Radiation Crosslinking of Films

New Applications in the Thermoforming of Filled Materials

Irradiating semi-crystalline thermoplastics induces three-dimensional crosslinking in the macromolecules. Radiation crosslinking has long been used in the production of injection molded parts. Radiation crosslinking of films, on the other hand, offers hitherto untapped potential for new applications in the thermoforming of filled materials.

Thermoforming generally refers to the stretch forming of heated thermoplastic semi-finished articles by means of compressed air or vacuum. The thermoforming process can be divided into four phases: heating, forming, cooling and demolding [1]. It occupies a special position in polymer processing due to the low wall thicknesses that can be achieved even in the case of large, flat parts. Compared with injection molding or blow molding, thermoforming has a low capital investment cost for machines and tools, because usually only single-sided molds made from readily machinable materials are needed. This is offset by the additional cost of the semi-finished articles and the limited availability of materials and geometric design options [2]. Nevertheless, thermoforming is one of the most economical and efficient processes in polymer processing today. Modern machines and tools are capable of efficiently producing large quantities.

Main Applications in Thermoforming

The main application area for thermoformed products is in the production of packaging. Technical products, such as decorative surfaces and items of luggage, have a much smaller market share because there is a limited availability of materials that meet the high requirements profile which they impose. Contrast this with radiation-crosslinked injection-molded parts made from semi-crystalline thermoplastics, such as polyamide 6 (PA6), polyamide 66 (PA66) or polybutylene terephthalate (PBT), where the number of applications in the automotive, electrical, electronics and mechan-

Radiation source: an electron accelerator of 3 MeV maximum energy, operated by BGS Beta-Gamma-Service at its Wiehl site near Cologne, Germany. Electrons released from a hot cathode are collimated into a beam and accelerated via alternating electric fields (© BGS/M. Steur)

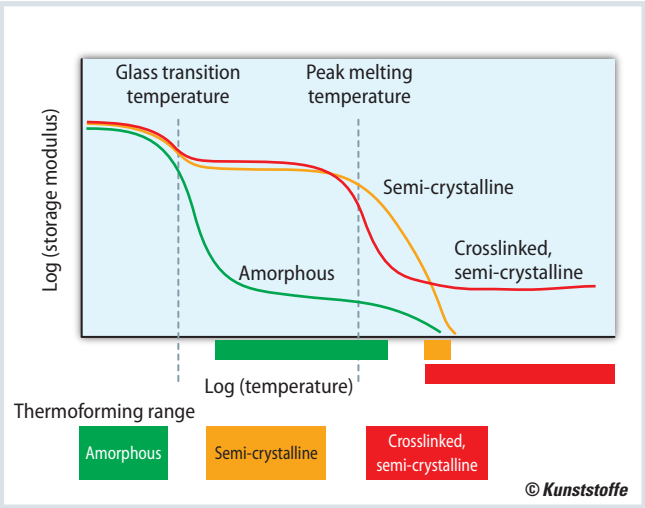

Fig. 1. Melt strength: comparative storage modulus of amorphous, semi-crystalline and semi-crystalline radiation-crosslinked polymers

(source: [5, 6])

ical engineering sectors keeps growing [3]. These semi-crystalline engineering thermoplastics are unsuitable for thermoforming in the unmodified state because they are more difficult to process than amorphous thermoplastics. As a result, the advantages associated with the use of engineering semi-crystalline thermoplastics in various applications, such as toughness, wear, and chemical resistance, usually cannot be exploited for thermoformed parts, which is why many applications are not accessible through thermoforming. This is precisely where electron or gamma radiation crosslinking comes in (**see Box p. 116**), because it offers a way to widen the process window for semi-crystalline thermoplastics.

Little scientific research has been done so far on the thermoforming of filled films. All kinds of properties can be introduced into the matrix material by adding fillers [4]. Inactive fillers, such as talcum, can help to lower costs while functional fillers can serve to specifically boost mechanical properties or dimensional stability.

The benefits of radiation crosslinking on the forming behavior of filled films are evident from the following research results obtained at the Chair of Polymer Technology in Erlangen, Germany, together with BGS Beta-Gamma-Service, a company which specializes in radiation crosslinking.

