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# Styrolux[+] and Styroflex[+] - From Transparent High Impact Polystyrene to New Thermoplastic Elastomers

## Syntheses, Applications and Blends with other Styrene based Polymers

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SUMMARY: Styrolux and Styroflex are styrene and butadiene based block copolymers prepared by butyllithium initiated anionic polymerization. Styrolux is a transparent, tough and stiff thermoplastic material for high speed processing. Its specially designed molecular structure allows homogeneous mixing with general purpose polystyrene maintaining the transparency. Styroflex is a newly commercialized product with the mechanical behavior of a thermoplastic elastomer, e.g. low modulus and yield strength, high elongation and excellent recovery. High transparency and thermal stability give the competitive edge over conventional styrene-butadiene elastomers. Styroflex, Styrolux and general purpose polystyrene form a unit construction system e.g. for transparent film materials and injection molded parts with fine-tunable hardness and toughness.

### Introduction

Basic properties of noncrystalline polymers are determined by the value of the glass transition temperature $T_g$ in respect to ambient temperature. Polymers with low $T_g$ are referred to as rubbers and behave as viscoelastic liquids. Typical properties comprise elastic recovery, large elongation at break, and softness. To avoid tack and cold flow chemical crosslinking (vulcanization) is required for many applications. On the other hand high $T_g$ resins are stiff and hard, but commonly break when elongated beyond a few %. Well defined block copolymers with at least one block sequence hard-soft-hard offer the chance to combine the advantages of both groups of commonly incompatible materials while maintaining transparency (Fig. 1).

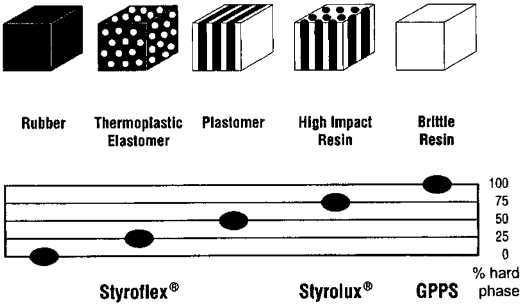

Fig. 1. Mechanical property range of block copolymers. Note: Styroflex contains ~70% soft phase, but only ~35% butadiene.

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The matrix phase basically determines the bulk properties like mechanical behavior and polarity. Thus thermoplastic elastomers exhibit predominantly elastic deformation. They are characterized by a rubber matrix containing inclusions of the hard spheres or cylinders consisting of high $T_g$ end blocks as molecular anchors. The ratio of plastic to elastic deformation increases with the content of the hard phase. Fairly soft "plastomers" with a 50/50 hard-soft ratio and cocontinuous morphology do not have substantial elastic recovery and no pronounced yield point, but show extended plastic deformation due to shear yielding[1). Reduction of the rubber content to 25% in simple symmetrical triblock copolymers leads to high modulus but brittle thermoplastic materials. The challenge has been to develop stiff resins with a low rubber content while preserving the ability of plastic deformation[1) and in consequence impact strength.

## Styrolux

Styrolux, the transparent and tough polystyrene of BASF with styrene butadiene block structure, is used in applications like packaging film, beakers and injection molded parts. This type of polymer was introduced in the late fifties[2) and has subsequently been improved. It is now a steadily growing specialty in a.m. applications. Roughly 80% of Styrolux is blended with general purpose polystyrene (GPPS)[3).

In order to understand the role of transparent and tough polystyrene like Styrolux as blend component, its molecular design is briefly discussed. All Styrolux grades except the later described KR 2691, a linear, symmetrical S-B-S triblock, consist of unsymmetrical star block copolymers. When Styrolux without further specification is mentioned later in the text the term always refers to star polymer grades. The Styrolux grades cover a butadiene content from about 20 to 30%, differing in their toughness/stiffness ratio. Styrolux combines a substantial yield point (25-35 MPa) with plastic deformation up to 300%.

