Replacement of Conventional Elastomers

Application Range of Styrene-Based Thermoplastic Elastomers Expanded

Thermoplastic elastomers (TPE) are finding increasing use, as both manufacturers and processors come under constant pressure to innovate. A major disadvantage of TPE as compared with conventional vulcanizates is their tension set, which it has now been possible to minimize by post-crosslinking of the elastomer phase. This opens up opportunities for processors to develop further applications for commercially available TPE.

The reduction in tension set provided evidence of the partial crosslinking of TPS (figures: LBF)

In the engineering plastics class, thermoplastic elastomers are recording exceptional growth [1]. Because of their property profile, they are used, for example, as a replacement for plasticized PVC when plasticizers are undesirable. Thanks to their melt processability, they can be processed by extrusion and injection molding to achieve new designs and faster cycles not possible with conventional vulcanized elastomers. Another advantage of their suitability for melt processing is recyclability. The fields of application for TPE range from auto manufacture to household goods and the medical sector.

At the present time, there is a steady movement of the TPE market into the Asian region. Compounders and processors based in Germany are also competing primarily with Chinese suppliers of end products [1].

Since styrene-based TPE (TPS) occupy a dominant market position among thermoplastic elastomers, they are the starting point for the innovations described here, which give TPE processors an edge over international competitors [1].

Among styrene-based thermoplastic elastomers, SEBS (styrene-b-ethylene-co-butylene-b-styrene), in particular, has the advantage over SBS (styrene-b-butadiene-b-styrene) and SIS (styrene-isoprene-styrene) of being more stable to thermooxidative degradation and unwanted crosslinking because of the elimination of double bonds in the soft phase. SEBS is produced by hydrogenation of SBS, during which the double bonds in the soft phase are over 99 % saturated.

The lack of chemical crosslinking in TPE does, however, give rise to some limitations. As a consequence, they cannot replace irreversibly crosslinked elastomers in all fields of application. TPE, for example, swell more in non-polar media. A certain amount of tension and compression set can also be observed with high strain rates or frequent strain.

The aim of the work described here was to reduce both effects by partial chemical crosslinking of the soft phase. The degree of crosslinking is restricted so that only branched polymers are produced in order to retain melt processability.

Crosslinking Methods

To achieve a defined and reproducibly low degree of crosslinking, the starting point for irreversible chemical crosslinking of the soft phase was to link the individual polymer chains via the remaining double bonds (less than 1 %) present in commercially available SEBS grades. In this way, gelling and hence a loss of melt processability could be prevented. The crosslinking reactions tested included accelerated sulfur vulcanization and various radical-initiated reactions during processing in different twin-screw extruders or kneading chambers. To ensure better processability, the SEBS was processed with 150 % paraffinic white oil in all trials.

Accelerated sulfur vulcanization is an established process for crosslinking elastomers and was adapted here for partial crosslinking of SEBS [2]. Through the addition of sulfur combined with different accelerators during the compounding

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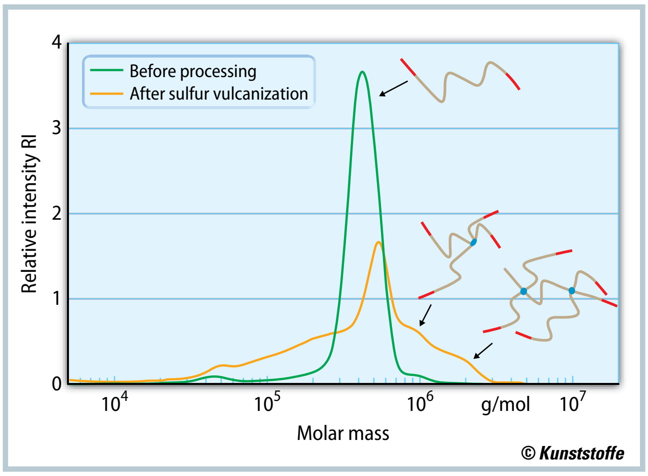

Fig. 1. Evidence of the increase in the molecular weight of SEBS achieved through sulfur vulcanization as determined by GPC

process, it could be demonstrated that partial crosslinking of SEBS is possible in principle. In the molar mass distribution of the specimens processed in this way, fractions with double and triple molar mass of the starting material can be seen (**Fig. 1**). Mechanical tests on these specimens confirmed that in this way tension set (**Title figure**) can be substantially reduced. But since there was an unpleasant odor from the reagents used both during and after processing, the field of application for these end products is severely limited. This process was not therefore further optimized but may be regarded as general confirmation of the assumptions previously made.

Various polymers that contain double bonds, such as ethylene-propylene-diene rubber (EPDM), can be crosslinked through the addition of peroxides. An attempt was therefore made to use this process for partial SEBS crosslinking. The problem here is that radical formation is thermally induced, i.e. during the compounding process, and the radicals formed react non-specifically with the polymer chains. Despite the use of a wide variety of peroxides in different concentrations, a degradation reaction always occurred simultaneously to the desired crosslinking. Because of the small number of double bonds, the degradation reaction predominated here. This resulted in a wide molar mass distribution with a high content of diblock copolymers (**Fig. 2**), leading in turn to a loss of elastomeric properties.

