Macromol. Symp. **2006**, 245-246, 641–650 DOI: 10.1002/masy.200651391

Crosslink Density of Peroxide Cured TPV

Norbert Vennemann, Klaus Bökamp, Dirk Bröker*

Summary: EPDM/PP model compounds were dynamically vulcanized by use of varying amounts of an organic peroxide and a trifunctional methacrylate to produce thermoplastic vulcanizates (TPV) materials with different properties. Tensile strength and ultimate elongation as well as compression set data of these materials are comparable to existing commercial TPV products. Although, crosslinking of the elastomer phase is the most important step during the production process, there is a lack of suitable test methods until now to determine the cross link density precisely. Therefore, a new test method, Temperature Scanning Stress Relaxation (TSSR) was examined to determine the crosslink density of the EPDM – phase. The results are in good agreement with results obtained from conventional swell measurements. The advantages of TSSR measurements over swell measurements are quite obvious. Whereas swelling measurements are very time consuming, TSSR tests are much easier and faster to perform. Additionally, information about the relaxation behavior and degradation of the PP - phase was obtained from TSSR measurements.

Keywords: crosslinking; dynamic vulcanization; elastomers; relaxation; temperature scanning stress relaxation (TSSR)

Introduction

Crosslink density is one the most important parameters of elastomers and dynamic vulcanizates. Almost all mechanical properties, e.g. modulus, hardness, tear and tensile strength, creep, relaxation and compression set, depend strongly on crosslink density. For this reason, knowledge of this parameter is of major interest for the production and usage of these materials. Until now, there are only few methods available for the determination of crosslink density. For conventional elastomers, equilibrium swelling measurements, mechanical tensile tests in combination with Mooney-Rivlin-plots[1] and magnetic resonance techniques (NMR)[2] are used for this purpose. Due to the more complex morphological structure of dynamic vulcanizates tensile tests, as well as NMR techniques are not suitable in terms of crosslink density of TPV or have had only limited use, until now. In this work, a new test method for the determination of the crosslink density of dynamic vulcanizates is introduced. The suitability of this method is examined at the example of polyolefinic model compounds, which were dynamically vulcanized by means of a peroxide cure system. Generally, dynamically vulcanized polyolefin elastomers TPV are produced by use of phenolic cure systems or by sulfur and an appropriate sulfur accelerator.[3,4] Free radical vulcanization initiators such as organic peroxides have had limited use for crosslinking polyolefin-based TPV due to the tendency for the peroxide to degrade polypropylene.[5–7] This degradation of polypropylene results in poor melt strength and decreased physical properties. Recent studies show that the use of methacrylate coagents in peroxide crosslinked EPDM/PP based TPV can help to minimize degradation of PP.[8,9] These TPV exhibit lower color and lower toxicity than phenolic cure TPV products, while maintaining good mechanical properties and good

---

University of Applied Sciences of Osnabrück,
Albrechtstr. 30, D-49076 Osnabrück, Germany
E-mail: N.Vennemann@FH-Osnabrueck.de

compression set. The test method presented in this study may help to determine the crosslink density of the elastomer phase of these dynamic vulcanizates (TPV).

Theoretical Background

Rubber exhibits a rather complex behavior with respect to temperature changes. Whereas the coefficient of linear expansion α of most materials is positive, that of vulcanized rubber changes from positive to negative values, if the strain is increased. This change in sign of α is known as thermoelastic inversion and is observed under the condition of constant load at strain ratios $\lambda > 1.1$.[10] Another aspect of thermoelastic behaviour of rubber is closely related to this. Under the condition of constant strain an increase of stress σ with temperature T is also observed,[11] if the strain ratio λ exceeds a value of 1.1. In this work the coefficient κ is defined as the derivative of mechanical stress with respect to temperature.

$$\kappa = (\partial\sigma/\partial T)_{\lambda,p} \tag{1}$$

According to the well known theory of rubber elasticity the mechanical stress σ is proportional to the absolute temperature T[12,13] and can be expressed by equation (2).