**Synthesis, Structure and Morphology of Styrolux.** Transparent and tough polystyrene is prepared by sequential anionic polymerization, where butyllithium may be added in more than one charge. A possible synthesis consists of the formation of a long styrene block in the first step, followed by further addition of butyllithium and styrene, thus yielding short styrene blocks. The molar ratio of short to long chains is significantly larger than 1. In Styrolux, a mixture of styrene and butadiene is finally added, resulting in a butadiene/styrene block with a tapered block transition. This mixture consisting of short, butadiene-rich and long, styrene-

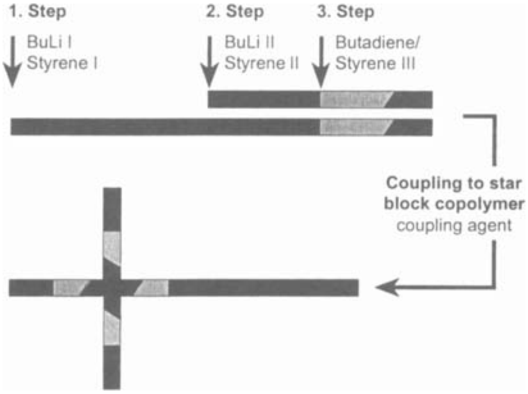


Fig. 2. Synthesis of Styrolux.

rich triblocks is coupled with an oligofunctional coupling agent giving on average an unsymmetrical star polymer with about 4 arms (Fig. 2)[4]. The coupling reaction is of course a statistical process and all possible combinations of long and short arms are observed in an amount predicted by Pascal's triangle, taking the molar ratio into consideration.

The morphology of Styrolux does not fit into the common morphology scheme of styrene/butadiene block copolymers with spheres, cylinders and lamellae as basic morphologies. Fig. 3 left and center shows TEM micrographs of a compression-molded Styrolux sample. At first glance, the impression is one of an irregular, wormlike morphology. Styrene and butadiene form an interpenetrating network with styrene as the predominant phase (Fig. 3 left). A closer look reveals that the butadiene "lamellae" are often split and appear to contain small styrene cylinders and spheres. The difference in scale is remarkable (diameter): large styrene "worms": 25 nm, small styrene inclusions in butadiene: 6 nm, butadiene "lamellae": 8 nm. One explanation might be that long and short styrene blocks partly demix. In particular the short styrene block in the core of the star polymer might form a separate phase. [This notion is also supported by DSC measurements discussed later. The glass transition temperature of the hard phase is unusually broad and stretches from 105 down to 30°C suggesting at least an inhomogeneous polystyrene phase.]

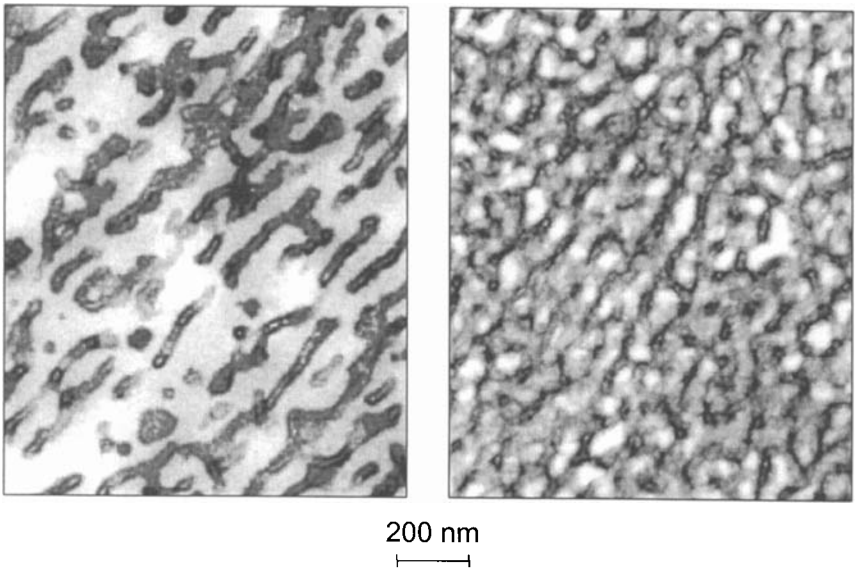


Fig. 3. TEM micrographs of Styrolux/GPPS blend (40/60) (left) and neat Styrolux (right).

**Styrolux/GPPS Blends.** In blends with polystyrene the "double lamellae" continue to exist unchanged. Only the large styrene domains are widened (Fig. 3 right). Apparently the long styrene blocks of Styrolux are directed towards the GPPS containing domains.

Transparency runs through a minimum for 30/70 Styrolux/GPPS blends (Fig. 4), but for film applications the drop is negligible. GPPS is added both on grounds of economy and to modify specific properties. Stiffness (modulus of elasticity), hardness and heat distortion resistance (Vicat B) increase when GPPS is added, whereas the toughness decreases.

