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Characterization of Thermoplastic Elastomers by Means of Temperature Scanning Stress Relaxation Measurements

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1. Introduction

Thermoplastic elastomers (TPE) and, in particular thermoplastic vulcanizates (TPV), are a new class of materials, combining the properties of conventional elastomers (rubber) and the processibility of thermoplastics. Compared with conventional rubber elastomers, these materials can be more easily processed and more easily recycled. TPE are often used to replace conventional thermoset rubber, but those are also used for a great variety of new applications and products, particularly in hard/soft combinations with other thermoplastics. Due to the advantages over conventional thermoset rubber, the commercial uses for thermoplastic elastomers are growing rapidly (Schäfer, 2001; Bittmann, 2004).

Beside many advantages, some disadvantages do exist, also. In comparison to chemically crosslinked elastomers (e.g., EPDM or natural rubber), TPE materials have stronger limitations with respect to upper service temperature, which is caused by softening or melting of the hard phase. Furthermore, TPE exhibit higher creep and stress relaxation, than thermoset rubber, even at ambient temperatures (Holden et al., 2004). Thus, new demands on polymer testing arise from the assessment of thermoplastic elastomers (TPE) with respect to their rubber elastic use properties and stress relaxation behaviour, particularly at elevated temperatures.

Due to the complex molecular structure and phase morphology of TPE, traditional test methods normally used for characterization of elastomers give only limited information about the unique properties of TPE. For this reason, temperature scanning stress relaxation (TSSR) test method has been developed, recently (Vennemann et al., 2001, 2003). In this work, the basic principle of the TSSR test method as well as the theoretical background will be described. Furthermore, an overview of numerous results obtained from selected TPE materials, will be presented to demonstrate the versatility of the TSSR method. In addition, further development of the method will be presented, in particular for rapid determination of crosslink density of TPV.

2. Theoretical background

2.1 Stress relaxation and determination of relaxation spectra

Polymers exposed to constant strain exhibit the well known phenomenon of stress relaxation, i.e. a more or less strong decrease of stress as a function of time. The microscopic

mechanisms, leading to the macroscopic recognizable decrease of stress, may result from physical and/or chemical processes. In contrast to thermoset rubber, where the thermal - mechanical behaviour is dominated by chemical reactions resulting in cleavage of polymer chains and network junctions, in case of thermoplastic elastomers physically induced stress relaxation processes are most important with respect to usage properties.

For the simple Maxwell - model, as represented in Figure 1, the relaxation time constant τ is defined as the period of time, after the stress has dropped down to the value of σ_0/e . Here, σ_0 indicates the initial stress at time zero when the strain has been applied to the sample. Unfortunately, the real behaviour of materials is more complicated and cannot be described by the simple Maxwell - model. According to the well known theory of linear viscoelasticity the entire relaxation process can be described by means of the generalized Maxwell - model, which consists of an infinite number of individual spring - dashpot - elements. Under isothermal conditions ($T = \text{const.}$) the relaxation modulus E_{iso} is a function of time t and given by Eq. (1), for this model (Ferry, 1980).

$$E_{iso}(t) = E_{\infty} + \int_{-\infty}^{\infty} H'(\tau) \cdot e^{\frac{-t}{\tau}} d \ln \tau \quad (1)$$

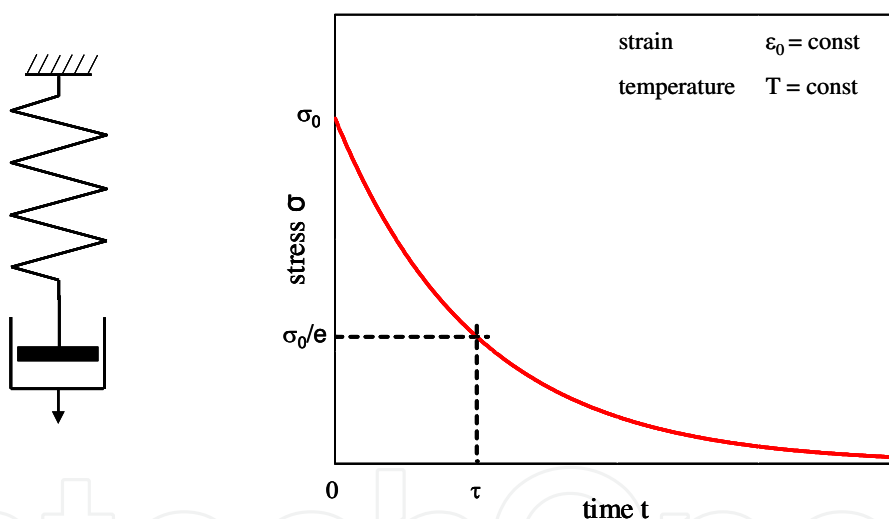


Fig. 1. Maxwell - Model and stress as a function of time after a constant strain ϵ_0 has been applied at $t = 0$.

The relaxation modulus is also directly related to the experimentally observable stress $\sigma(t)$ and can be easily calculated by dividing the stress by the applied strain ϵ_0 . In this equation the relaxation spectrum $H'(\tau)$ is a steady function describing the probability of the relaxation time constants τ of the model which may be associated with the population of relaxation mechanisms of the system. The constant E_{∞} is added in Eq. (1) to allow the system to approach an equilibrium state higher than zero, as observed normally for viscoelastic solids.

According to Alfrey's rule (Alfrey & Doty, 1945) the value of the relaxation spectrum $H'(\tau)$ at point $\tau = t$ is obtained in first approximation by differentiating $E_{iso}(t)$ with respect to $\ln t$, by Eq.(2).

$$H'(\tau) = -\left(\frac{dE_{iso}}{d\ln t}\right)_{t=\tau} = -t \cdot \left(\frac{dE_{iso}}{dt}\right)_{t=\tau} \quad (2)$$

All relaxation mechanisms, and thus the relaxation time constants, are strongly depending on temperature, i.e. the higher the temperature, the lower the relaxation time constants and vice versa. Therefore, the relaxation spectrum covers a very wide range on time scale and it is practically impossible to determine the entire function by means of a single stress relaxation measurement. Usually, a set of measurements at several temperatures have to be executed, to create a master curve, based on time - temperature superposition principle (TTS). That means, high effort is required to obtain full information of the stress relaxation behaviour.

With temperature scanning stress relaxation (TSSR) measurements, an alternative strategy has been introduced recently (Vennemann et al., 2001; Vennemann, 2003; Barbe et al., 2005). In contrast to traditional isothermal tests, during TSSR measurements the temperature is not kept constant, but is increasing linearly with a constant heating rate β , e.g. $\beta = 2 \text{ K/min}$. As a result, the non-isothermal relaxation modulus $E_{non-iso}$ as a function of temperature is obtained. Analogue to isothermal stress relaxation measurements, the spectrum $H(T)$ can be calculated in first approximation by Eq. (3).

$$H(T) = -\Delta T \cdot \left(\frac{dE_{non-iso}}{dT}\right)_{\beta=\frac{\Delta T}{t}=const} \quad (3)$$

$$\text{with } T - T_0 = \Delta T = \beta \cdot t$$

In this equation T_0 stands for the initial temperature at which the test is started and β is the heating rate of the temperature scan. Although this function is not defined on time scale, the relaxation mechanisms the polymer sample undergoes during the test can be identified, clearly, because the relaxation time constant τ decreases monotonously with increasing temperature T . Due to its very strong temperature dependence, the relaxation time constant τ drops down to small values rapidly, within small temperature range. Thus, the entire spectrum is observable on temperature scale within a relative short period of time during a temperature scan of a TSSR test.

Beside stress relaxation, two other phenomena, i.e. thermal expansion and rubber elasticity of the sample, have to be taken into consideration, if a sample, mounted between two sample holders having constant distance, is heated up linearly. In the following sections, those effects will be described in detail.

2.2 Thermal expansion of the sample

Due to thermal expansion of the material the initial length l_0 of the sample is increasing, if a temperature scan is performed starting at initial temperature T_0 up to higher temperatures T . In consequence, the thermal expansion of the sample contributes to a decrease of stress, if a stretched sample is mounted between sample holders with constant distance. The thermally induced variation of strain $\varepsilon = (l - l_0)/l_0$ during TSSR tests can be easily calculated by

$$\varepsilon(T) = \frac{l}{L_0(1 + \alpha \cdot \Delta T)} - 1 \tag{4}$$

where L_0 is the initial distance of the sample holders at temperature T_0 and α is the coefficient of linear thermal expansion of the sample. For rubber typical values for α are in the range of 1 to $3 \cdot 10^{-4} \text{ K}^{-1}$ (Gent, 2001). In Figure 2 the relative strain $\varepsilon/\varepsilon_0$ is plotted against temperature for certain values of initial strain ε_0 . It becomes obvious, increasing temperature results in decreasing strain. However, the influence of temperature on relative strain is more or less negligible, if the strain is sufficiently high. To minimize the influence of thermal expansion, TSSR experiments should be performed at initial strains not below 50 %.