$$\sigma = \frac{\rho \cdot R \cdot T}{M_c}(\lambda - \lambda^{-2}) \tag{2}$$

Where ρ is the mass density, $\lambda = l/l0$ the strain ratio of the sample and R the universal gas constant. M_c is defined as the average molar mass of the elastically active network chains, which is proportional to the reciprocal value of the crosslink density ν of the network. At constant strain the slope of the stress vs. temperature plot reveals the crosslink density. From equation (3), obtained by a combination of equations (1) and (2), the crosslink density ν can be easily calculated from the experimentally obtained value of the temperature coefficient κ.

$$\nu = \frac{\kappa}{R \cdot (\lambda - \lambda^{-2})} \quad \text{with} \quad \nu = \frac{\rho}{M_c} \tag{3}$$

Experimental

Materials and Preparation of the Samples

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 were produced in a two-step mixing process using a Haake Rheocord 600 laboratory internal mixer (Thermo Electron Corporation, Karlsruhe). 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 1.

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 2. At a fixed EPDM volume fraction of $\phi_{EPDM} \approx 0.77$ the compound compositions differ only in the content of crosslink agents. At first the pre-blend were put into the mixer at a

Table 1.
Composition of the pre-blends in parts per hundred rubber (phr).

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 2.
Composition of the TPV compounds 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.

temperature of 130 °C and a rotor speed of 40 rpm. Due to internal friction, a temperature increase inside the mixer occurred. After achieving a temperature of approximately 155 °C the polypropylene was added. Simultaneously, the rotor speed was increased, successively up to 160 rpm, in order to reach a temperature range of 180 °C–190 °C. At this temperature the mixing was continued for additional 8 minutes enabling the dynamic vulcanization process to occur. At the end of the mixing process the compound was removed from the mixer and cooled down to room temperature.

Test plates of all compounds were produced in a pneumatic injection molding press. At a barrel temperature of 190 °C the material was heated up for 10 minutes and then rapidly transferred into the cavity of a mold, which had a temperature of 70 °C. The dimensions of the plates were $100 \times 75 \times 2$ mm^3. Test specimens were die-cut from the injection molded plates and used for testing, after at least 24 hrs of storage at room temperature.

Thermoset rubber samples for comparison purposes were produced with the same composition as the pre-blends. Vulcanization of these samples identified with Ex (where x is a number of 1 to 6) was performed in the injection molding press at 160 °C for about 40 minutes. The proper vulcanization time were determined before with a rheometer test.

Tensile, Hardness, and Compression Set Testing

From the test plates, type 5A testing rods were cut and then tensile testing was performed according to ISO 527 using a Zwick Z 1545 tensile testing machine (Zwick GmbH & Co., Ulm). Shore A Hardness was measured according to ISO 868 using a hardness testing machine (Frank GmbH). Compression set was determined according to ISO 1653, using an oven temperature of 125 °C for a period of 22 h, and a subsequent relaxation time of 30 minutes.

Swelling Measurements

Rectangular test pieces with dimension of $70 \times 10 \times 2$ mm^3 were used for testing. After immersion in cyclohexane the samples were stored at 23 °C in the liquid. After 24 h the cyclohexane was refreshed to remove extracted components. After another 24 h the swollen samples were weighed, dried and weighed again. Drying of the samples was performed at 50 °C for 48 h in order to remove the solvent. The relative gel content with respect to the initial mass m_0 was calculated from the difference between m_0 and m_d, where m_d is the mass after drying of the sample. Considering the density of the polymer ρ_P and the density of the solvent ρ_S, the mass m of the swollen sample was used to calculate the polymer volume fraction ϕ_P according to equation (4).

$$\phi_P = \frac{V_P}{V} = \frac{1}{\left(1 + \frac{m - m_d}{m_d}\right) \cdot \frac{\rho_P}{\rho_S}} \qquad (4)$$

The ratio of total volume V of the swollen sample and the volume V_P of the dry polymer sample is defined as the swell ratio Q.

$$Q = \frac{V}{V_P} \qquad (5)$$

The reciprocal swell ratio 1/Q can be taken as a measure of the crosslink density. From the comparison of equations (4) and (5) it becomes obvious that *1/Q* is also identical with ϕ_P.

