phys. Chem. 2004, 69, 239-244
- [10] N. A. Andreucetti, C. Sarmoria, O. A. Curzio, E. M. Valles, Effect of the phenolic antioxidants on the structure of gamma-irradiated model polyethylene. Radiat. Phys. Chem. 1998, 52(1-6), 177-182
- [11] A. Rivaton, S. Cambon, J.-L. Gardette, Radiochemical Aging of Ethylene-Propylene-Diene monomer elastomers. I. Mechanism of degradation under inert atmosphere. Journal of Polymer Science: Part A: Polymer Chemistry. 2004, 42, 1239-1248.
- [12] N. Getoff, Radiation chemistry and the environment. Radiat. Phys. Chem. 1999, 54 377-384.
- [13] C. von Sonntag, Free-radical-induced chain scission and cross-linking of polymers in aqueous solution-an overview. Radiat. Phys. Chem. 2003, 67, 353-359
- [14] B. Krause, D. Voigt, L. Häußler, D. Auhl, H. Münstedt, Characterization of Electron Beam Irradiated Polypropylene: Influence of Irradiation Temperature on Molecular and Rheological Properties. Journal of Applied Polymer Science 2006, 100, 2770-2780
- [15] Gedan-Smolka, M.; Müller, A.; Gohs, U.; Calvimontes, A.: Electron pre-treatment of sheet molding compounds (SMC). In: Progress in Organic Coatings, 2011, 72, S. 159-167.
- [16] Müller, M. T.; Zschech, C.; Gedan-Smolka, M.; Pech, M.; Streicher, R.; Gohs, U.: Surface modification and edge layer post curing of 3D sheet moulding compounds. In: Radiation Physics and Chemistry, 2020, 173, 108872, <https://doi.org/10.1016/j.radphyschem.2020.108872>.