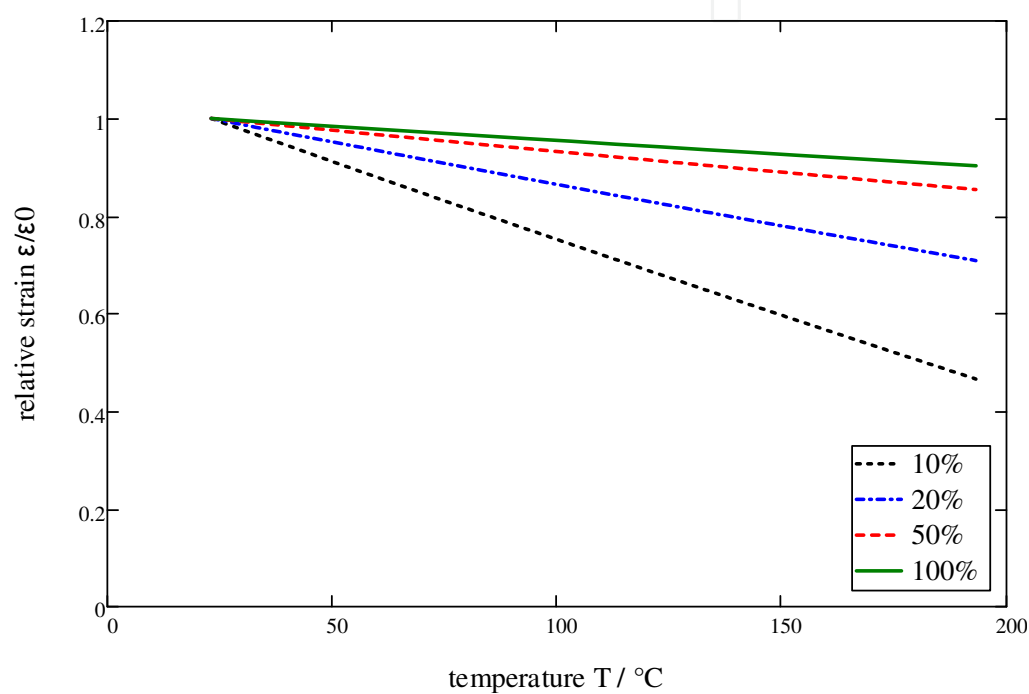


Fig. 2. Influence of thermal expansion of the sample on relative strain. Curves were calculated for certain initial strain values, as indicated, by means of Eq. (4) with $\alpha = 3 \cdot 10^{-4} \text{ K}^{-1}$.

2.3 Rubber elasticity

According to the well known theory of rubber elasticity in case of an ideal rubber network, the mechanical stress σ is proportional to the absolute temperature T and can be expressed by Eq. (5) (Mark, 1981).

$$\sigma = \nu \cdot R \cdot T \left(\lambda - \lambda^{-2} \right) \tag{5}$$

Where ν is the crosslink density of the network and R is the universal gas constant. The strain ratio λ is defined as $\lambda = l/l_0$, where l is the length and l_0 the initial length of the sample. According to Eq. (5) the stress should increase with increasing temperature, if the strain ratio λ is kept constant. The slope of the stress - temperature - curve at constant elongation can be obtained from the derivative of stress with respect to temperature which is assigned as temperature coefficient κ in the following.

$$\kappa = \left(\partial \sigma / \partial T \right)_{\lambda} = \nu \cdot R \cdot \left(\lambda - \lambda^{-2} \right) \quad (6)$$

For high elongations, the temperature coefficient κ is positive, however at low strain ratios, i.e. $\lambda < 1.1$, a negative value of κ was found experimentally. The transition from a negative to a positive value of the temperature coefficient is known as thermoelastic inversion (Pellicer, 2001). The phenomenon of thermoelastic inversion is not predicted by theory but, it was shown early (Anthony et al., 1942) and has been confirmed by own measurements (Vennemann & Heinz, 2008), this apparent contradiction results only from thermal expansion of the sample. Considering the temperature dependence of the strain, as described by Eq. (4), the relation of Eq.(5) can be rewritten as

$$\sigma = \nu \cdot R \cdot T \left(\frac{\lambda_0}{1 + \alpha \cdot \Delta T} - \left(\frac{\lambda_0}{1 + \alpha \cdot \Delta T} \right)^{-2} \right) \quad (7)$$

where λ_0 is the initial strain ratio at temperature T_0 . The influence of thermal expansion on the stress - temperature - curve is shown in Figure 3, where the uncorrected curve as calculated from Eq. (5), is represented in comparison to the corrected curve, as calculated from Eq. (7). Obviously, the initial slope is slightly reduced due to thermal expansion. Furthermore, the corrected function is no longer strictly linear, but exhibits a slight curvature with increasing temperature. From Eq. (7), by derivation with respect to temperature T , the corrected temperature coefficient κ is obtained, which is now also a function of temperature. The initial value of κ at temperature T_0 is given by Eq. (8) (Vennemann et al., 2011).

$$\kappa_0 = \kappa(T_0) = \nu \cdot R \cdot \left[\left(\lambda_0 - \lambda_0^{-2} \right) - T_0 \cdot \alpha \cdot \left(\lambda_0 + 2 \cdot \lambda_0^{-2} \right) \right] \quad (8)$$

2.4 General remarks

It has been shown; macroscopic recognizable increase of stress is recognizable if an elongated piece of rubber is heated up linearly. The macroscopic reaction of the material is caused by the change of entropy on microscopic scale and thus, it becomes possible to easily determine the crosslink density of a rubber sample, which is an important microscopic parameter of the system. But, it is important to notice, that the above equations are only strictly correct for ideal rubber networks. Real systems, such as filled elastomers and thermoplastic elastomers, are more complex, and cannot be fully described by this simple theory. Therefore, further development of theory is required to better understand the behaviour of those materials. Recently, a model has been developed to describe the thermoelastic behaviour of carbon black filled elastomers (Vennemann et al., 2011).

In case of thermoplastic elastomers the situation is even more difficult, because these materials consist of at least two phases and in case of commercial grades additionally of fillers, plasticizer and other additives. Although most elastomers and also thermoplastic elastomers (TPE) exhibit thermoelastic behaviour similar to ideal rubber, calculation of true crosslink density is not possible, but only apparent values because of lack of adequate theory. Nevertheless, the characterization of thermoelastic behaviour by TSSR measurements is very useful, in particular in case of thermoplastic vulcanizates, because properties which are closely related to the structure of the polymer network become recognizable. Furthermore, additio-

nal information about the composition, morphology and structure of the sample can be deduced from the entire relaxation spectrum.

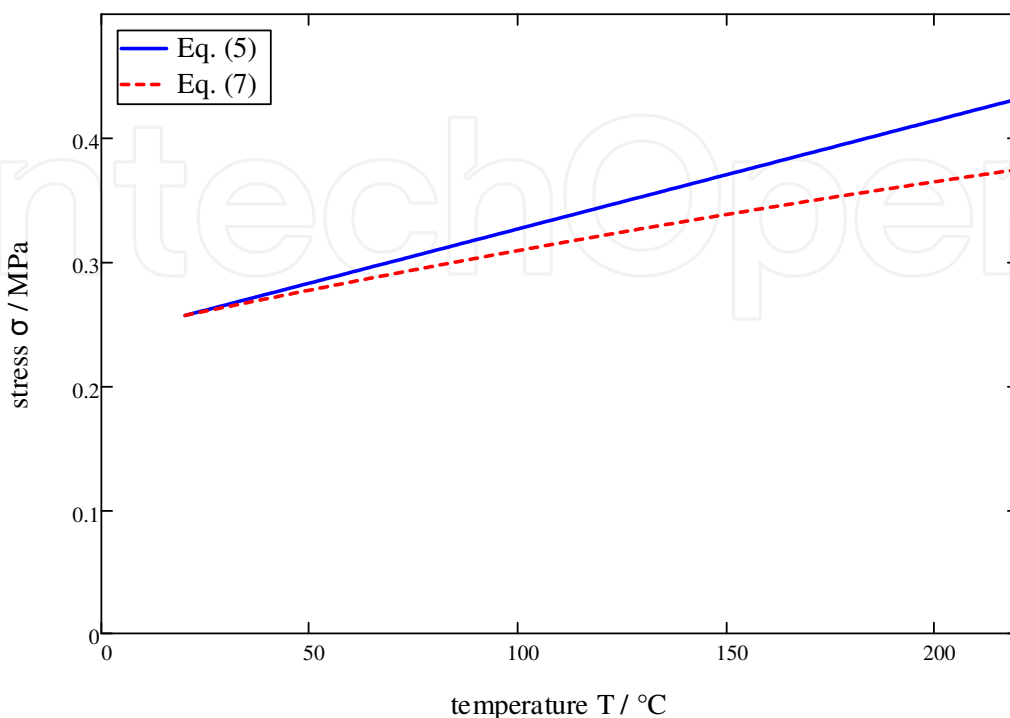


Fig. 3. Theoretical stress - temperature - curves, calculated by use of Eq. (5) and Eq. (7) with $v = 100 \text{ mol/m}^3$, $\lambda_0 = 1.5$ and $\alpha = 3 \cdot 10^{-4} \text{ K}^{-1}$.

3. Experimental

3.1 Materials and preparation of the samples

3.1.1 Thermoplastic elastomers based on Styrene Block Copolymers (SBC)

High molecular weight poly(styrene-*b*-ethylene/butylene-*b*-styrene) (SEBS) with a polystyrene (PS) content of 33%, a molar mass of the PS-blocks of 29000 g/mol and a total molar mass of $M_w = 174000 \text{ g/mol}$ were used as the basis for the compounds prepared. In SBC/polyolefin blends a standard isotactic polypropylene and, alternatively a standard high density polyethylene were used as the polyolefin component of the compounds. In SBC/PPE blends high molecular weight poly(*p*-phenylene ether) (PPE) with $T_g = 215^\circ\text{C}$ and molar mass of $M_w = 38900 \text{ g/mol}$ was used as the modifier. Additionally, high purity medicinal paraffin oil was used as the extender oil for all compounds and a small amount of stabilizer was added to protect the polymers against degradation during the mixing process.

SBC/polyolefin compounds were produced using a twin-screw extruder (L/D: 32/1, 25 mm diameter; Berstoff GmbH). SBC/PPE compounds were produced by means of a single-screw extruder (Göttfert GmbH, L/D: 15/1). In all cases the ingredients were mixed together prior feeding to the extruder, having a barrel temperature of 260°C . Test plates of 2mm thickness of all compounds were produced in a pneumatic injection moulding press. Further details are described in earlier papers (Vennemann et al., 2004) and (Barbe et al., 2005).