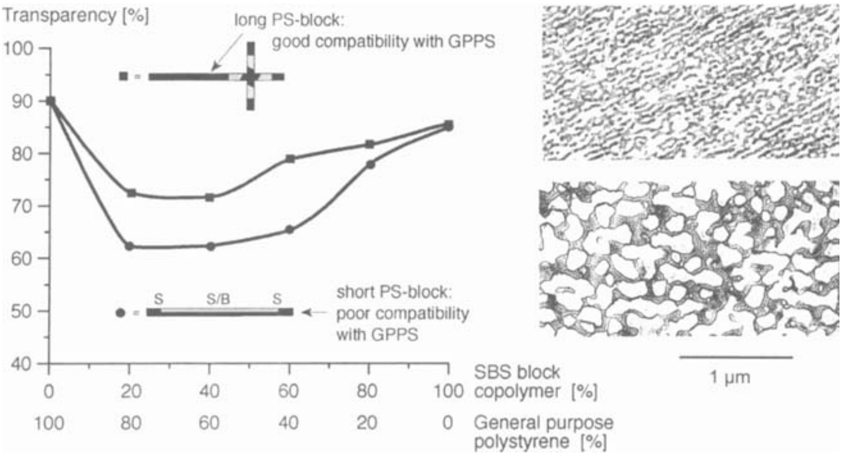


Fig . 4. Transparency of SB block copolymer / GPPS blends: Influence of long styrene block. $M_w$ (SBS) 135,000 g/mol. Butadiene content: star shaped SBS 26%; linear SBS 32%.
TEM (SBS/GPPS 60/40): Note demixing of linear SBS on length scale of visible light.

**Styroflex**

Styroflex is a newly commercialized product based mainly on styrene and butadiene. Our goal was to create a resin for extrusion and injection molding with similar or even improved characteristics compared to plasticized PVC. It should exhibit the mechanics of a thermoplastic elastomer, e.g. low modulus and yield strength, high elongation and excellent recovery and should be suited for high speed processing, especially for thin films. The latter aspect requires an intrinsic high thermal stability in order to avoid gel formation during processing.

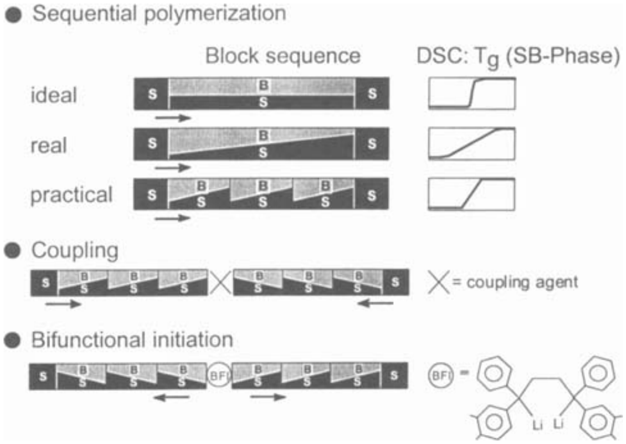


Fig . 5. Synthesis routes to Styroflex. The bars indicate the chemical composition along the polymer chain. The light gray areas within the bars symbolize butadiene, the dark areas styrene.

**Structure and Synthesis.** To meet these goals we chose a symmetrical hard-soft-hard structure typical for TPEs with a block length ratio of about 15:70:15^5). The hard segments consist of polystyrene, but instead of a butadiene soft segment we introduced a statistical SB sequence with a glass transition temperature of approx. -30°C and an S/B ratio of approximately 1. Thus the overall styrene content of Styroflex reaches almost 70% which is in a range known for transparent, impact modified polystyrene like Styrolux. The benefit of this structural variation is a drastically increased molecular weight (140,000 vs. 70,000 g/mol) while retaining the same viscosity or melt flow rate^6-8). Furthermore, a low 1,2-vinyl content is required for superior thermal stability due to reduced crosslinking.

The polymer is prepared by butyllithium-initiated sequential anionic polymerization in cyclohexane (Fig. 5). In order to generate the statistical SB block the presence of a randomizer is required^9). Commonly at least 0.2 to 0.5 vol% of tetrahydrofuran (THF) are added, based on cyclohexane. Using less THF renders a styrene end block which changes the hard-soft-ratio and results in the loss of elastic recovery. Unfortunately THF changes the butadiene microstructure by raising the 1,2-vinyl content from about 8 % in pure cyclohexane up to 30% in the presence of 0.25 vol% THF. Since 1,2-vinyl units undergo crosslinking more readily than 1,4 units, the thermal stability of the SB rubber is reduced. In this respect the THF content has to be kept as low as possible, accepting some gradient from butadiene to styrene. Dividing the SB block into several short blocks, supports however the formation of a homogeneous soft phase. As an alternative, potassium alkoxides can be added as randomizers. Most favorable are sterically hindered tertiary alkoxides like triethyl carboxide^10). Best results are obtained with a K/Li molar ratio of 1:30^10,11). The even incorporation of styrene and butadiene could be shown by taking samples during the copolymerization and analyzing the butadiene content.