Temperature Scanning Stress Relaxation (TSSR)

The Temperature Scanning Stress Relaxation test method has been developed recently to characterize the thermal-mechanical behavior of thermoplastic elastomers[14–16] (TPE). During the TSSR test a constant tensile strain of at least 50% is applied to dumbbell test piece (type 5A, ISO 527). After the initial strain is applied, the sample is allowed to pre-condition for two hours at room temperature. 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 2 K/min, until the stress relaxation has been fully completed or rupture of the sample has occurred.

The tests were performed by use of a commercial available TSSR instrument obtained from Brabender GmbH (Duisburg, Germany). The TSSR instrument consists of an electrical heating chamber where the sample 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 actual temperature the thermocouple is placed near the center 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.

From the obtained force – temperature curve certain characteristic quantities such as T_{10}, T_{50}, T_{90} and the rubber index RI are calculated. The temperature Tx stands for the temperature at which the force F has decreased about $x\%$ with respect to the initial force F_0. The rubber index RI is a measure of the rubber like behavior of the material and is calculated from the area below the force – temperature curve according to equation (6). A full description of the method can be found in earlier publications.[17,18]

$$RI = \frac{\int_{T_0}^{T_{90}} F(T)/F_0 dT}{T_{90} - T_0} \tag{6}$$

Temperature Coefficient Measurements

Stress – temperature curves obtained from TSSR measurements were used to calculate the temperature coefficient κ by numerical differentiation according to eq. (1). For TPV – samples thermo elastic inversion is a minor effect and only recognizable at low temperatures in the initial part of the stress temperature curve (Fig. 1). Above 40 °C, the effect of stress relaxation overcompensates the entropy effect. The behavior of

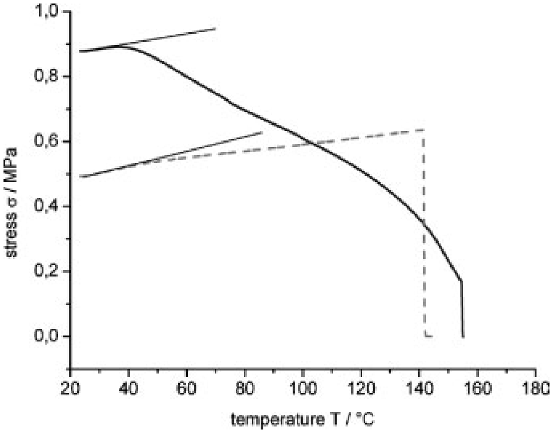

Figure 1.

Typical stress - temperature curve obtained from TSSR measurements of a TPV (solid line) and a thermoset rubber (dashed line). The temperature coefficient κ corresponds to the slope of the curves in the initial part as indicated by the straight lines.

thermoset rubber is significant different compared to TPV. As also shown in Fig. 1 the stress increases over a wide range of temperature before it drops down to zero, in the case of an unfilled EPDM thermoset rubber. In all cases, the maximum slope of the stress temperature curve in the initial part of the curve was used for the determination of the crosslink density ν according to eq. (3).

Results and Discussion

Morphology of the TPO and TPV Samples

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 2. Samples for these micrographs were cut parallel to flow from an injection molded plaque, stained with ruthenium oxide, and cryo-microtomed into thin sections. In Figure 2A, 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 Figure 2B. Here, the elastomer appears as dark discrete particles with diameters of less than one micron, embedded in the continuous PP phase (lighter color). From Figure 2C and 2D it is recognizable, that the use of higher amount of curatives does not alter the morphology significantly.