3.1.2 Thermoplastic polyolefin blends (TPO) and dynamic vulcanizates (TPV)

a. Commercial grades based on EPDM/PP

Several commercial grades of thermoplastic vulcanizates based on EPDM/PP covering a wide range of hardness were obtained from Solvay Engineered Polymers (TX/USA) and tested as received. The novel TPV-AP materials were produced via a dynamic vulcanization process using a new curative system and DVA process developed by Solvay Engineered Polymers (Reid et al., 2004). The new cure system results in a material with non-hygroscopic behaviour, white colour, and low odour. Properties of TPV-AP are compared to two other commercially available TPV materials. TPV-HS is a commercial TPV based upon EPDM and PP where the elastomer is crosslinked with a hydrosilation process. TPV-PH is also a commercial TPV based upon EPDM and PP where the elastomer is crosslinked with a phenolic resin curing process. The samples of both TPV-HS and TPV-PH were not produced by Solvay Engineered Polymers, but commercial grades, produced by other suppliers.

b. Model compounds of peroxide cured TPV based on EPDM/PP

Commercial available EPDM rubber and isotactic polypropylene homopolymer (PP) were used as the basis for the dynamic vulcanizates (TPV). The EPDM contains 50 wt % ethylene and 4 wt % ethylidene norbornene (ENB). It has a Mooney viscosity ML(1+4) at 125 °C, of 36. The melt flow rate of the polypropylene, measured at 230 °C and 2.16 kg is 12 g/10 min. The crosslink system consists of di(tert-butylperoxyisopropyl)benzene (abbrev.: DTBPIB) as peroxide and trimethylolpropane trimethacrylate (abbrev.: TRIM) as co-agent. The peroxide and co-agent are supplied commercially on a silica carrier, with active agent content of 40 wt % and 70 wt %, respectively. The TPV samples are designated as TPV1 to TPV6, whereas the total amount of curatives (DTBPIB and TRIM) is increasing from 1 phr to 6 phr in steps of 1 phr. The volume fraction of polypropylene was $\phi_{PP} = 0.23$ in all compounds. An uncured compound of identical EPDM/PP ratio was also produced and tested as reference sample. All samples were produced in a two-step mixing process using a Haake Rheocord 600 laboratory internal mixer (Thermo Electron Corporation, Karlsruhe). Further details of the production process are published elsewhere (Vennemann, 2006).

c. Model compounds of phenolic cured TPV based on EPDM/HDPE

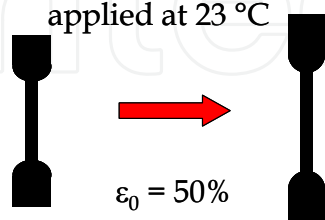
Two different commercially available EPDM rubber and two different grades of high density polyethylene (HDPE) were used as the basis for the dynamic vulcanizates, in this study. Crosslinking of the EPDM in all compounds was performed with a phenolic resin cure system, consisting of stannous chloride ($\text{SnCl}_2 \cdot 2 \text{H}_2\text{O}$), zinc oxide (ZnO) and SMD 31214. The latter is a commercially available solution of paraffinic mineral oil and 30 wt % of phenolic resin SP 1045. Further details of the composition and preparation of the compounds are published elsewhere (Vennemann, 2009).

3.2 TSSR instrument and test procedure

The temperature scanning stress relaxation tests were performed by use of a commercial available TSSR instrument obtained from Brabender GmbH (Duisburg, Germany). The TSSR instrument (Fig. 4) consists of an electrical heating chamber where the sample, a S2 testing rod, is placed between two clamps. The clamps are connected to a linear drive unit to apply

a certain uniaxial extension to the sample. A high quality signal amplifier in combination with a high resolution AD-converter is used to detect and digitize the analogue signals of the high-resolution force transducer and the thermocouple. In order to detect the current temperature the thermocouple is placed near the centre of the sample. All signals are transferred to a personal computer. A special software program is used for treatment and evaluation of the data as well as for the control of the test procedure.

1. Step: Initial strain is applied at 23 °C



2. Step: Isothermal relaxation at $T_0 = 23\text{ °C}$ for 2 hrs

3. Step: Temperature scan with constant heating rate

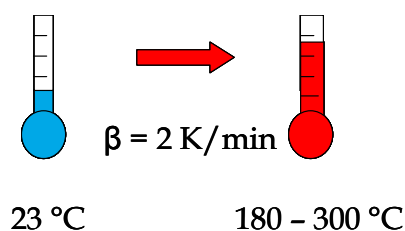


Fig. 4. TSSR instrument and test procedure

The test procedure starts with placing the sample in the electrical heated test chamber, which is controlled at the initial temperature T_0 of 23 °C. After the initial strain of $\epsilon_0 = 50\%$ is applied, the isothermal relaxation period starts, whereas the temperature remains constant at 23 °C within $\pm 0.1\text{ °C}$. During this time most of the short time relaxation processes occur and the sample reaches a quasi equilibrium state. Then the sample is heated linearly at a constant rate of $\beta = 2\text{ K/min}$, until the stress relaxation has been fully completed or rupture of the sample has occurred.

From the obtained force – temperature curve certain characteristic quantities such as T_{10} , T_{50} , T_{90} and the TSSR index RI can be calculated. The temperature T_x stands for the temperature at which the force ratio F/F_0 has decreased about $x\%$ with respect to the initial force F_0 . The TSSR index RI is a measure of the rubber like behaviour of the material and is calculated from the area below the normalized force – temperature curve, as represented in Figure 5 and given by Eq. (9). Additionally, the temperature coefficient κ and the relaxation spectrum $H(T)$ are calculated from the initial slope and the derivative of the stress–temperature curve, respectively, as described in chapter 2, in more detail.

$$RI = \frac{\int_{T_0}^{T_{90}} F/F_0 dT}{T_{90} - T_0} \tag{9}$$

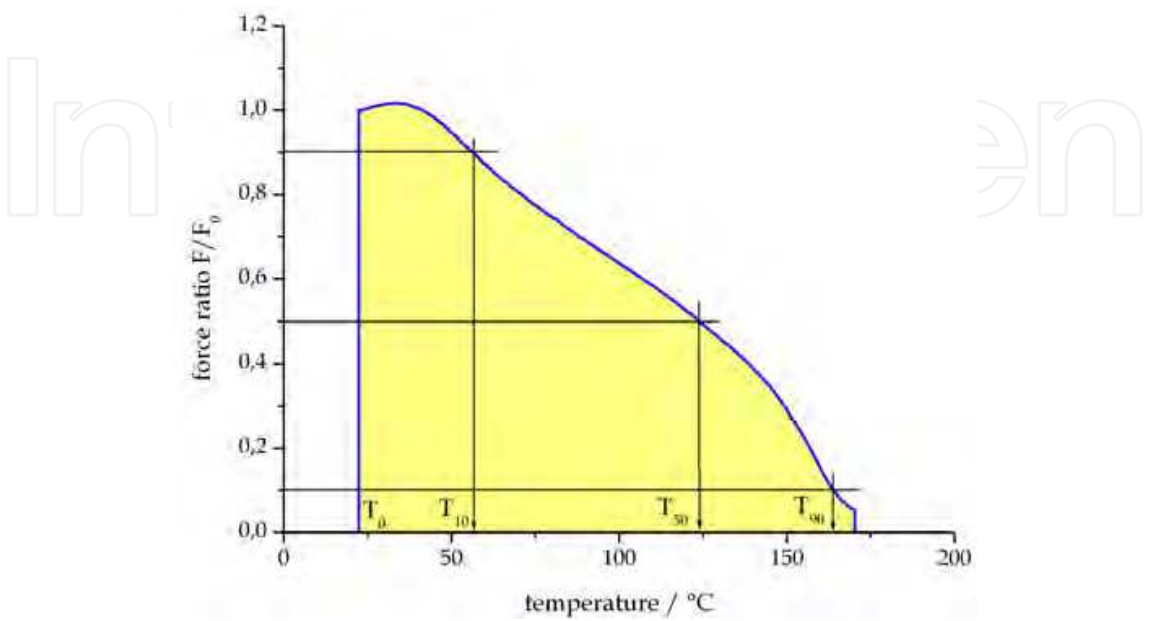


Fig. 5. Normalized force as a function of temperature and determination of characteristic temperatures T_{10} , T_{50} and T_{90} .

4. Results and discussion

4.1 Thermoplastic elastomers based on Styrene Block Copolymers (SBC)

Commercial available TPE-S materials are generally a compound of a styrene block copolymer, commonly poly(styrene-b-ethylene/butylene-b-styrene) (SEBS) or poly(styrene-b-butadiene-b-styrene), and a thermoplastic polymer, mostly polypropylene (PP). Additionally, plasticizer, mineral fillers and other components are used to achieve the demanded properties. In Fig. 6 (left) force - temperature curves and the corresponding relaxation spectra of two different types of SBC - compounds are represented. Up to 110 °C, both materials behave almost identical, but at higher temperatures the force of the SEBS/PE compound drops down to zero close to 120 °C, whereas the force of the SEBS/PP compound decreases more or less slightly until the base line is approached at about 165 °C. In the relaxation spectrum of both materials a significant peak at about 100 °C is observable which corresponds to the glass transition temperature of the styrene hard phase of the SEBS. At higher temperature (120 °C or 160 °C) an additional peak appears which is caused by the melting of the thermoplastic component, i.e. polyethylene or polypropylene, respectively. From these measurements it becomes clearly obvious; the upper service temperature range of SBC compounds is limited by the glass transition of the polystyrene hard phase. An increased upper service temperature limit may result from the existence of a co-continuous phase of a thermoplastic component having a higher melting temperature. In case of polyethylene as the thermoplastic component, an improvement up to 120 °C can be achieved, whereas by use of polypropylene higher temperature, up to a maximum value of 160 °C, is possible.