There are three basic synthesis routes to Styroflex (Fig. 5): sequential polymerization, coupling of a living S-SB diblock, or bifunctional initiation^12). Bifunctional coupling agents X such as dichlorodimethylsilane and butanediol diglycidyl ether give almost quantitative coupling yields. Carboxylic esters like ethyl acetate work only well when donor solvents are absent. In the presence of THF the coupling yield drops to 30-40%.

Essentially ether-free bifunctional initiators for highly bifunctional growing polymers have been developed by BASF^13). At the time our goal was to find a starting system for the preparation of 1,4-polybutadienediol. Starting materials for the bifunctional initiators are alkylated, particularly methylated, 1,1-diphenylethenes, and β-alkylstyrenes. Reductive coupling with lithium metal in an ethylbenzene/ethyl ether mixture yields the desired 1,4-dilithiobutane derivatives in quantitative yield. The ether serves as charge transfer catalyst. In the case of 1,1-diphenylethylene derivatives at least two methyl groups are required to achieve solubility in ethylbenzene. Best suited in terms of accessability and side reactions is 1-(3,4-dimethylphenyl)-1-phenylethene, which can readily be made by addition of ortho-xylene to styrene in the presence of sulfuric acid followed by dehydrogenation. After the reductive coupling the ether and ethylbenzene are stripped under reduced pressure leaving the dilithiobutane as a deep red, viscous liquid, which tends to crystallize after several hours. Hydrolysis and GC analysis did not show any residual ether. At least one equivalent THF per dilithiobutane remains ligated however, if THF instead of ether is used. The dilithiobutane derivatives themselves proved to be poor bifunctional initiators. About 60% monofunctional growth has been observed. A possible explanation is fast lithium hydride elimination during the initiation step. In order to obtain a useful bifunctional initiator the dilithiobutane is reacted at 0°C with 10 equivalents of butadiene which plays the role of both activator and solvent. The resulting pale yellow oligomeric initiator, which is obtained as a viscous liquid, can be diluted with cyclohexane, and virtually quantitative bifunctional initiation of butadiene and/or styrene is observed.

**Morphology.** Fig. 6 shows the TEM micrograph of a compression-molded Styroflex sample. Due to the phase/volume ratio of about 30% polystyrene in the block polymer, the transmission electron micrograph of Styroflex depicts spherical morphology with the SB rubber as matrix and polystyrene as spheres. The fuzzy borders of the spheres indicate an extended interphase typical of a system close to the order-disorder transition (ODT). The repulsive interaction between the polystyrene and the SB phase is greatly diminished compared to a polystyrene/polybutadiene system. Styroflex has a higher molecular weight than commercial SBS TPEs however, which in turn favors phase separation. When cooling from the melt within a few minutes no long range order develops, but the arrangement of the styrene domains is quite regular yet. Styrene domains are surrounded predominantly hexagonally by their neighbors. The domain identity period is about 39 nm.

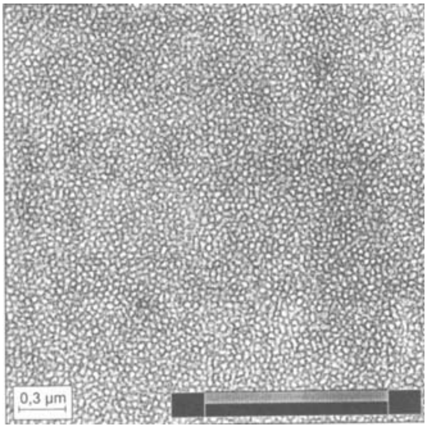


Fig . 6. Transmission electron micrograph of Styroflex.

