Crosslinked Plastics. Thanks to improved properties, plastics crosslinked by irradiation are increasingly offering an economic alternative to high-performance thermoplastics. Dr. Andreas Ostrowicki and Uwe Stenglin have been involved with this process since the very beginning and speak here about rapidly developed applications, promising ideas and how mid-size companies can keep up with the chemistry giants.

» A Radiant Future for Materials Properties «

Twenty years ago, applications in the electro-industry stood at the beginning of a development that has spread to many industries in the meantime: the use of economical radiation-crosslinked plastics with improved materials properties. Among others, BGS Beta-Gamma-Service GmbH & Co. KG, Wiehl, Germany, was active, having specialized in radiation crosslinking and sterilization for more than 25 years. They aim to expand the area of application among plastics products by improving, for example, thermal and wear resistance.

Interview partners were Managing Director Dr. Andreas Ostrowicki, and Dipl.-Ing. (FH) Uwe Stenglin, his managing partner at PTS Plastic-Technologie-Service, Marketing und Vertriebs GmbH, Tauberzell, Germany, where radiation-crosslinked high-performance compounds are manufactured.

Kunststoffe: The molecular structure of plastics can be crosslinked by beta and gamma radiation, thereby improving several of their materials properties. What actually occurs during radiation crosslinking?

Dr. Andreas Ostrowicki: For the most part, beta radiation from powerful electron accelerators is used with an energy as high as 10MeV. When it penetrates a polymer, the electron beam is attenuated and transfers kinetic energy to the material via a cascade of secondary electrons. The macromolecules, thereupon, break up into radicals that effect crosslinking with additional macromolecules. Radiation crosslinking is an essentially physical phenomenon that leaves no residue in the material. When it is used, numerous materials properties, such as temperature stability, chemical resistance and/or tribiological behavior can be improved and set precisely. By this means, low-cost types of plastics can replace high-performance plastics for any number of application areas.

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Kunststoffe: In the production process, radiation crosslinking is a final processing step following shaping. PTS Plastic-Technologie-Service (PTS) manufactures radiation-crosslinked high-performance compounds. How did your cooperation with Beta-Gamma-Service (BGS) come about?

Uwe Stenglin: Right from the start, the company was originally founded with the idea in mind of developing engineering thermoplastics that were crosslinkable by means of radiation. We were aware that, e.g., polyethylene (PE) can be improved for use in underfloor heating, shrink tubing or wire insulation by irradiation. But for other materials, such as polyamide (PA) or polybutylene terephthalate (PBT), there were no established raw material mixtures. The raw material compound has to be equipped with stabilizers and additives to support, or even enable the radiation crosslinking process.

I recall at the time following up on a suggestion by BGS, that polyamide might possibly be crosslinked by using triallyl isocyanurate (TAIC). In those days, it was available only in liquid form, so it was out of the question to process such a material by injection molding. One of our first challenges was to apply

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Dr. Andreas Ostrowicki is Managing Director of BGS Beta-Gamma-Service GmbH & Co. KG, Wiehl (figures: BGS/Zillmann)

and laid the cornerstone for many years of joint developmental work.

Kunststoffe: How have radiation-crosslinked plastics fared in competition with high-performance plastics in the meantime?

Stenglin: After our successes in the electro industry, one thing followed another. For example, it suddenly turned out that electrical components made from radiation-crosslinked PA66 were not only temperature reliable, but had a longer mechanical life. In very involved experiments, scientists in the Department of Polymer Technology (LKT) at the University of Erlangen-Nuremberg, Germany, were able to solve the issue: The weaker, amorphous phases in the PA matrix that were left on the surface of the part due to slower cooling sequences in the mold are crosslinked by irradiation. That is, a part has a weak spot right where it is mechanically loaded, this spot is more stable following irradiation. Due to this discovery, we became more involved with questions of tribiology and then deliberately crosslinked, e.g., the running surfaces of plastic gear wheels and bearings.

Another example of how this radiation crosslinking of a surface effects astounding results is the propeller blades in pumps. Previously, polyether ether ketone (PEEK) had to be used for this application – at some EUR 90/kg. We have developed an alternative material that costs only EUR 24/kg including radiation crosslinking. Such successes from radiation crosslinking keep moving us ahead, not only in the electro industry, but also in the auto industry or in mechanical engineering.

Ostrowicki: And sometimes, necessity is the mother of invention. During a production interruption in Germany several

> **»Low-cost types of plastics can replace high-performance plastics for any number of application areas.«** Ostrowicki

TAIC to a powdery carrier. When we began developing compounds, we were looking for easy-to-process additives to support crosslinkability. Nowadays, we supply masterbatch types based on carrier polymers made from PA6, PA66, PA66/6, PA11, PA12, PBT, COPE (copolyester) or COPA (copolyamide).

Kunststoffe: What were your first applications in the mid-eighties?