Increased Melt Strength Due to Crosslinking

Electron or gamma radiation leads to the formation of a three-dimensional polymer network in semi-crystalline thermoplastics. This radiation-induced crosslinking takes place mainly in the amorphous state due to the greater mobility of the macromolecules. It shifts the glass transition temperature to higher temperatures and lowers crystallization temperatures and melt enthalpy. A schematic diagram of the effect on melt strength is shown in **Figure 1**. What is more, the crosslinking nodes formed during radiation crosslinking promote the development of »

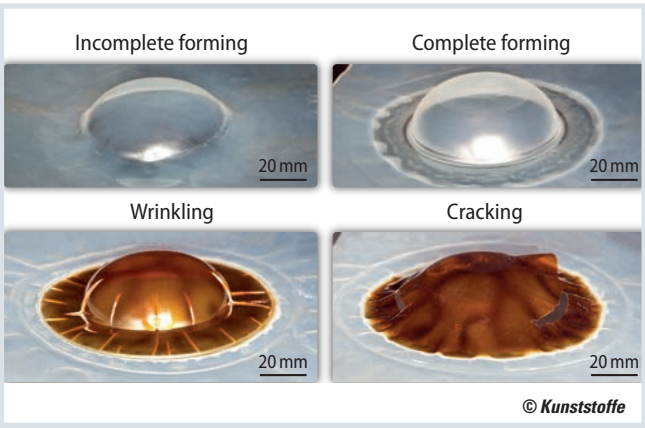

Fig. 2. Thermoformed polyamide 12 semi-finished products: sample parts to illustrate the thermoforming studies

(source: [5])

rubber-elastic behavior above the crystallite melt temperature [5]. This increase in melt strength is essential for the thermoforming process.

Semi-Crystalline Thermoforming of Thermoplastics

Polyamide is generally difficult to form because, on account of its low melt strength, it tends to drip when heated, causing damage to plant components such as radiant heaters. Studies [5] have shown, however, that electron irradiation improves the thermoformability of polyamide 12 (PA12). In a nutshell, the main results of these are: varying the content of triallyl isocyanurate (TAIC) crosslinking agent and the irradiation dose enabled the numerous interactions between crosslinking and formability to be elucidated. It transpired that crosslinking leads both to an increase in melt strength and to greater elongational hardening as well

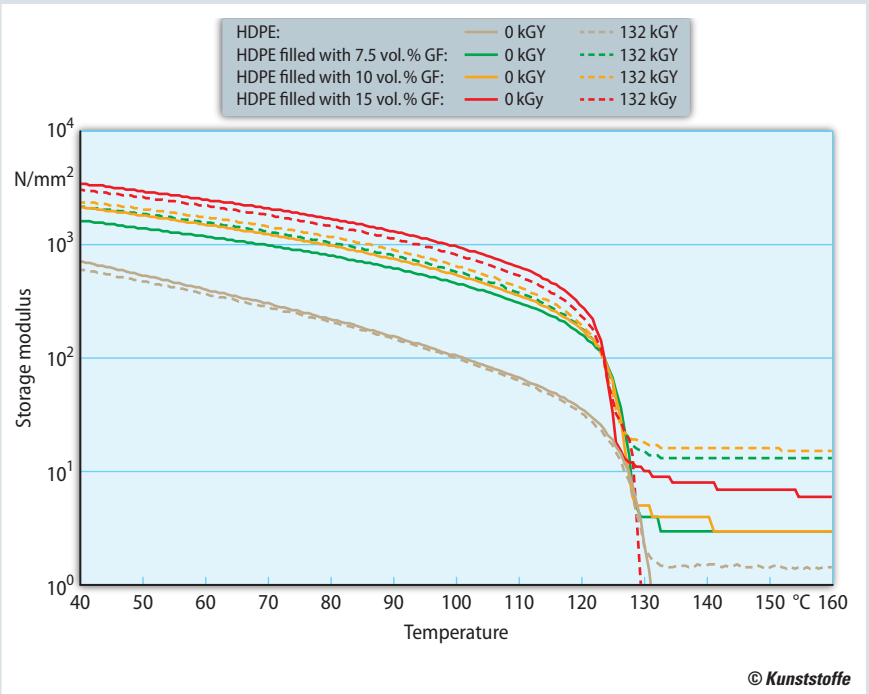

Fig. 3. Dynamic-mechanical analysis of glass-fiber filled radiation-crosslinked films of different filler content and energy doses (absorbed energy per mass; unit: Gray) (source: [8])