**Thermal Properties.** The DSC analysis (Fig. 7) shows the glass transition temperature of the soft phase at around -17°C. The long flat slope up to 80°C indicates an extended interphase ending in a barely separated hard phase. We proved that this is not an

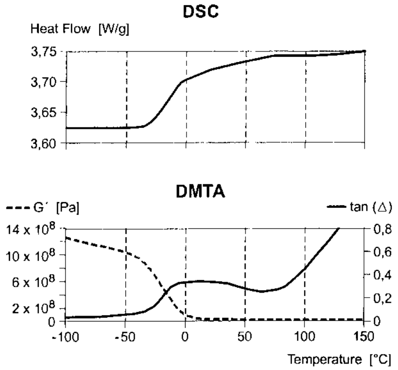


Fig . 7. Top: DSC analysis of Styroflex. Sample quenched from melt; heating rate 20 K/min. Bottom: Dynamic mechanical thermoanalysis (DMTA) of Styroflex.

effect of the heterogeneity of the SB rubber phase by synthesizing and analyzing the pure rubber block. In this case the glass transition was limited to a temperature range between -30 and 0°C.

DMTA measurements (Fig. 7) on Styroflex show two softening points around -20°C and +70°C, which are in good agreement with the DSC measurement.

**Rheology.** Fig. 8 depicts the relationship between the melt viscosities at 190°C and the shear rate for three different triblock copolymers. Styroflex is compared with Styrolux KR 2691 (BASF), which is a symmetrical SBS triblock with a molecular weight (MW) of approx. 70 000 g/mol and a butadiene content of about 26%, and with Kraton D 1102 (Shell), an SBS-type thermoplastic elastomer with a MW of approx. 70 000 g/mol and a butadiene content of about 70%. It can be seen that the three triblock copolymers behave quite differently. At low shear rates the melt viscosities of both Styroflex and Kraton D show little rate dependence in contrast to Styrolux KR 2691, where a decreasing rate is accompanied by a pronounced increase in viscosity, which is characteristic of thixotropic behavior. At high shear rates both Styrolux KR 2691 and Styroflex show significantly more shear thinning compared to Kraton D 1102, indicating good processability. Rheological measurements have been performed between 110 and 220°C in order to determine the ODT, which is found at 145°C. This temperature is well below the favored Styroflex processing temperature (170 - 210°C). Thus, the production of thin films with diminished residual melt history is facilitated. The low ODT is a key advantage over conventional SBS block copolymers.

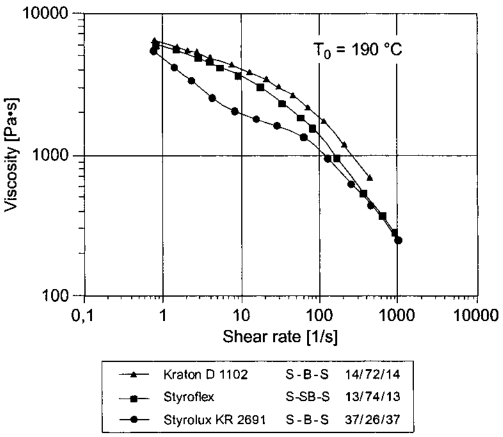


Fig . 8. Rheological behavior of different symmetrical triblock copolymers at 190°C.

**Mechanical Properties.** The mechanical behavior of Styroflex is that of a typical thermoplastic elastomer (Fig. 9). It appears to be somewhat harder than a classical SBS TPE. With an annealed specimen, an ultimate elongation at break of approx. 900% can be achieved, whereas typical SBS polymers fail at elongations of about 1000%. Similar behavior is observed with metallocene polyethylene.

At elongations well below failure, Styroflex follows Hooke's law. In contrast Styrolux KR 2691, a highly transparent and stiff polystyrene with symmetrical SBS triblock structure and a butadiene content comparable to that of Styroflex, has a pronounced yield point followed by plastic deformation. The tensile strength of PVC depends on the annealing time -

indicated by the dashed line. Styroflex films achieve a similar hardness to plasticized PVC due to molecular orientation.

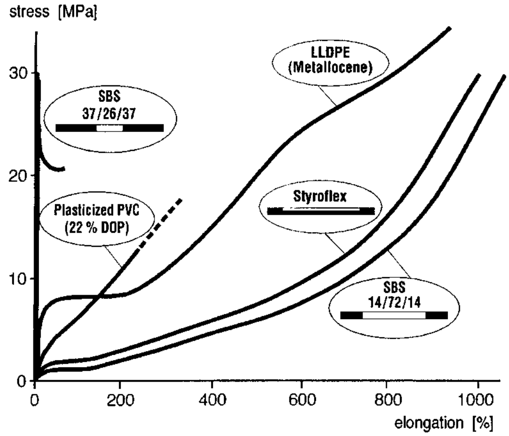


Fig . 9. Stress-strain diagram of compression-molded flexible materials.