Mechanical Properties

The mechanical properties of the TPO and TPV samples are summarized in Table 3. Hardness is increasing from 61 to 77 Shore A due to dynamic vulcanization. For the

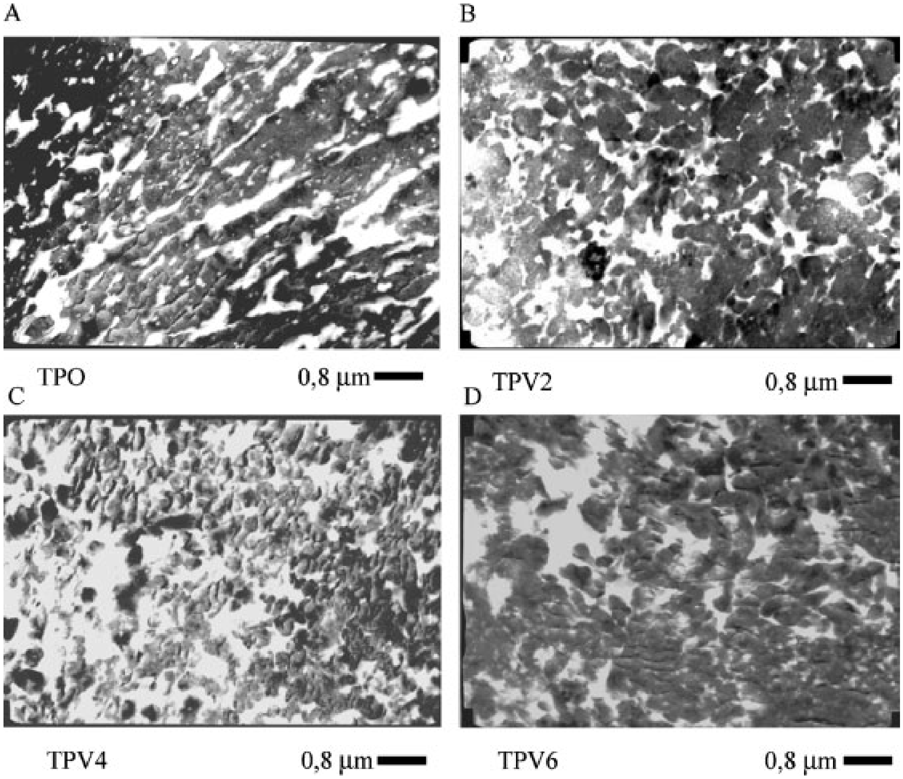

Figure 2.
TEM micrographs of selected TPV samples.

Table 3.
Mechanical properties and TSSR results of the TPO and TPV samples.

Sample ID	Sh A	CS 22 h /125 °C	Tensile strength	Elongation at 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

same reason, tensile strength and elongation at break also gain significantly, and reach levels comparable to commercial TPV materials. Maximum values of about 8 MPa for tensile strength and 380% for ultimate elongation are obtained by use of 1.5 phr peroxide in combination with 1.5 phr co-agent.

Compression set value is one of the elastomeric properties widely used to characterize TPV products. In the case of a single-phase rubber, compression set value is mainly related to the crosslink density of the tested material. In a two-phase TPV material, the compression set is not only related to the crosslink density of the elastomer phase, but also depends on the properties of the thermoplastic matrix. Due to the fixed EPDM/PP ratio of the investigated compounds, the influence of the dynamic vulcanization on the compression set values can be examined. The uncrosslinked TPO sample exhibits almost fully plastic behavior, recognizable at a high compression set value of almost 90% (22 h/125 °C). Significantly improved properties were found for the dynamic vulcanizates, where the TPV containing the highest peroxide content exhibits the lowest compression set value of 59%.