However, the latter values have to be considered as theoretical maxima. For obvious reasons, the upper limits of the service temperature have to be significantly lower than those maximum values. Because the melting temperature of polypropylene is considerably higher than of polyethylene, PP is favoured as thermoplastic component for commercial TPE-S materials. Normally, it is not possible to detect the glass transition temperature of the PS hard phase of commercial SBC compounds by means of traditional DSC and DMA measurements, because of the complex compound composition and the limited sensitivity of the instruments. In contrast, TSSR measurements are very sensitive with respect to relaxation processes of the hard phase and therefore more suitable, to characterize and improve those materials.

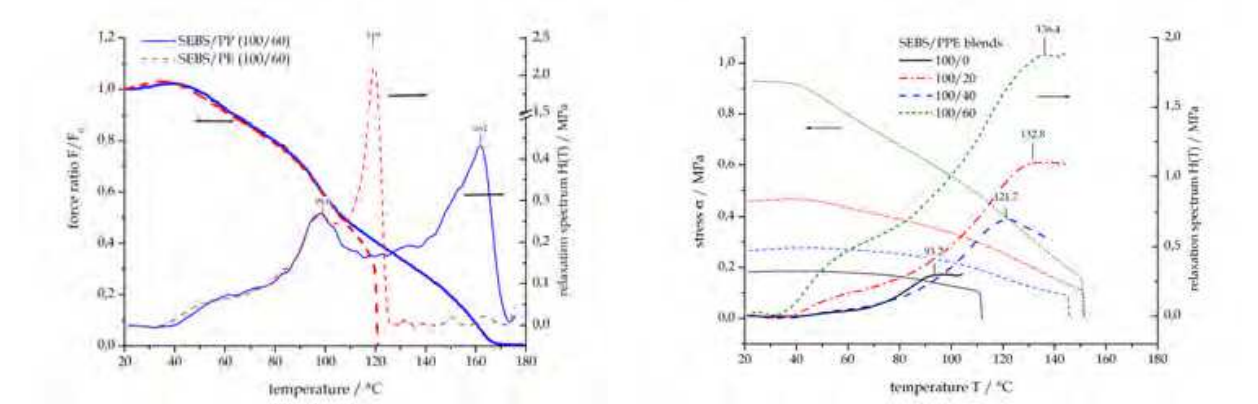


Fig. 6. *Left:* Force - temperature curves and relaxation spectra obtained from SEBS/PE and SEBS/PP blends. *Right:* Stress - temperature - curves and relaxation spectra obtained from SEBS/PPE blends with increasing proportion of PPE.

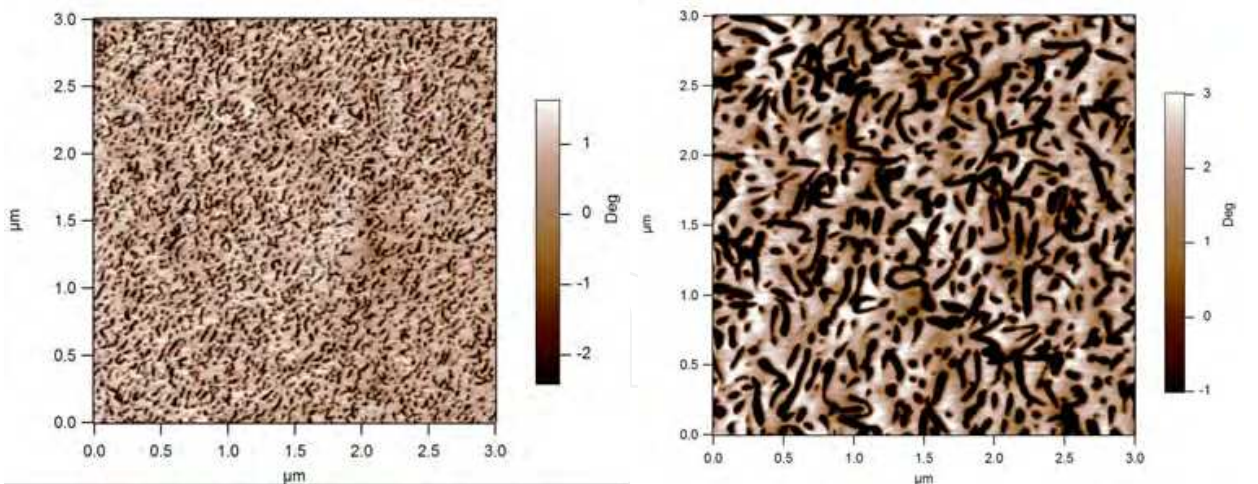


Fig. 7. AFM phase images of pure SEBS (left) and SEBS/PPE blend (right) with blend ratio of 100/20.

An alternative route to improve the heat resistance of TPE-S materials, i.e. TPE based on SBC, exists by blending the SBC with poly(p-phenylene ether) (PPE). PPE and PS are known to be thermodynamically miscible over the entire composition range, i.e., they form a blend with only one glass transition temperature (Tucker et al., 1988). Thus, by blending with PPE the glass transition of the SBC hard phase may be increased up to 150 $^{\circ}\text{C}$ (Barbe et al., 2005).

In Figure 6 (right) a series of stress - temperature - curves and relaxation spectra is also represented, which were obtained from SEBS/PPE blends, containing increasing proportion of PPE. Due to increasing content of PPE, the glass transition of the SEBS hard phase is shifting to higher temperatures and thus makes the hard phase more heat resistant. Furthermore, the level of the stress - temperature - curves is also increasing, caused by the reinforcing effect of the hard domains. As can be seen from the AFM phase images shown in Figure 7, the size of the hard domains (dark) is increasing, after PPE was added to the system. Obviously, the hard domains of the SEBS and also of the SEBS/PPE blends act as physical network junctions and additionally as filler particles. In this case, no co-continuous phase of the thermoplastic component exists, as in case of the SEBS/PP blends. The stress - temperature - curves and the relaxation spectra reveal the failure of the samples occurred slightly above the glass transition temperature of the hard phase. If combining the SEBS/PPE system with an additional thermoplastic blend component, e.g. polypropylene or polyamide 12, the thermal mechanical behaviour of the material can be improved on further (Barbe et al., 2005).

4.2 Thermoplastic polyolefin blends (TPO) and dynamic vulcanizates (TPV)

a. Commercial grades based on EPDM/PP

Most of the commercial available thermoplastic vulcanizates (TPV) are produced from polyolefin blends, in particular EPDM/PP, by the process of dynamic vulcanization. TPV exhibit several advantages over simple thermoplastic polyolefin blends (TPO). Due to selective crosslinking of the EPDM rubber phase, almost all material properties are improved. Especially compression set, creep, stress relaxation and swell behaviour are highly important for automotive applications, e.g. all kinds of sealing systems. As shown in Figure 8 for different types of commercial TPO and TPV, dynamic vulcanization has strong impact on relaxation behaviour (Reid et al., 2004). Whereas the stress - temperature - curve of a simple TPO blend exhibits a strong decrease of stress with increasing temperature, the decrease of stress of a TPV material of comparable hardness is significantly lower. As it becomes also obvious from Figure 8, the differences between TPO and TPV depend on hardness; the lower the hardness, the bigger the differences, and vice versa. Only one significant peak is observable in the relaxation spectra of the TPV, which is assigned to the melting of the PP matrix.

Sample	Shore - A	σ_0	T_{10}	T_{50}	T_{90}	TSSR - Index RI
		MPa	°C	°C	°C	
SEBS/PP (100/60)	69	1.098	63.7	107.5	159.0	0.655
SEBS/PE (100/60)	70	1.106	61.9	106.2	120.5	0.796
SEBS/PPE (100/0)	22	0.183	80.6	111.1	111.8	0.922
SEBS/PPE (100/20)	28	0.269	90.5	128.1	145.7	0.844
SEBS/PPE (100/40)	43	0.460	69.9	125.7	151.3	0.765
SEBS/PPE (100/60)	64	0.929	54.0	112.6	150.7	0.659

Table 1. Results of the TSSR tests as represented in Fig. 6.

In case of low hardness TPO a smaller peak appears at about 40 to 60 °C, which might be related to the α -relaxation process of the PP phase. At higher temperatures, when the PP ma-

trix is melting, no significant peak can be detected in case of TPO, because the stress is almost zero due to relaxation. The results of the TSSR tests represented in Figure 8 are compiled in Table 1. For similar hardness TSSR - Index and T_{50} - values of the TPV are significantly higher than those of TPO materials.

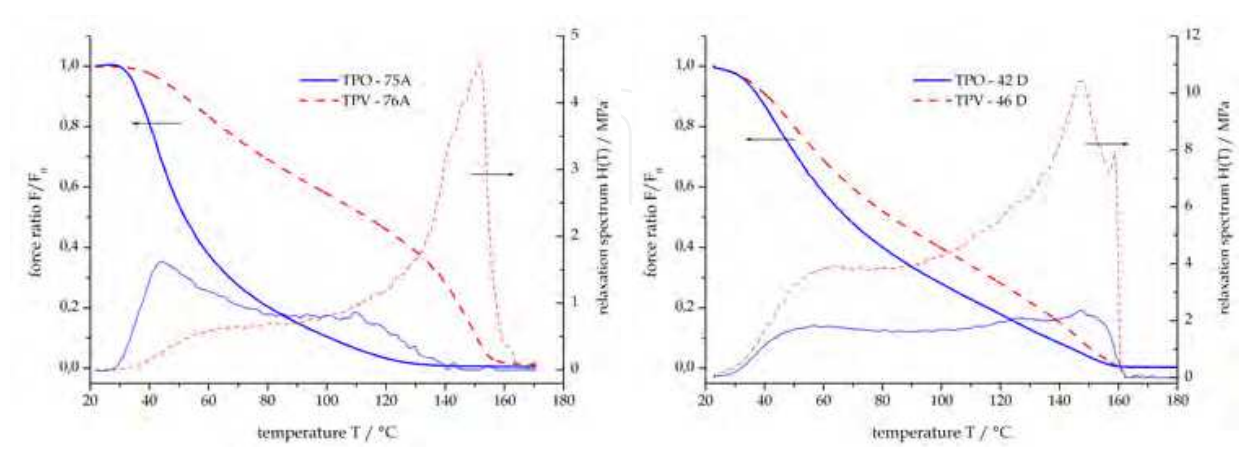


Fig. 8. *Left:* Force - temperature curves and relaxation spectra obtained from commercial TPO and TPV of 75 Shore A hardness. *Right:* Force - temperature curves and relaxation spectra obtained from commercial TPO and TPV of 40 Shore D hardness.

b. Model compounds of peroxide cured TPV based on EPDM/PP

Phenolic resin cure systems are mostly used for the production of commercial TPV materials. Although the phenolic resin cure system normally results in products with better compression set and oil swell than equivalent compositions produced with other cure systems, e.g. hydrosilation, peroxide, or sulfur, peroxide cured TPV materials were introduced into the market, recently (Reid et al., 2004). In EPDM/PP based systems serious problems result from degradation of the PP matrix, which may lead to deterioration of mechanical properties of the TPV. Thus, during the dynamic vulcanization by use of peroxides not only crosslinking of the EPDM rubber phase occurs, but more or less of the free radicals produce degradation of the PP matrix (Loan, 1967; Dickens, 1982), which has to be taken into consideration, also. Therefore, the producers have to find out the right balance between crosslinking of the EPDM phase and degradation of the PP phase; both reactions are initiated by free radicals, created by the curatives.