Films designed particularly for food wrapping should maintain their smooth, optically attractive surface over an extended period of time even after touching, stapling and other manipulations, which might cause indentations. Therefore a virtually complete recovery of the stretched film is desirable.

Adapted hysteresis experiments have been performed in order to compare the recovery of Styroflex with other film materials (Fig. 10). The sample is elongated to 200% and released to zero stress at a constant rate of 100% per min. The additional recovery is then monitored for five minutes. The experiment is repeated up to 300 and finally 400%. The measurements prove that the recovery of Styroflex is in the range typical of SBS-TPEs and far better than plasticized PVC. In fact after 30 min. the residual deformation is reduced to only 3%. In

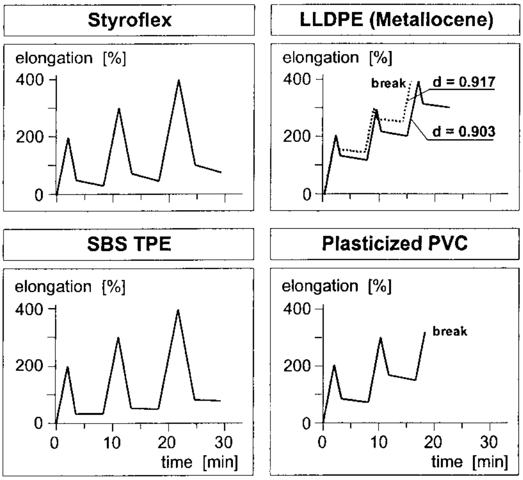


Fig . 10. Hysteresis of film materials.

comparison even the least crystalline metallocene linear low-density polyethylene (density 0.903) does not show a good recovery. The ratio of plastic to elastic deformation increases rapidly with density. Conventional SBS TPEs behave comparable to Styroflex, however their major drawbacks are poor thermoplastic processability and extensive thermal crosslinking. Thus, they are not applicable for sophisticated extruded and molded parts.

One of the predominant features of Styroflex is its high toughness. We compared Styroflex with plasticized PVC, metallocene PE and SBS elastomer (Tab. 1). The dart drop test proves its superior performance over plasticized PVC (note: oriented, extruded blown film was used for mechanical tests, see Tab. 1). Due to the orientation the Shore D hardness is roughly the same as that of PVC.

**Tab. 1. Properties of Styroflex vs. plasticized PVC( 20 w/w dioctyl adipate), metallocene PE and SBS elastomer (molded specimens)**

| | *Test Conditions* | *Styroflex* | *Plast. PVC 20 % DOA* | *Metallocene PE* | *SBS elastomer* |
|---|---|---|---|---|---|
| MVR (200°C/5kg) [ml/10′] | ISO 1133 | 10-15 | - | 5 | 8 |
| Dart drop [g] [a] | - | 600 | 290 | 500 | no film |
| Shore D hardness[b] | DIN 53505 | 39 | 36 | 42 | 20 |
| Vicat A[b] [°C] | ISO 306 | 40 | n.d.[c] | 87 | n.d.[c] |
| Elongation at break (%) | ISO 527 | >500 | approx. 300 | >500 | >500 |
| Transparency [%] | - | 80 | 85 | 85 | 20 |
| Elastic recovery | - | ++ | ++ | +/- | ++ |
| Time until crosslinking[d], 250°C, [min] | - | 19 | decompos. at T > 220°C | >60 | 4 |

[a]Weight (g) of a falling dart until failure of film sample. Film gauge 14 ± 5 µm
[b]Determined on compression-molded specimen (T = 200°C / 5 min). [c]n.d. = not detectable.
[d]Pressure increase of 5 bar in rheography experiment (explanation in text; see also Fig. 14).

Fig. 11 shows the improvements in thermal stability. A thermoplastic material at T = 250°C is extruded through a hole at constant rate. Pressure p increases with time due to crosslinking reactions in the melt. An (arbitrary) measure for "crosslinking" is the time after Δp = 5 bar.

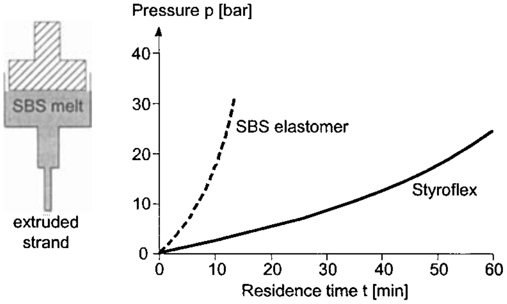


Fig. 11. Stability of SBS materials in melt. The time dependence of the extrusion pressure is a measure for the crosslinking rate.

