Introduction to styrenic thermoplastic elastomers - technical insights, advances and applications in the food packaging, medical and pharmaceutical Industry

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Introduction

Thermoplastic Elastomers (TPE) are a group of various plastic systems which inherent properties enable them to be used in numerous applications in the medical devices, pharmaceuticals and food packaging industry. Due to the high flexibility and the adjustable set of properties, TPE captured increasing market share in these areas over the past years. In 2008, over 55.000 tons of styrenic TPE were used in the regulated industry segments (medical devices, food packaging, toys, etc.). With an annual growth of 7,3% these markets still feature room for further innovations and expansion[1]. Such an innovation is the growing use of TPE as substitution of vulcanized rubbers, PVC or silicones. Today, sophisticated TPE formulations offer high temperature and media resistance, and therefore play out their strengths through easier processing, benefits in handling and recyclability.

With its main focus on regulated industries (food packaging, pharma, medical devices), Actega DS has been taking part in the use and development of TPE for more than 30 years and established a leading position as a supplier of plastic compounds.

Motivations of the medical devices market

The motivation and growth potential of the medical and pharmaceutical industry is of particular interest for a whole range of different sectors of industry.

A megatrend that emerged during the last 60 years and which is predicted to continue during the next decades in the Western world is the change in demographic structure. The percentage of German population aged <20 years decreased from 1950 to 2010 from 30% to 18% with an immense shift to the older population. At the same time, the percentage of population in the retirement age increased from 10% in 1950 to 21% in 2010[2] (See Figure 1). The progress in pharmaceutical and medical care of the population increased the anticipated average life span to 77 years (male) and 83 years (female) by 2010 and is estimated to further increase to 85 years (male) and 88 years (female) by 2040[2]. Not only does this severe change in the demographic structure raise questions about the funding of retirement pensions, it also produces massive increases in the cost of public health care. In 2006 the overall expenditures for healthcare in Germany were more than €245bn[2].

Figure 1: Demographic Change in Germany[2]

[1] Marktstudie “European Markets for Plastics in Medical Devices", Frost&Sullivan, 02/2009

[2] Statistisches Bundesamt, Destatis

A frequently consulted indicator of the developed healthcare system in Western countries is the amount of widespread diseases. The rise of diabetes is such an example. Within 9 years, the percentage of the German population being medicated with insulin rose from 5,9% (1998) to 8,9% (2007), to an absolute number of more than 7.000.000 people diagnosed with diabetes type I or II[3]. Certainly, an overall shift in life-style and nutrition adds to these numbers as well.

The sum of all patients, treatments and different therapies challenges the medical and pharmaceutical industry to design efficient and easy to use medical goods and solutions. New trends, which were developed due to the aforementioned changes in the social structures and overall healthcare state, are the increased use of pre-filled syringes, the advent of novel insulin infusion systems and the expansion of dialysis systems and associated disposables.

As versatile and diverse raw materials, plastics are widely used in the medical device industry today. Common arguments for the use of plastics are the ease of processing and molding, the compatibility with the human body, multiple ways of modification (coloration, bonding) and the recyclability. Flexible materials in particular, are used in disposable tubing systems, stoppers, sealing rings, flexible bags and pouches (nutrition and infusions) or as overmolding compounds for handles or surfaces.

Particularly Germany is a very attractive market for suppliers into the medical device business. Pan-European, Germany ranks on the first place in turnover (with €19,6bn. In 2008) in the medical industry before Italy (€7,45bn.), France (€7,22bn.) and the UK (€5,45bn.)[4]. Globally, a turnover of more than $296bn. (2010)[5] is achieved in the medical industry, with a share of about 40% realized in North America and 40% achieved in Europe. But also the outlook for the global segment is very promising. During the past years, average growth rates between 6% and 7%[3] were achieved.

In summary, several factors increase the need of the population for progressive and efficient medical and pharmaceutical supply. Over the past decade supply streams, development cycles and manufacturing processes especially in the medical devices industry became more and more sophisticated. This also affected the role of plastics as advanced materials for engineering of single use devices and instruments for specialized treatments.

Plastics and especially thermoplastic elastomers in the medical, pharmaceutical and food packaging industry

Beginning in the 1960's, the main driving force for the use of plastics in the medical industry was hygiene. By that time, most devices were intended for multiple operation (i.e. syringes) and needed to be sterilized after each use, but still bearing a risk of contamination. As an enabling technology, the use of plastics leaded to the commercially advantageous and more hygienic application of single use devices. The evolution and technical progress of modern polymers were key factors in the development of devices, which are considered a technical standard today. Examples can be as easy as the replacement of glass bottles by polyethylene pouches for packaging nutrition and infusion

[3] Deutscher Gesundheitsbericht Diabetes 2011, DiabetesDE, Berlin
[4] SPECTARIS Deutscher Industrieverband für optische, medizinische und mechatronische Technologien e.V., Berlin
[5] Studie „Medical Device Industry – Recovering from Recession", Frost&Sullivan, 06/2011

solutions, the development of modern catheterization systems or such complex and well researched materials for permanent implants like PEEK or silicones.
Compared to technical applications, the requirements on a “medical grade” plastic are much more driven by toxicological and hazard aspects.