Sample	Shore -Hardness	σ_0	T_{10}	T_{50}	T_{90}	TSSR - Index
		MPa	°C	°C	°C	
TPV- 76A	76A	0.9	52	114	151	0.66
TPO - 75A	75A	1.2	37	52	101	0.49
TPV - 46D	46D	4.7	41	83	146	0.54
TPO - 42 D	42D	2.0	38	68	136	0.49

Table 2. Results of the TSSR tests as represented in Fig. 8.

Because crosslink density is one of the most important parameters of elastomers and dynamic vulcanizates, the aim of this study was to investigate the crosslink density of peroxide cured TPV based on EPDM/PP. Until now, there are only few methods available for the determination of crosslink density (Eisele, 1979; Grinberg, 1999; Zhao, 2007). Most of these methods require high effort and are not suitable for daily use in product development or quality control. For this reason, a new test method for the determination of the crosslink density of dynamic vulcanizates was introduced. The suitability of this method was examined at the example of polyolefinic model compounds, which were dynamically vulcanized by means of a peroxide cure system (Vennemann, et al., 2006).

The TPV samples were produced in a two-step mixing process. In a first mixing step pre-blends containing EPDM and varying amounts of the crosslink agents were prepared at 100 °C and a rotor speed of 40 rpm. After a mixing time of 3 minutes the pre-blends were removed from the mixer and immediately cooled down to room temperature to avoid scorch of the material. The composition of the different pre-blends is summarized in Table 3. In a second mixing step the TPV compounds were produced, by melt mixing the pre-blends with the PP homopolymer. The composition of the TPV compounds is compiled in Table 4. At a fixed EPDM volume fraction of $\phi_{EPDM} \approx 0.77$ the compound compositions differ only in the content of crosslink agents.

The morphology of the samples was investigated by transmission electron microscopy (TEM). TEM micrographs of the phase morphology of selected TPV samples are shown in Figure 9. Samples for these micrographs were cut parallel to flow from an injection moulded plaque, stained with ruthenium oxide, and cryo-microtomed into thin sections. In Figure 9 (left), the co-continuous phase morphology of the thermoplastic polyolefin blend (TPO) is visible, where the EPDM is shown as dark and the PP is shown as light areas. Phase inversion already occurs at low curative content (1 phr peroxide/1 phr co-agent) as it becomes obvious from the TEM micrograph obtained from TPV2 as presented in Figure 9 (right). Here, the elastomer appears as dark discrete particles with diameters of less than one micron, embedded in the continuous PP phase (lighter colour).

Sample ID	E0	E1	E2	E3	E4	E5	E6
EPDM	100	100	100	100	100	100	100
DTBPIB	-	0.5	1.0	1.5	2.0	2.5	3.0
TRIM	-	0.5	1.0	1.5	2.0	2.5	3.0

Table 3. Composition of the pre-blends in parts per hundred rubber (phr)

Sample ID	TP0	TPV1	TPV2	TPV3	TPV4	TPV5	TPV6
Ex ^{*)}	100	100	100	100	100	100	100
PP	30	30	30	30	30	30	30

^{*)} Ex stands for the corresponding pre-blend, e.g. TPV1 contains pre-blend E1 etc.

Table 4. Composition of the TPV compounds in parts per hundred rubber (phr)

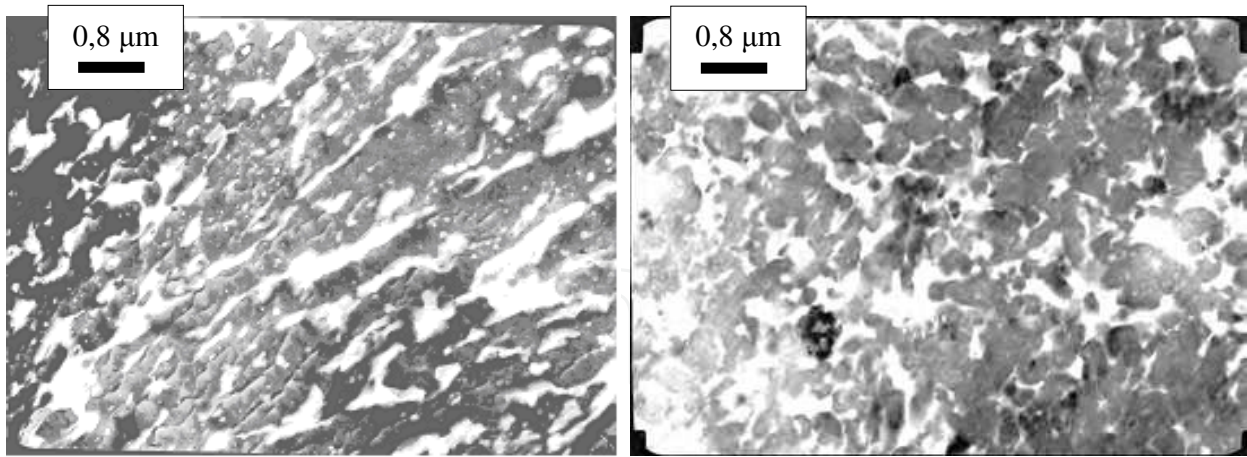


Fig. 9. TEM micrographs obtained from TPO (left) and TPV2 (right).

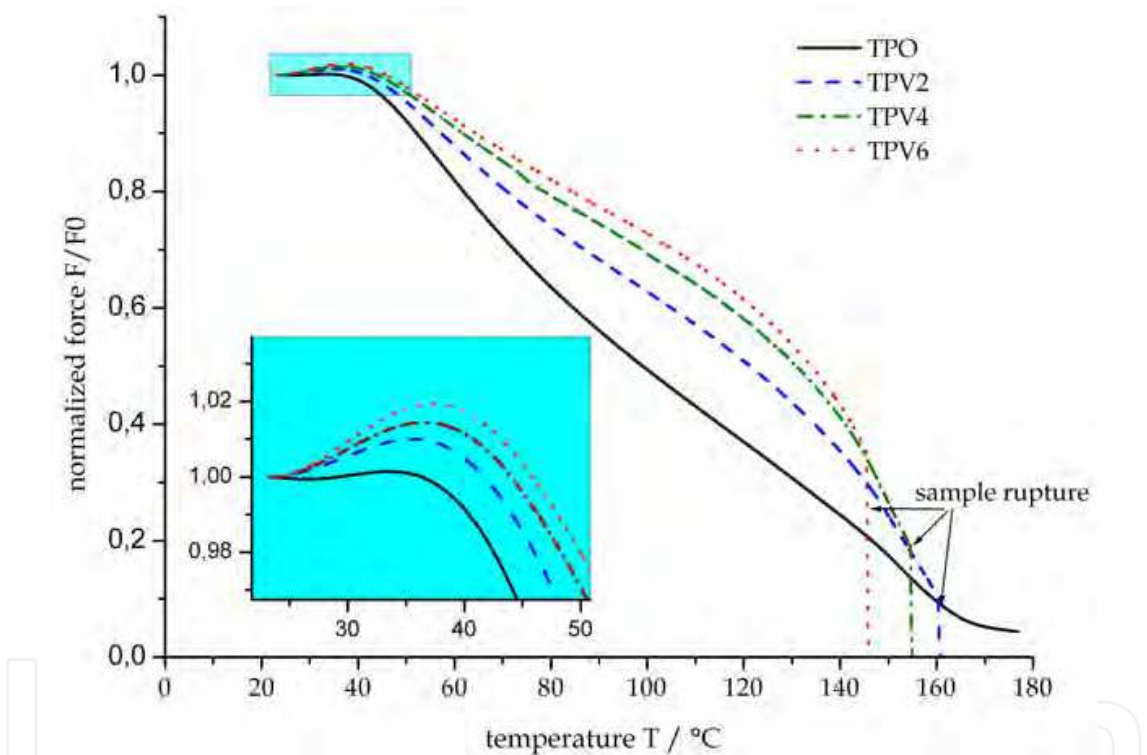


Fig. 10. Selected normalized stress – temperature curves of TPV samples obtained from TSSR measurements. TPO (solid line), TPV2 (dashed line), TPV4 (dashed dotted line) and TPV6 (dotted line).