## Blends containing Styroflex

**Styroflex/Styrolux Blend System.** Extruder blends of Styroflex and Styrolux have been prepared for a number of mixture ratios. The transparency was virtually unimpaired by the blend composition and remained at the high level of the pure materials (Fig. 12), indicating homogeneity of the blends well below the wavelength of visible light. The mechanical properties such as modulus and elongation at break vary almost linearly with composition. This enables fine-tuning of hardness, toughness and flexibility of films and injection-molded parts.

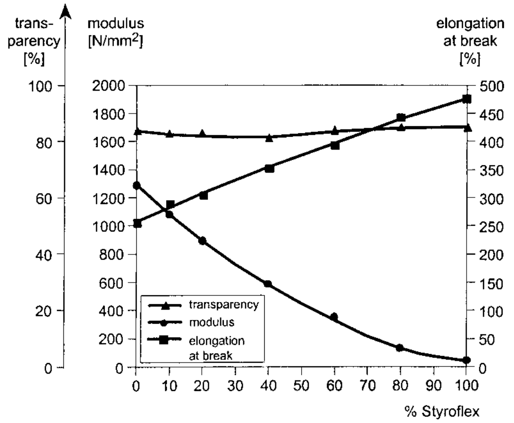


Fig . 12. Styroflex/Styrolux blend system: mechanical and optical properties.

In Fig. 13 the morphologies of pure Styrolux and Styroflex (top and bottom TEM) are compared with two blends. Styrolux (bottom) exhibits the already discussed complex wormlike morphology containing two different types of styrene domains with the long PS arms concentrated in the thick “lamellae“. In Styrolux/Styroflex blends two phases become apparent. One phase is butadiene-rich and contains spherical PS domains, the other phase large styrene worms. The phase ratio does not reflect the mixture ratio of Styroflex and Styrolux, but the “Styroflex phase“ seems to have a far larger volume ratio. The domain identity period is at roughly 15 nm less than half that of Styroflex. In view of the fact that the small styrene cylinders embedded in the butadiene lamellae disappear with increasing Styroflex content it appears most likely that Styroflex extracts the butadiene-rich stars containing only short arms and forms a new phase. Since this separation process occurs on a scale of about 80 nm transparency does not decrease.

The DSC analysis supports the conclusions from the TEM interpretations (Fig. 14). Only one soft phase is visible in both blends containing 20 and 60% Styroflex respectively, with average glass transition temperatures.

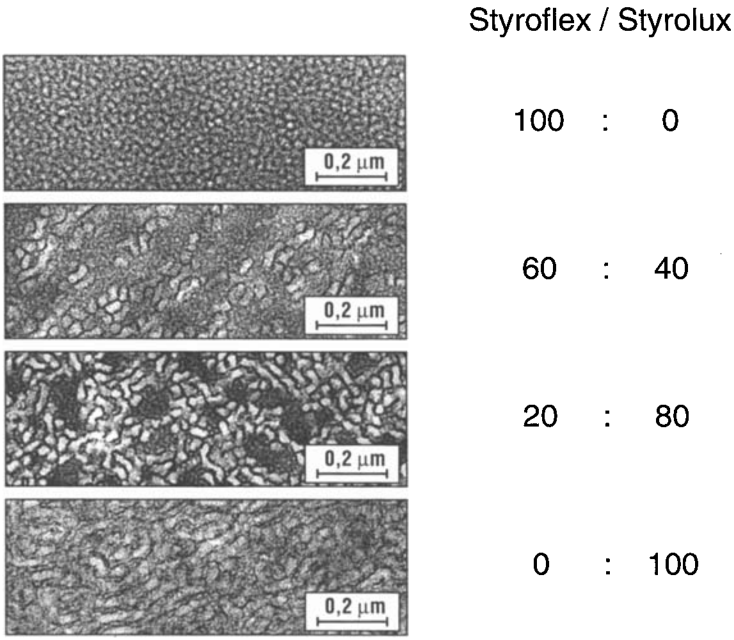


Fig . 13. Morphology of Styroflex/Styrolux blends.