Based on these requirements Actega DS outlined a set of specific demands which were finally translated into a medical grade plastics portfolio.

- Flexible materials, based on styrenic thermoplastic elastomers
- Shore hardness range from A20 to A80
- Elastic modulus in the range of 1MPa to 25MPa
- Elongation at break up to 1000%
- Transparency and/or translucency
- Sterilizable by gamma irradiation, ethylene oxyde gassing and autoclave without major changes in optical and mechanical properties
- No toxic or harmful effects on the human body, approved by biocompatibility standards like ISO 10993 or regulations in the United States Pharmacopoeia (USP)
- Adhesion performance in multi-component injection molding

Biocompatibility and regulatory demands
Especially in sensitive areas like medical devices, pharmaceutical and food packaging, factors like migration or leaching of potential toxic or harmful substances are big concerns. Thus, internationally accepted norms and testing conditions were created to evaluate raw materials and extractables for their hazard potential. Namely the ISO 10993 and the evaluation according to the United States Pharmacopoeia (USP) are common demands on plastic materials. Not only do the raw materials need very thorough screening and evaluation, but also the compounding process has the potential to contaminate a material with harmful substances if not done under accurate conditions. Process conduct, production hygiene and quality control need to go hand in hand to establish constant product quality and production according to the formulation. By evaluation of the material through the above mentioned norms and certification, the end-customer can be ensured to safely use the material in his critical applications.

Sterilization
To prevent the user and patient from infections with germs, viruses and bacteria, medical goods need to be delivered in sterile condition. To achieve the absence of these biological surface contaminations three main sterilization procedures were established as commercially interesting and technically feasible options: Gassing with Ethylene Oxyde, Irradiation with highly energetic rays (Gamma or Beta irradiation) and the sterilization via hot steam in an autoclave. All of these options have advantages and drawbacks which are not subject in this presentation. Nevertheless, all of these sterilization procedures do not only present a very fatal environment for biological contaminations but also have a dramatic impact on the involved materials of the medical or pharmaceutical good. Especially the irradiation with gamma rays has the potential to permanently alter the properties of plastic materials depending on the dose. These effects can range from a slight color change (yellowing) to increased stiffness or brittleness.

To overcome these issues with sterilization procedures, plastic materials need to be especially formulated and equipped with specialized stabilizers and other ingredients. Actega DS therefore developed a specialized TPE portfolio for medical applications which resists the sterilization by the above mentioned procedures. This resistance is illustrated through mechanical testing prior and after sterilization with gamma irradiation (doses 25 and 50kGy), ethylene oxyde and autoclaving.