To conduct the radical crosslinking reaction in a more controlled way, further trials were carried out, in which UV initiators were incorporated during compounding instead of the thermally degrading peroxides. This method has the advantage that the radical crosslinking reaction can be decoupled from processing step. The test specimens injection molded from these compounds were post-irradiated at room temperature with a UV lamp. Tension set was determined in tensile stress/strain tests over ten cycles of 200 % strain in each case, with residual strain being noted at the zero force point.

Successes with UV Light and UV Additives

To conduct a targeted UV-induced crosslinking reaction, several mutually influencing effects must be taken into account. Under the selected conditions, these effects can be explained very clearly with the example of the photoinitiator Irgacure 127 (manufacturer: BASF SE, Ludwigshafen, Germany): looking at residual strain as a function of additive concentration and UV exposure time (**Fig. 3**), it can be seen that from an irradiation time of 2 min upwards, there is a significant increase in residual strain in specimens without a UV initiator. This is caused by degradation of the polymer chains due to the UV irradiation. The effect is counteracted by crosslinking, which leads to a reduction in residual strain if the SEBS contains a UV initiator. This effect can be clearly observed at a concentration of 1 phr based on SEBS content and a UV exposure time of 5 min. The increase in residual strain occurring on further irradiation results from the above-mentioned degradation, which then predominates.

If the additive concentration is doubled, a third effect can be observed. The

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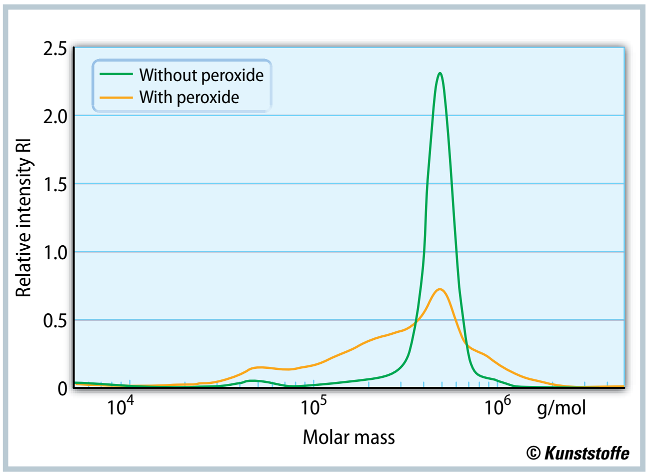

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Fig. 2. The decomposition of SEBS as a result of treatment with peroxides is evidenced by the wide molar mass distribution

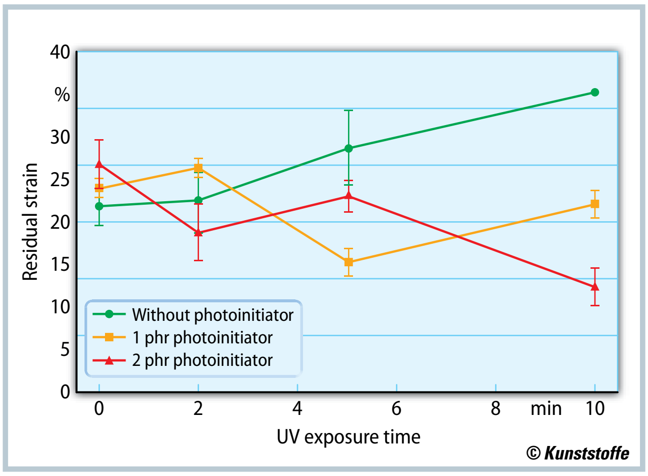

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Fig. 3. First evidence of the minimization of residual strain in SEBS in the presence of the photoinitiator Irgacure 127

higher concentration of UV-absorbing constituents results in a shift of the minimum residual strain to longer exposure times and increased residual strain on short-term UV exposure. This phenomenon can be explained in terms of an internal filter effect: at higher absorber concentrations, a greater amount of light is required to achieve complete activation in deeper layers. Consequently, the optimum shifts to longer UV exposure times given constant radiation intensity. In this series of trials, a decrease in residual strain from 21.9 to 12.5 % was achieved at 2 phr additive and 10 min UV exposure time. Residual strain is therefore reduced by more than 40 %.

The molar mass distribution values shown in **Figure 4** correlate with the residual strain curve and confirm the theoretical approach of crosslinking. It can be seen that, with rising initiator concentration and UV exposure time, the higher-molecular-weight content of the test specimen increases, which is attributable to crosslinking of the polymer chains.

Swelling tests on the specimens confirm the results of the mechanical tests and size-exclusion chromatography. The specimens were immersed in *n*-hexane, a selective solvent for the soft phase, and the amount of solvent absorbed was determined gravimetrically. It was noticed that with increasing crosslinking and decreasing residual strain, swellability also decreased. On the other hand, with the specimens degraded by UV radiation, higher swelling was observed.