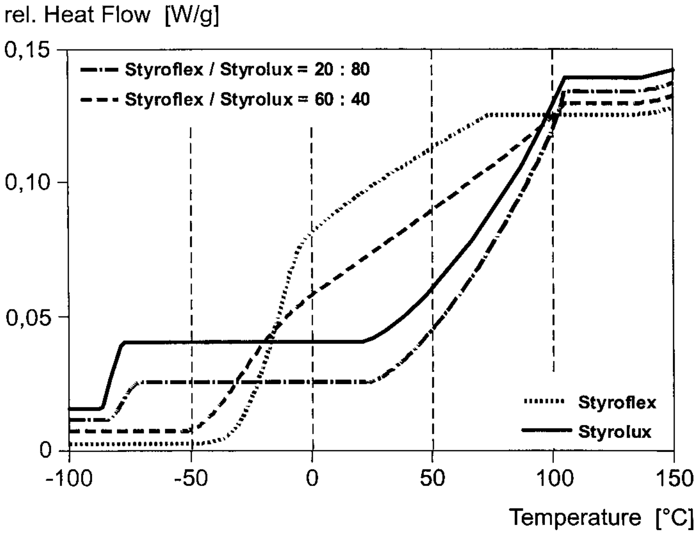
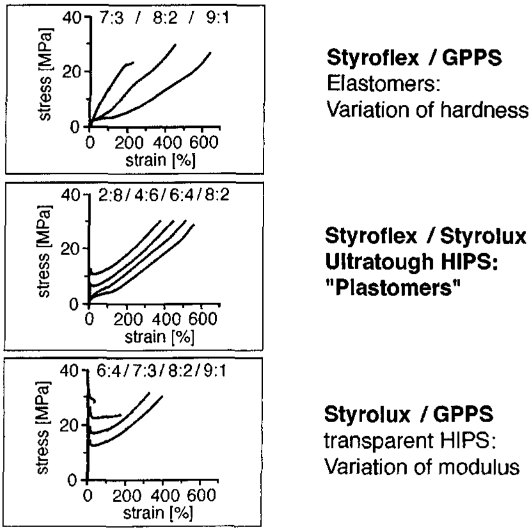


Fig . 14. Styroflex/Styrolux blend system: DSC analysis.

**Styroflex/Styrolux/Polystyrene Blend System.** Adding Styroflex as a third blend component to the established Styrolux/GPPS system opens up new possibilities. The already discussed Styroflex/Styrolux blend system enables the property range between transparent polystyrene and soft thermoplastic elastomers to be covered which has recently been named "plastomer" by metallocene LLDPE producers due to the characteristic large plastic deformation. The stress-strain diagrams for a series of blends is depicted in Fig. 15 center, showing how the balance of elastic to plastic deformation shifts with increasing Styrolux content. The bottom diagram elucidates the transition from a tough, relatively soft to a stiff, but fairly brittle thermoplast. Mixing Styroflex with small amounts of general purpose polystyrene (GPPS) increases the hardness but retains the elasticity (Fig. 15 top). We also investigated the ternary blend system and found it to be a predictable and calculable unit construction system e.g. for tailor-made film materials. Styrolux mainly plays the role of a compatibilizer between Styroflex and GPPS. The fact that a certain degree of toughness can be achieved with a higher GPPS content than with binary Styrolux/GPPS blends makes the ternary system particularly attractive in respect to thermal stability and cost reduction.



**Styroflex / GPPS**
Elastomers:
Variation of hardness

**Styroflex / Styrolux**
**Ultratough HIPS:**
**"Plastomers"**

**Styrolux / GPPS**
transparent HIPS:
Variation of modulus

Fig . 15. Styroflex / Styrolux / GPPS blend system: stress-strain diagrams.

## Conclusion

Styrolux and Styroflex are obtained by sequential anionic polymerization of styrene and butadiene. Styrolux is a stiff and tough resin, which retains its transparency when blended with general purpose polystyrene. Although containing only 25% butadiene it shows extended ductility explained by shear yielding processes. The highly unsymmetrical star block structure and the resulting complex morphology is thought to contribute to the favorable mechanical behavior.

Styroflex, the new BASF experimental styrenic polymer, combines the advantages of SBS elastomers (high toughness, recovery) with the properties of transparent, impact-modified SBS polymers like Styrolux (good processability, thermal stability, high transparency).

Together with Styrolux and general purpose polystyrene it forms a unit construction system e.g. for transparent film materials and injection molded parts allowing fine-tuning of hardness and toughness, representing the complete range of BASF's styrene/butadiene block copolymers (Fig. 1).

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