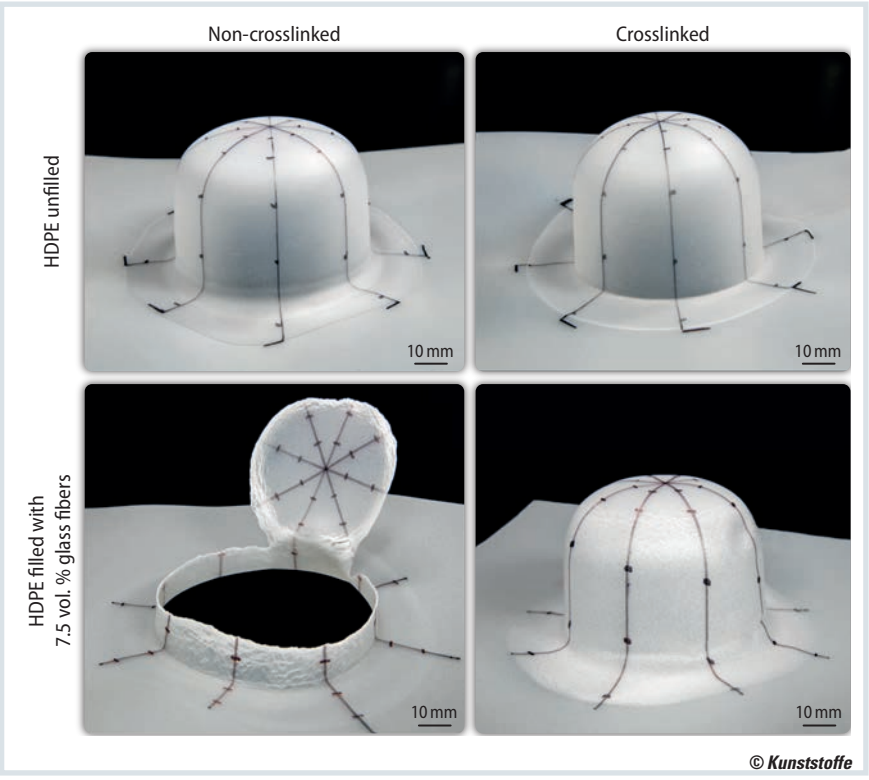

Fig. 4. Comparative thermoformability of unfilled and glass-fiber-filled as well as non-crosslinked and crosslinked HDPE semi-finished articles (source: © LKT)

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as to reduced elongation at break in the melt: degrees of crosslinking of less than 40% exert a positive effect on thermoforming. On the other hand, degrees of crosslinking above 40% impair forming, especially at higher draw ratios: the sharpness decreases or films tear.

Sample results from thermoforming studies on radiation-crosslinked polyamide 12 are shown in **Figure 2** for parts produced at low surface stretch ratios as a function of forming temperature and degree of crosslinking. It can be seen that a low forming temperature is accompanied by a drop in sharpness and that a high degree of crosslinking yields cracked or wrinkled parts. The overall, increased rigidity and strength in the finished part harbors high potential for highly stressed parts, such as covers, hoods, tubs and cladding. Furthermore, radiation crosslinking was found to benefit the development of wall thickness reductions, with more homogeneous distributions overall.

Thermoforming of Filled Systems

Aside from increasing the melt strength, radiation crosslinking enhances the bond between filler and matrix [7]. Filler bonding exerts a much greater influence in extensional rheology than in shear rheology: poor bonding causes the polymer to separate from the filler and the viscosity becomes lower than is the case for unfilled polymer. A good bond, on the other hand, prevents extension and raises the viscosity compared to the unfilled polymer. This is in contrast to shear behavior, where the fillers always hinder shear deformation, regardless of the bond [8].

For the purpose of achieving a separation of effects and avoiding overlap between filler addition and radiation crosslinking, the first step was to choose a model material made from high-density polyethylene (HDPE) and short glass fibers. The rationale for choosing this material system is that HDPE can be radiation-crosslinked without the need for additives and also lends itself to thermoforming. Different degrees of filling were then considered with a view to determining the influence exerted by the fillers on the end properties, e.g. wall thickness distribution or development of extension in radiation-crosslinked parts. Characterization of the melt strength of the semi-finished articles was achieved by conducting dynamic-mechanical analyses (**Fig. 3**) of polymer rigidity as a function of temperature. The results show that both filler addition and radiation crosslinking increase the melt strength [9].

The studies so far show that both an increased filler content [9] and an increased aspect ratio [10] impair thermoformability and that only low degrees of stretching can be achieved. To aid understanding, the forming results obtained for unfilled and glass-fiber-filled thermoformed parts under a higher surface stretch ratio are shown in **Figure 4**. No difference is found in the forming of non-crosslinked and crosslinked unfilled films. Non-crosslinked, glass-fiber-filled semi-finished articles, on the other hand, cannot be formed. If the chopped glass fiber content is below 15 vol.%, radiation crosslinking substantially widens »