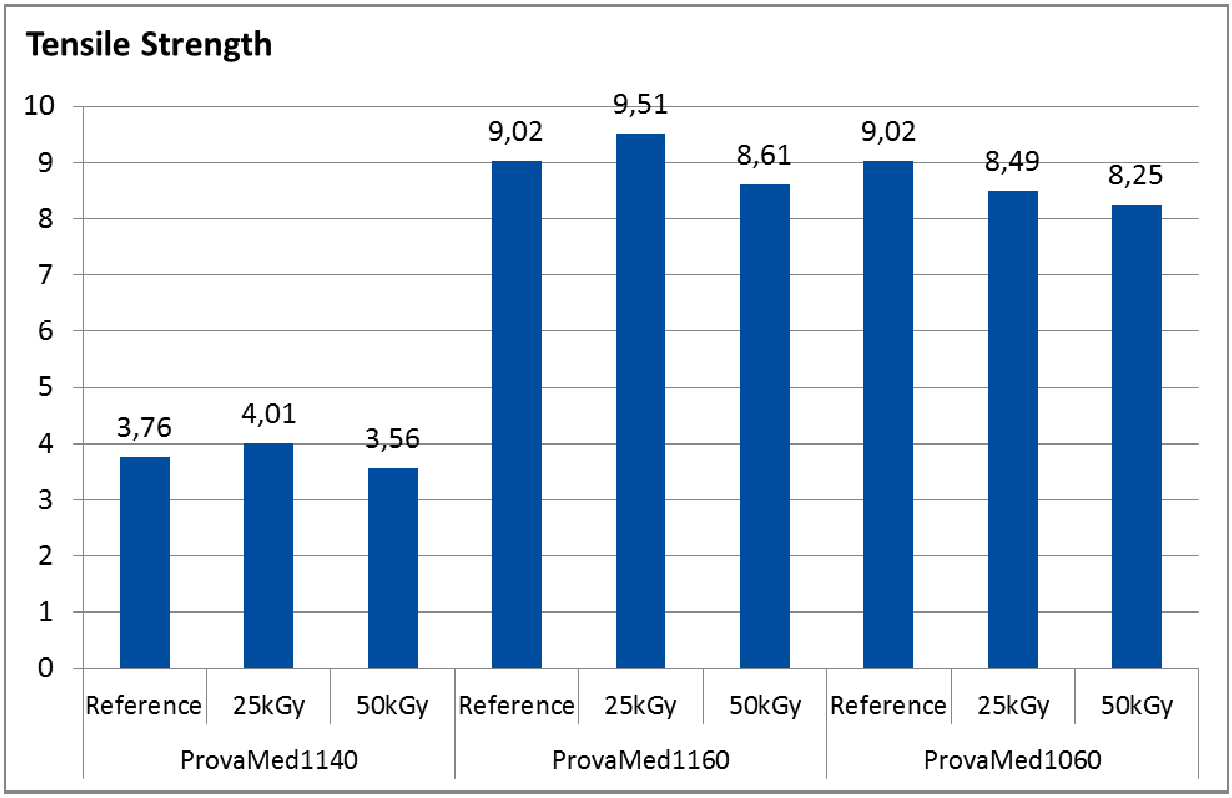

Diagram 1: Impact of gamma irradiation on tensile strength of ProvaMed® TPE

After irradiation with a dose of 25kGy the materials ProvaMed®1140 and ProvaMed®1160 show a slight increase in tensile strength. Due to the high energetic nature of the irradiation crosslinking effects occur in and between the polymer chains and increase the strength of the material. After further irradiation (dose: 50kGy) the damaging effect of the gamma rays exceeds this effect and the polymer chains are partially broken and lose tensile strength. But still the overall tensile strength even after such a high dose as 50kGy is very close to the original values and exceeds the mechanical demands in most applications and is therefore negligible.

Also treatment in an autoclave is a common procedure not only for multi-use medical goods. Materials are exposed to high humidity, pressure and temperatures of up to 134°C. These conditions can severely damage thermoplastic materials which do not exhibit sufficient resistance. Regularly observed effects are shrinkage, deformation or even melting of the plastic. The TPE materials ProvaMed®1060, 1070 and 1080 were especially designed, formulated and tested to resist the challenging conditions in an autoclave. As demonstrated in Diagram 2 by measuring the tensile strength of the materials, the resistance to the autoclave process is proven. The temperature has also the beneficial effect of inducing relaxation and crystallization processes in some of the polymers