TSSR Measurements

To better characterize the TPV materials, we also investigated the thermal-mechanical behavior by means of TSSR measurements. In Figure 3 selected force – temperature

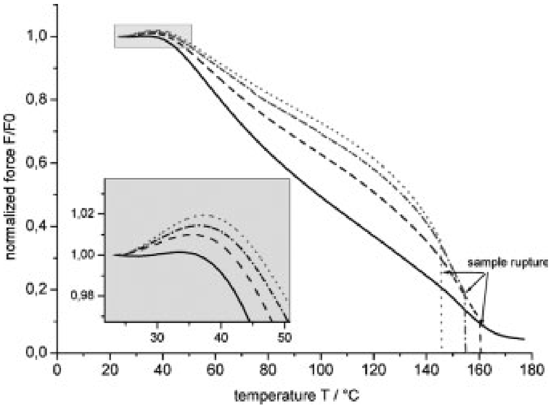

Figure 3.
Selected normalized stress – temperature curves of TPV samples obtained from TSSR measurements. TPO (solid line), TPV2 (dashed line), TPV4 (dashed dotted line) and TPV6 (dotted line).

curves obtained from TSSR tests are presented. For better comparison the current force F at temperature T is normalized by dividing with the initial force F_0. 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 3) are obtained. This behavior was expected, because dynamic vulcanization is well known as a process to improve the stress relaxation properties of polyolefine blends. Due to the reduced stress relaxation, the area below the normalized force–temperature curve increases. Consequently, the rubber index RI obtained from TSSR measurements increases also and is indicating an improvement of "rubber like" – behavior. From Fig. 3 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 peroxides, which is also a well known phenomenon. Although, at the start of the mixing process the total amount of peroxide is located in the EPDM-phase, a partial transfer of the peroxide to the PP-phase during the mixing process has to be considered. Thus, degradation of the matrix can occur and the thermal-mechanical properties deteriorate. Due to the consumption of peroxide crosslink efficiency is reduced and consequently, a decrease of the crosslink density of the dispersed rubber particles is obtained.

Crosslink Density Determined from TSSR Measurements

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 (Fig. 3) and thermoset rubber samples (Fig. 4). The crosslink density of all samples was calculated according to eq. (3) and is plotted against the total amount of curatives in Figure 5. 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 TPVx can be directly compared with sample Ex. Figure 5 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 efficiency in the rubber phase is reduced,

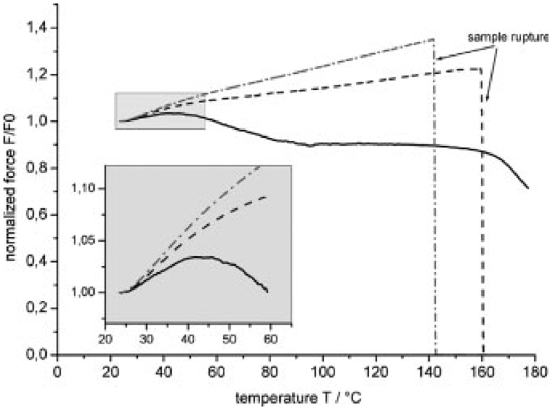

Figure 4.
Selected normalized stress – temperature curves of thermoset rubber samples obtained from TSSR measurements. E1(solid line), E3 (dashed line) and E5 (dashed dotted line).

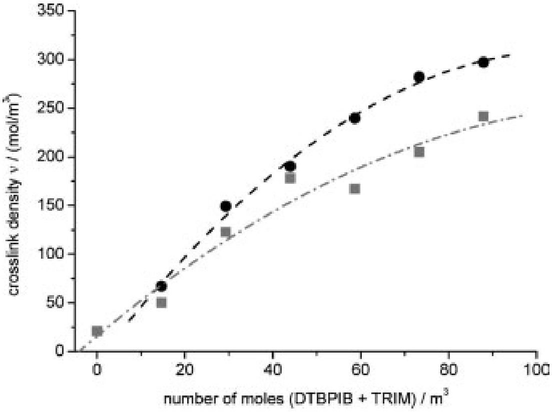

Figure 5.
Crosslink density obtained from TSSR – measurements. ● = E1– E6; ■ = TPV1 – TPV6.

due to partial consumption of the peroxide by the PP matrix.