In Figure 10 selected normalized force – temperature curves obtained from TSSR tests are presented. The influence of dynamic vulcanization is clearly recognizable from the shape of the curves. Whereas the uncrosslinked TPO sample exhibits the strongest stress decrease, this is significantly reduced in the case of the TPV samples and thus, higher values of T_{10} and T_{50} (Table 5) are obtained. This behaviour was expected, because dynamic vulcanization is well known as a process to improve the stress relaxation properties of polyolefin blends. Due to the reduced stress relaxation, the area below the normalized force-temperature curve increases. Consequently, the rubber index RI

increases also and is indicating an improvement of “rubber like” – behaviour. In Table 5 are also values of Shore A hardness, compression set, tensile strength and elongation at break summarized. From Figure 10 it can be also observed that rupture of the samples occurs if the peroxide content of the TPV increases. This is accompanied with a decrease of the TSSR T_{90} values. Unlike this, the force-temperature curve of the TPO sample approached zero, without rupture of the sample. The rupture of the samples can be explained with the degradation of the polypropylene matrix by peroxide, which is also a well known phenomenon. Due to the consumption of peroxide by the PP matrix, crosslink density of the dispersed EPDM particles is reduced. Figure 11 contains normalized force - temperature curves obtained from thermoset rubber samples, prepared by static vulcanization of the pre-blends. The behaviour differs strongly from that of the TPV samples, presented in Figure 10, although the crosslink systems are identical.

Sample ID	Shore A	CS 22h /125°C	tensile strength	elongation @ break	TSSR			
			MPa		T ₁₀	T ₅₀	T ₉₀	RI
					°C	°C	°C	
TPO	61	87.9%	1.9	102%	52.2	99.1	159.4	0.59
TPV1	69	74.2%	3.4	263%	53.7	106.7	159.3	0.62
TPV2	76	64.5%	6.3	328%	57.2	121.3	160.4	0.66
TPV3	74	62.5%	8.1	381%	61.6	131.4	156.9	0.72
TPV4	75	61.2%	8.1	366%	61.7	130.9	154.8	0.73
TPV5	77	60.5%	7.9	335%	63.3	133.3	149.2	0.76
TPV6	77	59.2%	8.1	309%	64.4	134.0	145.7	0.78

Table 5. Mechanical properties and TSSR results of the TPO and TPV samples

As described before, temperature coefficient values κ were determined from the initial part of stress – temperature curves, which were obtained from TSSR measurements at TPV (Figure 10) and thermoset rubber samples (Figure 11). The crosslink densities of all samples were calculated according to Eq. (6) and Eq. (8) and are plotted against the total amount of curatives in Figure 12. It should be noticed, that the compositions of the thermoset rubber samples E1 – E6 are identical with the rubber phase of the corresponding TPV samples. Thus, the crosslink density of TPV1 can be directly compared with sample E1, TPV2 can be compared with E2 and so on. Figure 12 clarifies that with the same amount of curatives a higher crosslink density is achieved in the thermoset rubber than in the rubber phase of the corresponding TPV compound. This result confirms the assumption that the crosslink density in the rubber phase of the TPV is reduced, due to partial consumption of the peroxide by the PP matrix. By comparison of the number of moles of curatives used in the recipe, the crosslink of efficiency of the cure system can be verified, also. The obtained results of crosslink density were also compared with the reciprocal swell ratio of the samples, which is a measure of crosslink density. It was shown that the crosslink density obtained from TSSR measurements, correlates well with the reciprocal swell ratio (Vennemann et al., 2006).

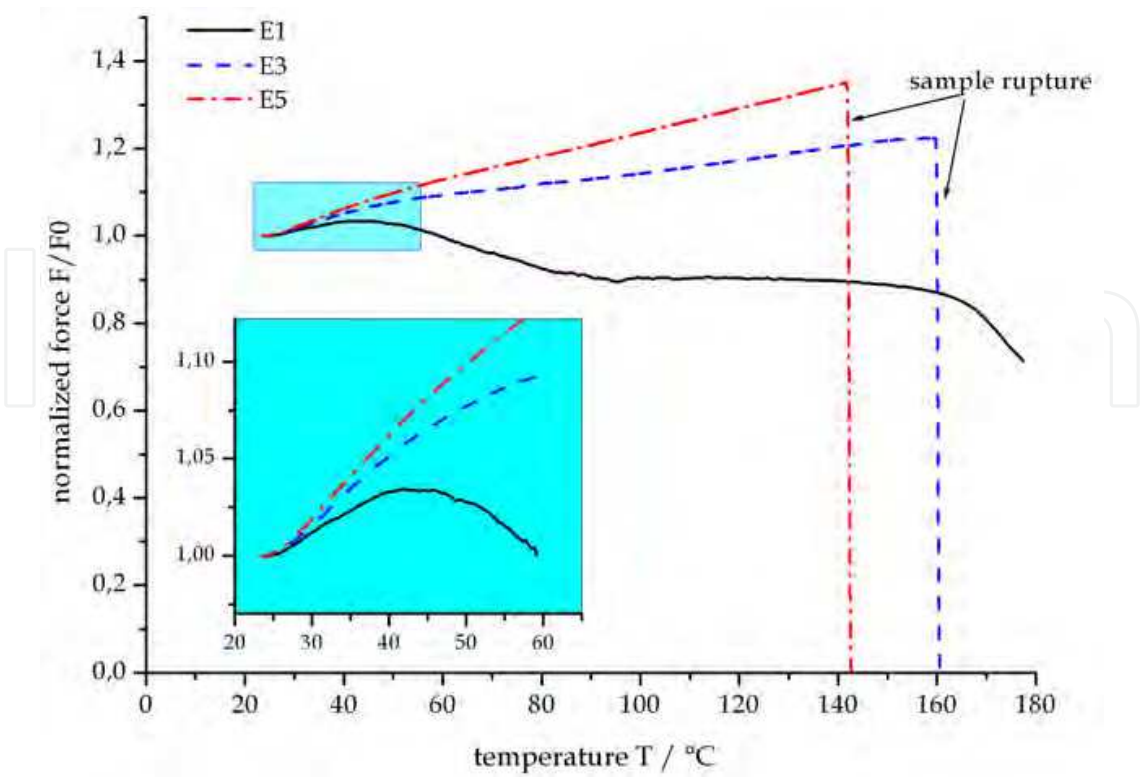


Fig. 11. Selected normalized stress – temperature curves of thermoset rubber samples obtained from TSSR measurements. E1 (solid line), E3 (dashed line) and E5 (dashed dotted line).

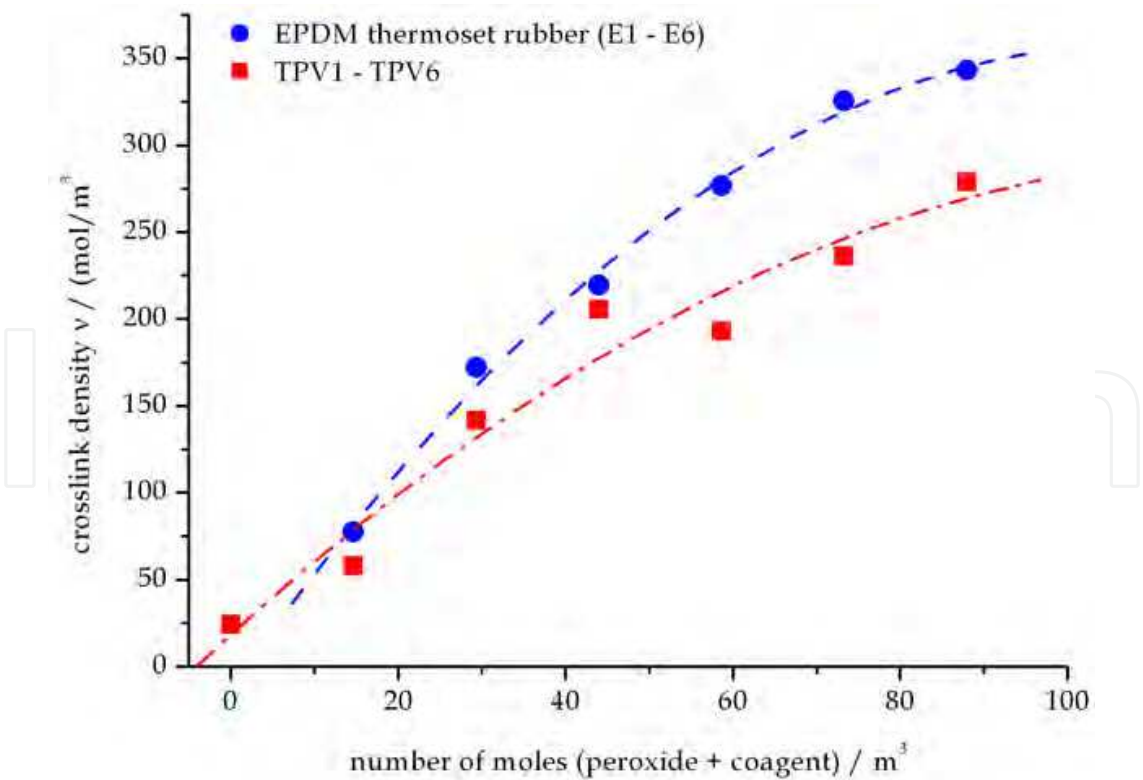


Fig. 12. Crosslink density of thermoset rubber samples E1 - E6 (●) and TPV1 - TPV6 samples (■) as obtained from TSSR – measurements.

- c. Advanced TPV based on EPDM/HDPE designed for hart/soft combinations with HDPE

Until now, most of the commercial available thermoplastic vulcanizates are based on the EPDM/PP system. Thus, good adhesion is achieved to components made of polypropylene (PP), due to inherent compatibility of the TPV matrix and commonly used PP materials. In combination with other polymers the bonding strength is more or less poor, particularly in case of more polar engineering thermoplastics. Even with other polyolefins bonding strength to TPV may deteriorate because of incompatibility of both partners. PP and HDPE are generally considered immiscible (Shanksa, et al., 2000). Thus, adhesion at the interface of EPDM/PP based TPV and HDPE or UHMW-PE components is lower than in the case of miscible polymers and may have a negative effect on the functionality of the part.