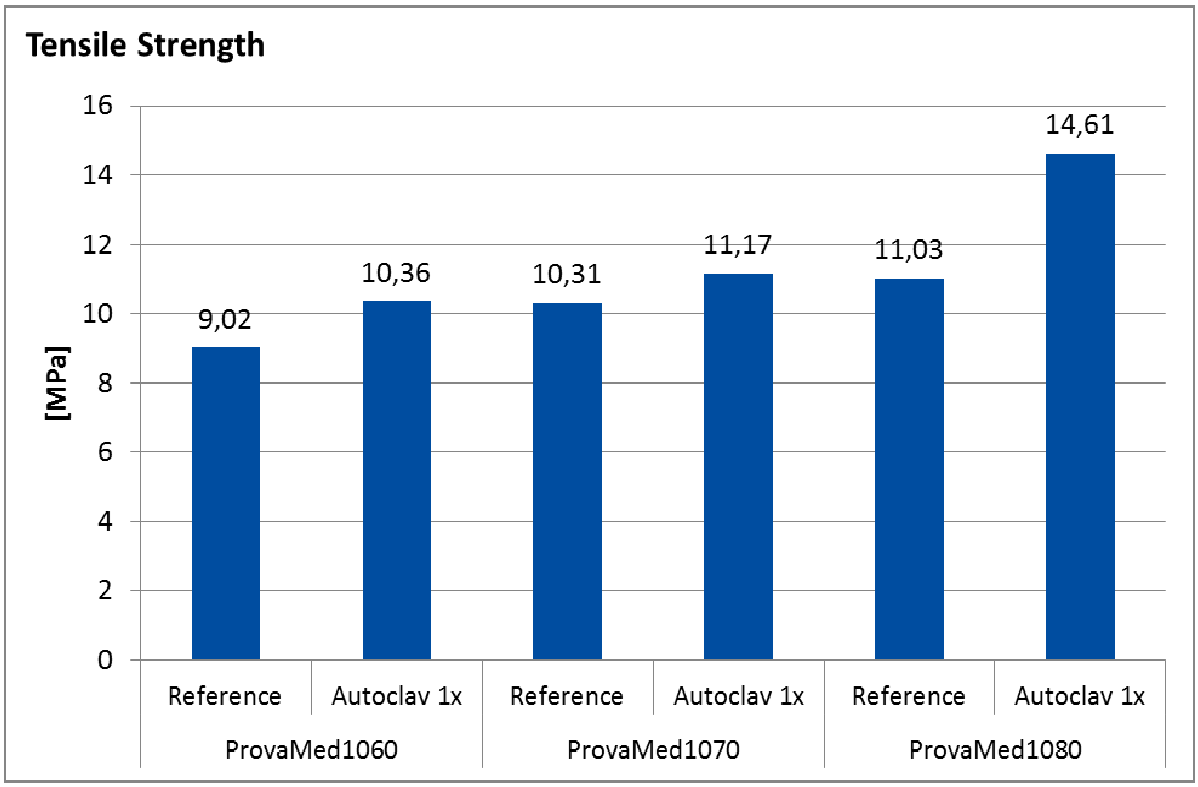

Diagram 2: Tensile strength after autoclave-treatment at 134°C for 15 minutes

which are part of the TPE formulation. This can cause a noticeable increase in tensile strength and elongation at break of the plastic. A similar effect appears during the sterilization with Ethylene oxide gas.

Overall, specific ProvaMed® TPE compounds were designed and tested for suitability in medical applications, which demand the sterilization of the final products. The change in mechanical properties is minimal and can be considered negligible in the design process.

New Developments in food contact applications

The majority of metal-vacuum closures worldwide is equipped with PVC based sealants and lacquers today. PVC, additives such as lubricants and stabilizers are dispersed in a suitable plasticizer to form plastisoles. These paste-like sealants can exhibit a wide viscosity range and are coagulated by thermal influence. The PVC paste is injected into the rim of the vacuum closure and cured in a 220°C temperated feed oven. During curing cycles between 60 and 80 seconds, the PVC paste solidifies and forms a circular sealant that helps maintaining the vacuum in glass jars. The completed closures are boxed and sold to fillers of food stuffs.

PVC as well as the additives and plasticizers are under immense pressure from ecology groups and therefore

Image 1: Metal-vacuum closure with PVC based sealant

also under legislative observation. Since 2004 a variety of EU-wide amendments regarding the approval of food contact materials and chemicals were adopted, causing certain additives and especially plasticizers based on phthalates to be limited or even prohibited.

Confronted with these regulatory adjustments the industry was ever looking for alternatives to be used as a replacement for the PVC-based sealant materials. But for a long time, the mechanical and processing conditions of PVC based sealants for vacuum closures were not met.

Based on its tradition and technical experience with thermoplastic elastomers, Actega DS invented a non-PVC solution for use in vacuum closures and brought it to market in 2011 in first commercial applications. Under the trade name Provalin®, a wide product range for use in conventional closures and applications as well as for specialized closures (i.e. baby food) was brought to market. These materials also fulfill the demanding regulatory requirements for long term food contact, even with fatty foods.

Besides the necessary fulfillment of regulatory aspects, the absence of PVC in the glass packaging also contributes to positive environmental effects. Since Provalin® is free of heavy metals, plasticizers or critical chemicals and can be thermally recovered, the overall footprint is minimized compared to PVC.

Image 2: Provalin® based, PVC-free sealants used in various lug caps

Provalin® grades have been developed for use in all kind of common applications like hot-fill, pasteurization and sterilization and are legally conforming with the 4th amendment to the Plastics Directive 2011/10/EC including the global migration limit of 10mg/dm². Since Provalin® is a solid thermoplastic material no oven is needed for curing. The cap is equipped with the sealant in a specialized compression moulding process.

Today the commercialization of Provalin® made good efforts with notable partners trusting in the material. The company “Feinkost Dittmann” for example equipped their food stuffs with high fat content with the novel blue Provalin® sealing and promoting the innovation with a designated logo on the cap.

Summary

Overall, Thermoplastic Elastomers showed a significant development over the past decades and expanded their technical and commercial capabilities allowing a variety of new applications. Actega DS, as a specialized compounder of TPE formulated these high performing polymers into TPE compounds for markets which have extraordinary demands on hygiene, migration and regulatory

aspects. In close collaboration with key customers, markets that were desperately looking for alternatives, suitable PVC and plasticizer-free materials were developed.