Besides the internal filter effect that can be caused by the additives, the polystyrene domains of SEBS can themselves also filter the radiation required for crosslinking. To find a way to exclude this effect and allow partial crosslinking in the deeper layers as well, further trial series were conducted. The UV initiators selected were products that are activated in a wavelength range outside the absorption spectrum of polystyrene (e.g. Irgacure 819 from BASF). **Figure 5** shows the residual strain values as a function of UV exposure time and initiator concentration (Irgacure 819). Here, again, effects due to degradation and crosslinking of the polymers are interfering. In this case, a significant reduction in residual strain was achieved after only 2 min exposure time and, after 5 min, strain fell to only about half its initial value. In these trials, too, degradation and crosslinking reactions were verified by determining molar mass distribution and swellability.

By way of example, **Figure 6** shows the tensile stress/strain graphs from the »

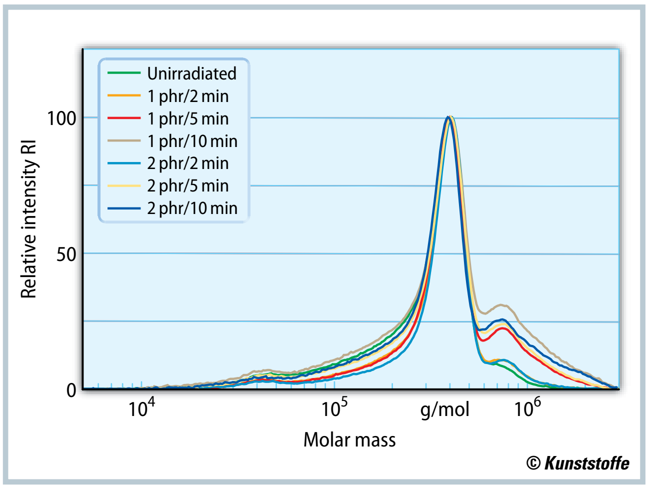

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Fig. 4. GPC analysis of SEBS provides evidence of the increase in molecular weight achieved with Irgacure 127

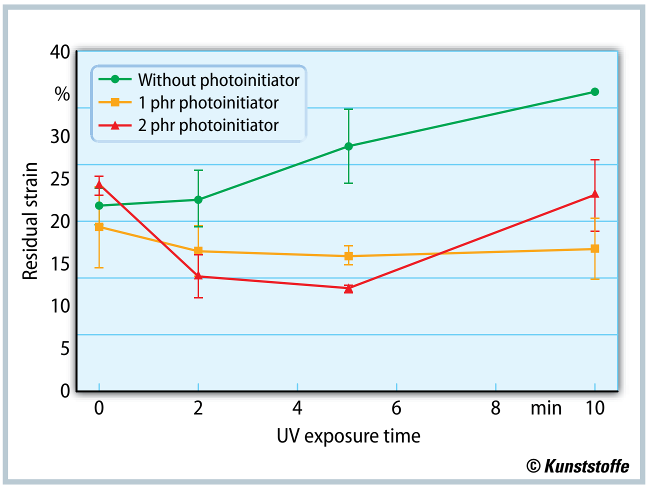

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Fig. 5. The photoinitiator Irgacure 819 shortens the UV exposure time required by SEBS as compared with Irgacure 127

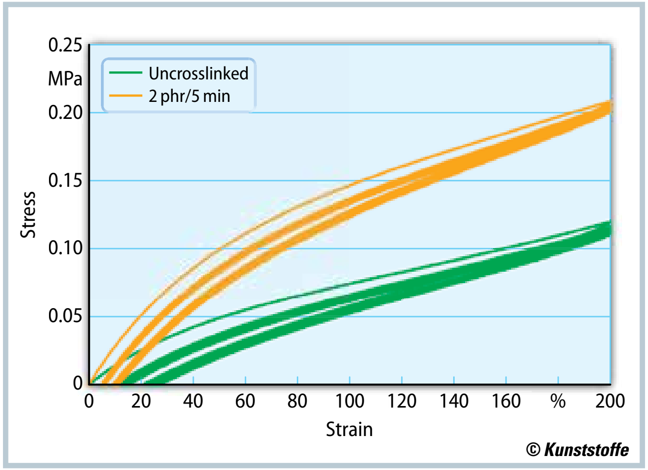

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Fig. 6. UV-induced crosslinking in the presence of Irgacure 819 leads to an increase in the stiffness of SEBS

hysteresis measurements for the specimen with the lowest residual strain and an untreated specimen. In addition to the reduced tension set in the partially crosslinked specimen, a significant increase in stiffness can be seen, which is also attributable to the partial crosslinking of the soft phase.

Conclusion

In the studies conducted, it has been shown that the tension set of SEBS can be significantly reduced by partial chemical crosslinking. It is sufficient just to crosslink part of the polymer chains without forming a complete network, so that melt processability is retained. Other effects caused by the partial crosslinking are increased stiffness and reduced swellability in the presence of non-polar media.

A particularly suitable crosslinking method has proved to be the use of UV initiators, so that the crosslinking reaction can be carried out in a controlled way, decoupled from processing itself.

With this development, TPE processors can adapt the property profile of SEBS for specific end uses and so expand the range of application for their products. ■