Stenglin: At the time, a large company in the electro industry was interested in using thermoplastic polymer materials instead of the thermosets they had been using in the production of electro-technical and electronic components. The company expected extraordinary savings from such a system change. The handicap for thermplastic polymers lay in the over 260°C temperatures that the material had to stand up to. Of course, they could have taken an expensive high-temperature polymer, but we succeeded with a glass fiber-reinforced radiation-crosslinked PA66. That was a breakthrough for both companies

years ago, PA12 was in very short supply. PTS seized this opportunity to develop a material for tubing on a PA6-blend basis that has become successful in the meantime. But that material is not just an equivalent replacement: the plastic plus crosslinking service now costs less than half of the tubing previously produced from PA12.

Stenglin: Not by chance was PA12 the favorite for automobile tubing. It is chemical resistant, turns out to be impact tough under mechanical loading and is insensitive to stress cracking, which proved to be of advantage when traveling on wintry roads where the tubing is loaded by saltwater and consequent corrosion due to stress-cracking. The radiation-crosslinked PA6 blend satisfies these requirements.

More yet: To receive their final shape, tubes are thermoformed. With PA12, this process goes on for a relatively long period of time, since, among other things, warm-up must be provided so that the material remains stable during the shaping process. Our radiation-crosslinked PA6 blend is compara- →

tively robust here: Shaping was, according to our estimation, capable of taking place much faster and at temperatures high above the previous melting point. Its users are still not exhausting PA6's easy-going behavior during thermofixation; there is still a gap for process engineering to fill.

Ostrowicki: Meanwhile, we can build on a great wealth of experience in the various areas of application for radiation crosslinking. We are pushing forward with many developments together with academic institutes and research organizations in business. One result of this cooperation is, for example, the marketability achieved meanwhile for thermoformable PA12 films, or new potential for joining different materials by means of vibration welding. I am quite convinced that radiation crosslinking will be found to have a great deal of undiscovered potential that I would very much like to realize together with our users.

Kunststoffe: How do your two mid-size companies manage to exist on the playing field of huge chemicals companies capable of supplying both the material and the crosslink technology from a single source?

Ostrowicki: With those typical virtues that make mid-size German companies successful: First of all, that means the flexibility to want to accept unusual challenges and then closeness to our users that our responsible employees strengthen by being directly addressable at all times.

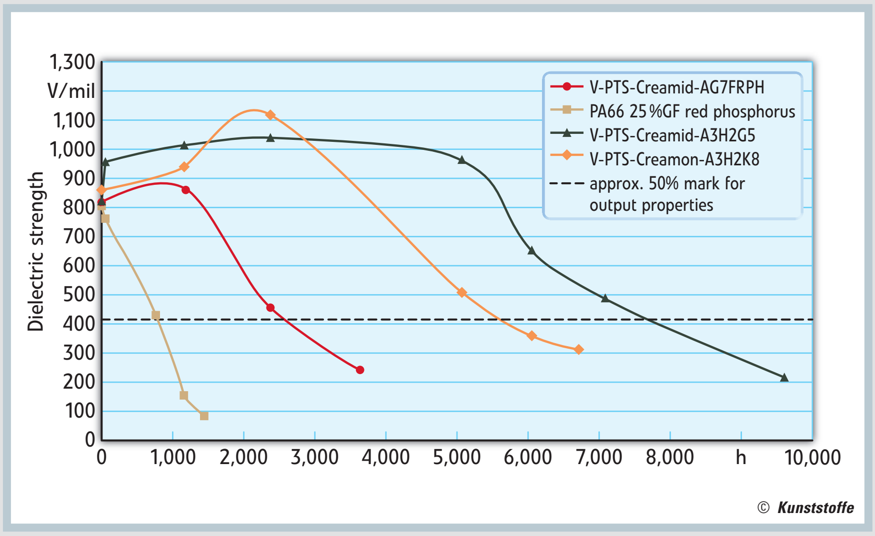
Stenglin: I would like to underline that with an example: There was a multinational company that marketed a polybutylene terephthelate (PBT). This was a really good material. But after only three years, it was sacked, because the profitability threshold hadn't been reached. Private, mid-size companies tick differently, they trust in their ability and their products. After three years, PTS still hadn't made money. In the fifth year following start-up, it got exciting, and today we are the worldwide leader for radiation-crosslinkable engineering plastics. I find this stick-to-itiveness only among personally run companies.

Ostrowicki: That's true for us, too. In 1981, the company was founded with the idea for a business that would supply the radiation technology required by many user companies for whom purchasing, equipping and operation are too complicated and expensive. This strategy has worked us as a service provider. In the meantime, the capacities of our radiation lines are so great that an individual company would scarcely be able to utilize them fulltime. Moreover, we offer our users the assurance that they don't have to limit themselves to a traditional materials supplier for a long time. With our broad knowledge of what is possible with these technologies and together with a competent supplier of radiation-crosslinked materials, we offer suitable solutions.

> ***» Mid-size companies tick differently, they trust in their ability and their products. «*** **Stenglin**

Kunststoffe: What stands in the way of even more rapid development of applications for radiation-crosslinked plastics?