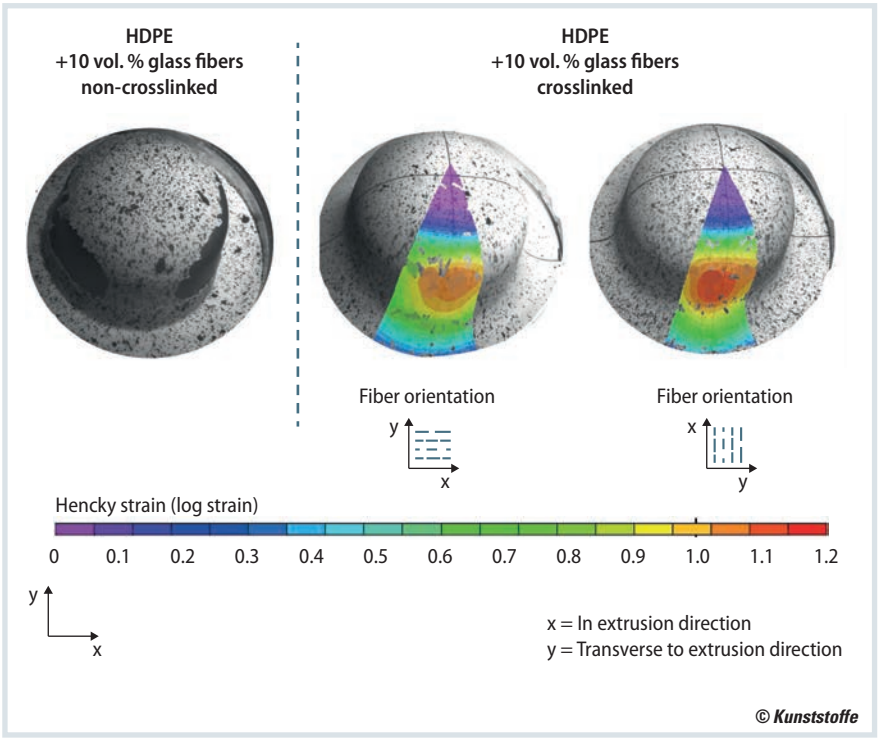

Fig. 5. Hencky strain in the final thermoformed part as a function of fiber orientation (HDPE containing 10 vol. % glass fibers) (source: [9])

Radiation Crosslinking

Radiation crosslinking is based on the interaction of high-energy electrons (beta radiation) which have been generated in electron accelerators. During crosslinking, the material absorbs the radiation energy, chemical bonds are broken and free-radicals are formed. The polymer chains crosslink by recombination, forming a multidimensional polymer network. Targeted use of additives enables or promotes the crosslinking of thermoplastics. For applications in which beta radiation has limited penetrating depth, crosslinking is effected with gamma radiation, which can penetrate more deeply. Radiation crosslinking can thus be used to specifically achieve thermal, mechanical, chemical and tribological property changes in all kinds of polymer applications.

A key process variable is the radiation dose. Defined doses are used to control crosslinking of the polymer or polymer chains. Electron accelerators apply the required dose within seconds, but gamma systems usually require several hours due to the lower dosing power.

Handling technology for irradiating polymer components on the 10 MeV electron accelerator at the Bruchsal site in Germany (© BGS/M. Steur))

the thermoforming window for high degrees of stretching as well. However, if the films are filled with 15 vol. % short glass fibers, substantial widening of the window is only possible for low degrees of stretching. Fiber orientation (**Fig. 5**) is also found in the evaluation to exert a substantial influence on elongation in the thermoformed part [10]. The images show the results of fiber orientation transverse to the stretching direction (**Fig. 5, center**) and in the stretching direction (**Fig. 5, left**). It can be seen that, when the fibers are oriented transverse to the stretching direction, the matrix participates much more in the stretching process, as maximum elongations are found over a wider range. Where the fibers are oriented in the stretching direction, their reinforcing effect comes into play and the maximum elongations extend over a smaller range.

Radiation crosslinking enables the forming window of filled films to be widened up to a volume fraction of 15 % and allows much higher degrees of stretching to be reliably attained. The reason for this is that radiation crosslinking creates a tighter three-dimensional network of molecular chains, which both improves the melt strength and prevents crack growth starting from the fillers.

Conclusion and Outlook

The studies performed on the HDPE model material show that the process window during thermoforming of filled films can be significantly widened by radiation crosslinking the semi-finished film articles. This is particularly advantageous for applications in which low weight, low cost and freedom of design are required for forming.

So far, there is limited scope for transferring these results to engineering materials such as polyamide 6, because the volatility of the TAIC, the additive most commonly employed in radiation curing, makes it difficult to extrude a radiation-crosslinkable polyamide 6 grade. The additive evaporates and gives rise to defects both within the film and on its surface.

Current research is focusing on developing more thermally stable crosslinking additives that can also be used in extrusion. The possibility of transfer to polypropylene (PP) or polyamide 12, which are important materials in thermoforming, still needs to be examined. The ability to modify these materials would open up new fields of application for thermoforming of filled film systems. ■