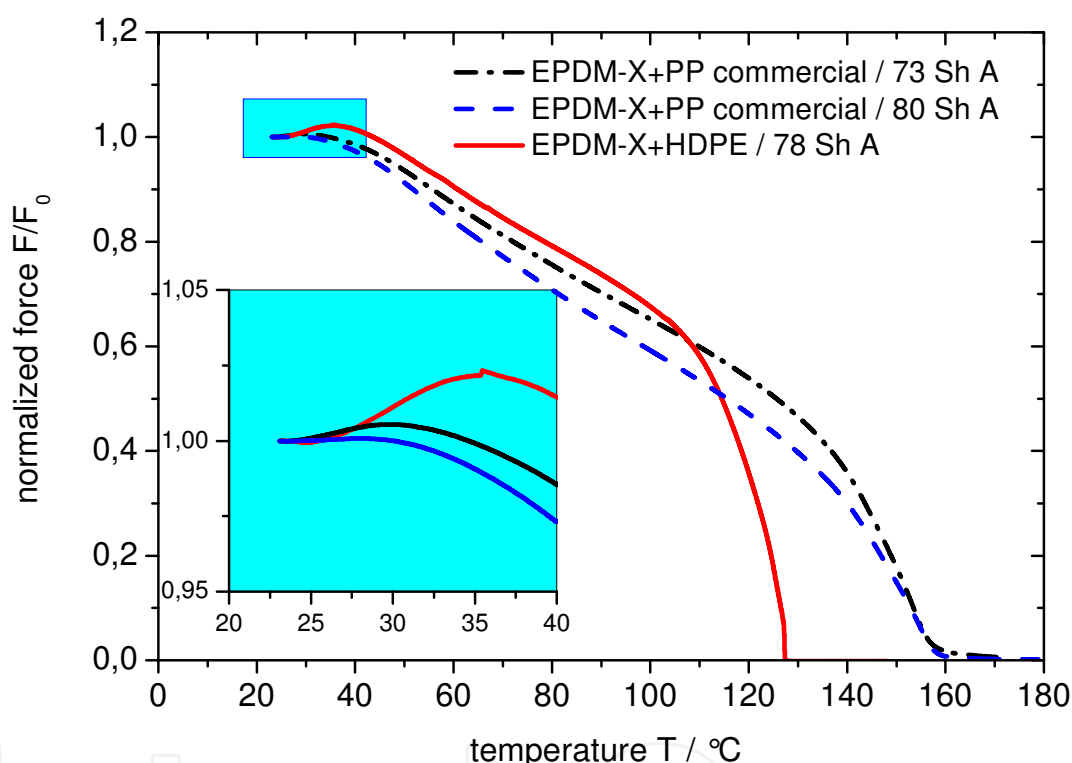


Fig. 13. TSSR force - temperature curves of a model TPV based on EPDM/HDPE (—) and commercial TPVs based on EPDM/PP of 73 (— · —) and 80 (— · —) Shore A.

Only a few papers have been published about dynamic vulcanization of EPDM/HDPE blends (Gosh et al., 1994) (Machado & van Duin, 2005), until now. A strongly increased compound viscosity as a result of dynamic vulcanization has been reported, particularly at higher EPDM contents. Therefore, one aim of this work was to optimize the blend composition of EPDM/HDPE dynamic vulcanizates with respect to mechanical properties and processibility, in order to produce TPVs with improved rubber elasticity and compatibility to rigid HDPE thermoplastics (Vennemann et al., 2009). In Figure 13 TSSR force - temperature curves of a model TPV based on EPDM/HDPE and of commercial TPVs based on EPDM/PP are shown for comparison. From the initial part of the curve it becomes obvious, that the entropy elastic behaviour of the EPDM/HDPE material is more pronounced than of the EPDM/PP based materials.

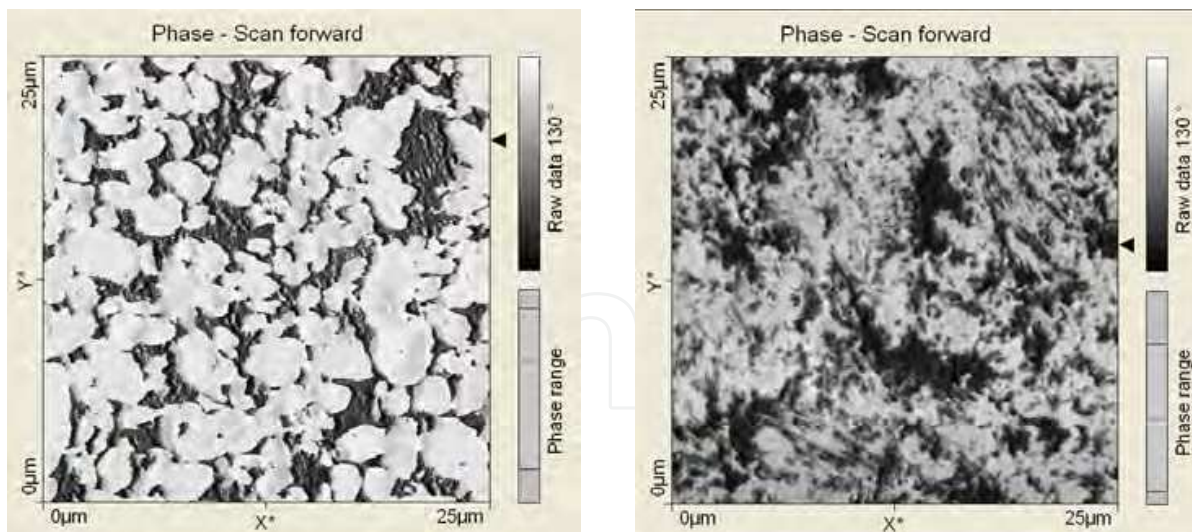


Fig. 14. AFM phase images of TPVs based on EPDM/PP (left) and EPDM/HDPE (right)

This observation corresponds to results from DMA measurements, in particular loss tangent, which is significantly lower at room temperature in case of EPDM/HDPE compared with EPDM/PP (Vennemann et al., 2009). At higher temperatures, above 100 °C, the EPDM/HDPE exhibits stronger stress relaxation due to the melting of the HDPE matrix. But, at moderate temperatures, up to 70 °C, compression set and rubber elasticity of these materials are equal or even better than existing products based on EPDM/PP. Thus, TPVs based on EPDM/HDPE might be an alternative to well known EPDM/PP products if enhanced rubber elastic properties are required. Furthermore, in hard/soft combinations with HDPE these compounds may have advantages over other TPEs due to their good compatibility, which results in excellent adhesion. The phase morphology of TPVs based on EPDM/PP and EPDM/HDPE having the same blend ratio and similar composition are shown in Figure 14. In these AFM phase images the EPDM rubber phase is light coloured, whereas the thermoplastic hard phase appears dark. In the case of the EPDM/PP sample (left), sharp boundaries between the light coloured EPDM domains and the dark appearing PP matrix phase are recognizable. The size of the EPDM domains is less than 5 µm, which is typical for this type of material. The AFM phase image obtained from the EPDM/HDPE sample differs significantly from the EPDM/PP sample. Obviously, micro-phase separation also occurred, but the phase boundaries are not as sharp, as in case of EPDM/PP. Apparently, both polymers are interpenetrating each other at the phase boundaries, because of good compatibility of EPDM and HDPE. This might be also an explanation for higher interaction and higher viscosity of the EPDM/HDPE material, which results in better rubber elasticity but also in poorer processibility.

Recently, a novel powdery EPDM/HDPE material has been developed, which can be produced by means of a special two-step mixing process (Vennemann et al., 2009). Consistency and processibility of the powdery raw material is similar to UHMW-PE powder. That means, the only way of processing is compression moulding. But, due to the almost identical consistency and the very good compatibility of the EPDM/HDPE powder and the UHMW-PE, the production of double-layer or multi-layer plates is possible, by a simple compression moulding process. Thus, hard/soft combinations can be produced easily which combine the extraordinary high toughness and abrasion resistance of UHMW-PE with the rubber like behaviour of a TPV, based on EPDM/HDPE.

4.3 Determination of crosslink density by means of rapid TSSR - tests

Although TSSR measurements are significantly faster and easier to perform than other methods to characterize the crosslink density of thermoset rubber and TPV, further improvement of the method is desired from industry, in particular by reduction of the test duration, without deterioration of the reliability of the results. High potential for the reduction of test duration is included by the isothermal relaxation period. During the isothermal test period, which lasts normally 2 h, the short time relaxation processes occur and the sample reaches a quasi equilibrium state before the non-isothermal test starts. If the isothermal test period is reduced to shorter values, the entropy effect will be partially compensated by stress relaxation and thus the obtained temperature coefficient κ is diminished, systematically. This problem can be solved by considering the effect of stress relaxation on the experimentally observable temperature coefficient κ . Generally, the total value of κ can be divided into two parts, as described in Eq. (10). It should be mentioned, that the entropic part of κ is positive, whereas the contribution of stress relaxation is negative.

$$\kappa = \kappa_{\text{relax}} + \kappa_{\text{entropy}} \quad (10)$$

Under the condition of sufficiently long duration of the isothermal testing period, the influence of stress relaxation on the initial slope of the non-isothermal stress - temperature curve is negligible. But, if the isothermal test period is shorter, the contribution of κ_{relax} can no longer be neglected. For this reason a theoretical approach was developed, which is suitable to estimate the contribution of the isothermal stress relaxation. In this approach it is considered that under isothermal conditions the decay of stress can be described by the empirical function given in Eq. (11), which fits the experimental values very nicely.

$$\sigma(t) = a + b \cdot t^{-c} \quad (12)$$

Differentiation of Eq. (12) with respect to time t and by considering the linear relationship between t and temperature T leads to Eq. (13), from which the theoretical contribution of stress relaxation κ_{relax} on the experimentally obtained temperature coefficient κ can be estimated.

$$\kappa_{\text{relax}} = \frac{-c}{\beta} \cdot b \cdot t_{\text{max}}^{-c-1} \quad (13)$$

Where β is the heating rate and t_{max} is the duration of the isothermal test period. The empirical parameters a , b and c of Eq. (12) are easily calculated from least - square fits by non-linear regression.