Ostrowicki: We have to move faster up into the spheres of sound scientific knowledge. For numerous single issues we are already working together with science and research and have elucidated and documented many mechanisms of radiation crosslinking. But we keep running into new, amazing effects that ought to be investigated further, but for which we unfortunately lack the capacities. For instance it has turned out in some cases that the properties of several fiber composite plastics (FCP) are quite obviously improved under radiation. How-



The improvement in electrical puncture resistance stands out when radiation-crosslinked polyamide types are compared with non-crosslinked flame resistant PA66 materials. In one extreme case, electrical life at 170 °C improves tenfold due to radiation crosslinking

Dipl.-Ing. (FH) Uwe Stenglin laid the cornerstone for a family company to produce polymer materials in 1986 when he founded PTS Plastic-Technologie-Service, Marketing und Vertriebs GmbH, Tauberzell. He is Managing Director of the PTS Group

ever, this isn't always the case. We don't yet know why. So we would like to invite scientists to cooperate with research papers on this and many other issues.

Stenglin: We have already made considerable progress; there are quite a lot of technical data sheets are available from radiation-crosslinked plastics. Thermal aging behavior (without mechanical loading) has already been extensively documented by the auto industry. We still need to catch up with long-term values, such as isochronous stress-strain curves. Especially clear advantages can be expected in this field. Unfortunately, there are bottlenecks at the testing institutes.

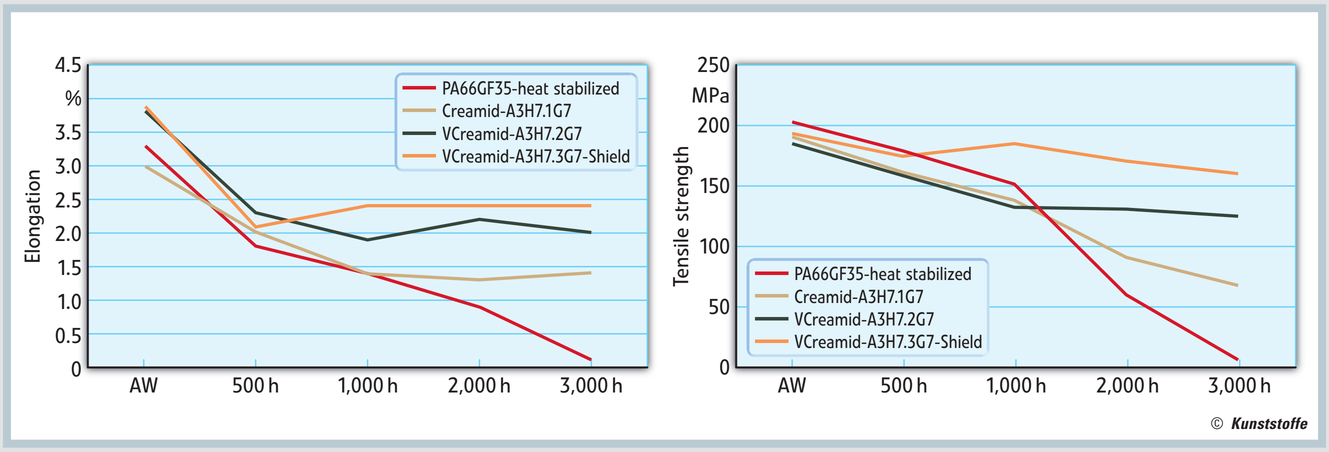
Kunststoffe: How will radiation-crosslinked plastics develop?

Stenglin: In the beginning, there was the improvement of temperature reliability for electrotechnical components. To this came tribiological topics in mechanical engineering. Currently, the auto industry is interested in chemical resistance, acid resistance and repeatedly in temperature reliability. Our PA66 materials have been shown to survive over 3,000 hours at 220 °C in an automobile.

Based on their advantages, these radiation-crosslinked PA66 types have been successful with glass fiber-reinforcement. A radiation-crosslinked thermoplastic is not a thermoset, but, depending on its degree of crosslinking, a thermoelastic material with a softening point that lies above its previous melting point. Thus it's somewhere between a rubber and a thermoset. Radiation-crosslinked PA66 doesn't melt, but it becomes thermoelastic at 260 °C, PA6 does this at 220 °C and PA12 even at 180 °C, which is why PA66 is often the material of preference. Most of all under mechanical loads in the temperature range between 205 and 245 °C.

Ostrowicki: In the past, our companies have done the groundwork toward equipping existing materials with new properties. In fact, entirely new materials were created. Here you can't always draw from what is known, but have to reckon with repeated surprises. What is so exciting, is that an enormous wealth of materials versions can be achieved though a variety of possible combinations. ■

Interview: Dieter Beste



These two diagrams show thermal aging of 35 % glass fiber-reinforced, non-crosslinked PA66 compared to radiation-crosslinked V-Creamid polyamide types at 220 °C. The measurements prove that only the combination of stabilization and radiation crosslinking results in high and long-lasting elongation and strength values