The entire stress - curve, including the isothermal part, is presented as a function of time in Figure 15, as obtained from a TSSR - test of a standard commercial TPV sample of about 70 Shore A. In contrast to the standard test procedure, this test was performed with reduced duration of the isothermal test period of 60 minutes. As can be seen from the magnified part

of the curve in Figure 15 (right), the slope of the stress - curve increases immediately, after the non-isothermal test period has started. It becomes also obvious, that the slope of the non-isothermal stress - curve is partially reduced by the influence of the ongoing stress relaxation.

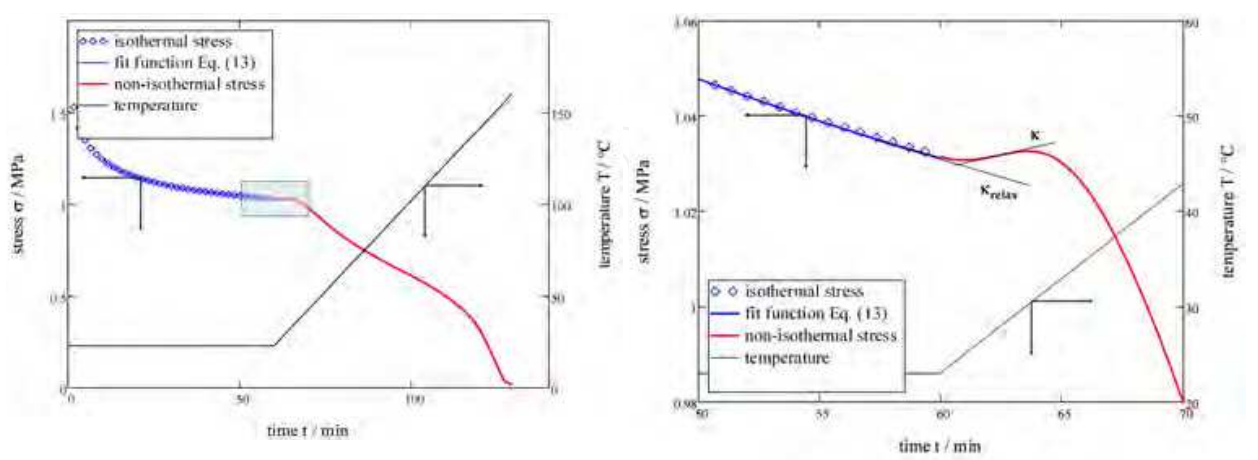


Fig. 15. Entire stress - curve (left) of a TSSR - test and zoomed part (right) of the curve, as indicated by the rectangle.

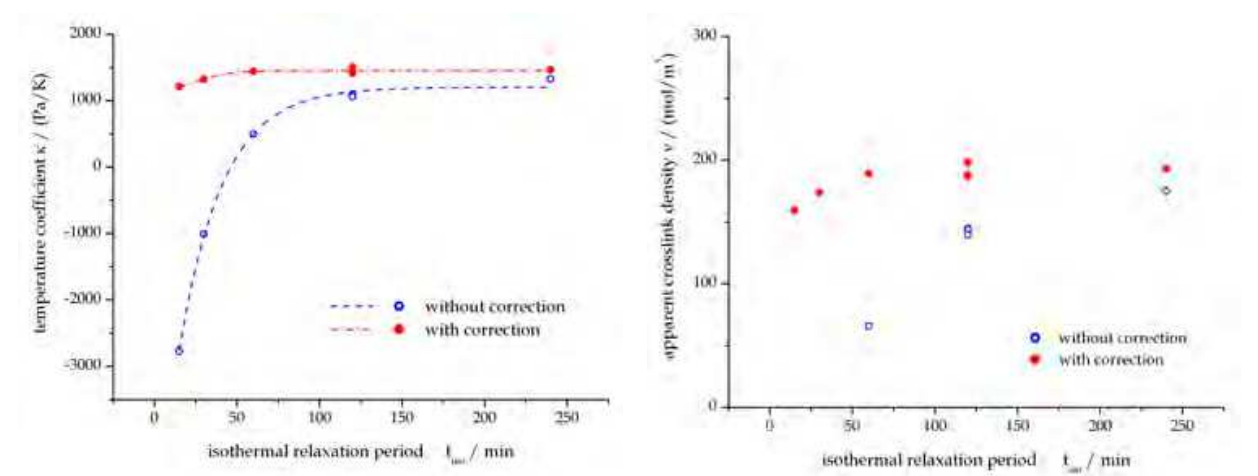


Fig. 16. Temperature coefficient (left) and apparent crosslink density (right), with and without correction, of a commercial TPV.

In order to determine the entropic part κ_{entropy} of the experimentally obtained temperature coefficient κ , it is necessary to eliminate the contribution of stress relaxation by means of Eq. (13). Thus, an apparent value of crosslink density of the sample can be calculated from Eq. (8) when κ_0 is replaced by the entropic part κ_{entropy} of the temperature coefficient. To demonstrate the influence of the correction, the experimentally obtained values of temperature coefficient are plotted as a function of isothermal relaxation period, with and without correction for comparison, on the left side of Figure 16. On the right hand side of Figure 16 the corresponding values of apparent crosslink density are presented, as calculated from Eq. (8) without and with correction by Eq. (13). Without correction, the values of temperature coefficient and crosslink density vary over a wide range, starting from negative values and ap-

proaching an almost constant level at long periods of isothermal relaxation. After correction by Eq. (13), the influence of the duration of the isothermal relaxation period has almost vanished. Therefore, rapid TSSR - tests with strongly reduced isothermal relaxation period give comparable results than standard TSSR - tests, but in shorter time, which might be advantageous, in particular for production control.

5. Conclusion

The aim of this paper is to describe the opportunities of a new test method, especially developed to characterize the stress relaxation behaviour and thermoelastic properties of TPE. In contrast to conventional stress relaxation measurements the new TSSR test method is less time consuming and requires only a minimum on manual effort. Generally, three phenomena have to be considered if a stretched rubber sample is annealed under the conditions of non-isothermal TSSR tests. Stress relaxation or decrease of stress, immediately occurs after the strain has been applied to the sample. Because relaxation time constants strongly decrease with increasing temperature, stress relaxation is accelerated when temperature is scanned during a TSSR test. An opposite effect results from entropy elastic behaviour of the rubber sample. Due to increasing temperature a stretched rubber sample tends to contract and therefore the stress increases if the strain is kept constant. Furthermore, stress relaxation and entropy elastic behaviour will be superimposed by a slight increase of sample length, caused by thermal expansion. It is shown that thermal expansion of the sample is negligible, if the strain is sufficiently high. Basic equations for evaluation have been developed, taking into account the specific conditions of TSSR tests.

The versatility of TSSR measurements has been demonstrated at several examples of commercial TPE and model compounds. The relaxation spectra of commercially available TPE based on SBC exhibit two significant peaks, which can be identified as glass transition temperature of the polystyrene end blocks and the melt temperature of an additional blend component, e.g. polypropylene. Blends of SBC and PPE were investigated to improve the heat resistance of the material. It has been shown that PPE and the polystyrene end blocks of SBC form a mixed phase with elevated glass transition temperature. The corresponding shift of glass transition temperature of the hard phase could be clearly identified from TSSR relaxation spectra. Thus, TSSR measurements are a suitable tool to determine the stress relaxation properties of such complex systems.

Results obtained from investigations of thermoplastic polyolefin blends (TPO) and dynamic vulcanizates (TPV) based on EPDM/PP and EPDM/HDPE, demonstrate the versatile opportunities of TSSR measurements to characterize stress relaxation behaviour and crosslink density. Comparison of commercial TPO and TPV of different hardness clearly show that the relaxation behaviour of the material is significantly improved by crosslinking of the rubber phase. It is also seen, the impact on stress relaxation is more pronounced for materials of lower hardness.

A model system of peroxide cured TPV based on EPDM/PP was investigated to determine the crosslink density of the rubber phase. By varying the amount of curatives the crosslink density of the samples has been altered within certain limits. These samples were subjected

to TSSR measurements and from the initial slope of the TSSR stress temperature curves the crosslink densities of the samples were determined, by considering the entropy effect. Additionally, TPV based on EPDM/HDPE which was designed for hard/soft - combinations with HDPE and UHMW-PE. Due to better compatibility of EPDM and HDPE, the phase morphology and also the properties differ from EPDM/PP based TPV. From the results of TSSR measurements the differences with respect to rubber elasticity and heat resistance become clearly obvious.

Although TSSR tests are relatively fast and easy to perform, an accelerated test procedure has been developed for rapid determination of crosslink density of TPV. Based on a theoretical approach a basic equation has been developed to separate the phenomenon of stress relaxation from the initial part of the experimentally observable stress - temperature curve. Thus, reliable values of crosslink density can be obtained even at strongly reduced test duration.

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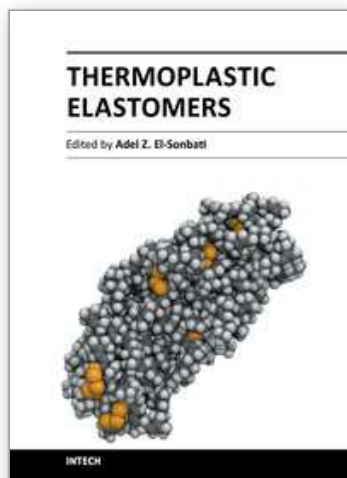
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Thermoplastics can be used for various applications, which range from household articles to the aeronautic sector. This book, "Thermoplastic Elastomers", is comprised of nineteen chapters, written by specialized scientists dealing with physical and/or chemical modifications of thermoplastics and thermoplastic starch. Such studies will provide a great benefit to specialists in food, electric, telecommunication devices, and plastic industries. Each chapter provides a comprehensive introduction to a specific topic, with a survey of developments to date.

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