Comparison with Swelling Measurements

Equilibrium swelling measurements are conventionally used if crosslink density of elastomers is of interest. Usually these tests are time consuming and require a lot of manual work and the use of organic solvents. Unlike this, TSSR tests are much faster and easier to perform and neither the use of solvents nor much effort for sample preparation is required. In order to prove the reliability of these tests with respect to crosslink density, the results will be compared with the results of conventional swelling measurements.

The results of the equilibrium swelling measurements in cyclohexane at 23 °C, obtained from the thermoset rubber samples (E1 – E5) and the thermoplastic vulcanizates (TPV1 – TPV6) are presented in Fig. 6. In this diagram, on the left y-axis the reciprocal swell ratio 1/Q, as a measure of crosslink density, is plotted against the total amount of curatives. The right y-axis of this diagram is used to plot the corresponding gel content values on the same x-axis. Taking the gel content as a measure of crosslinking degree, it can be deduced

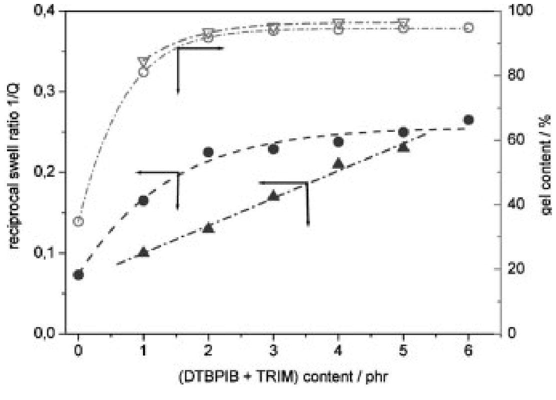

Figure 6.
Reciprocal swell ratio (filled symbols) and gel content (open symbols) as a function of curative content. Swelling measurements at the TPV (circles) and thermoset rubber samples (triangles) were performed in cyclohexane at 23 °C.

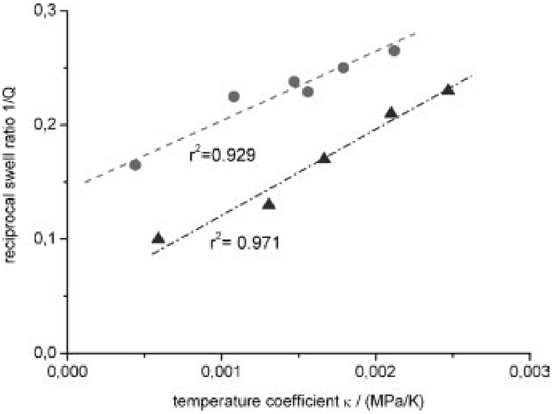

Figure 7.
Reciprocal swell ratio of TPV (circles) and thermoset rubber (triangles) samples as a function of temperature coefficient as obtained from TSSR measurements.

that almost fully crosslinked TPV is obtained if the compound contains at least 1 phr of DTBPIB in combination with 1 phr TRIM. This is in good agreement with the TEM results (Fig. 2), where a dispersed EPDM phase is recognizable at the same content of curatives.

Increasing values of the reciprocal swell ratio as also observable in Figure 6 are indicating an increase of crosslink density for the TPV as well as for the thermoset rubber. Obviously, the reciprocal swell ratio of the TPV is higher than of the thermoset rubber. This should not be misinterpreted in terms of crosslink density. In the case of the TPV, an apparent value of the overall crosslink density of the EPDM phase in presence of the PP phase is obtained. Due to the contribution of the PP phase to the swelling result, this value is not comparable with the swelling of a single-phase thermoset rubber.

In Figure 7 the results of the swelling measurements are compared with the temperature coefficients κ obtained from TSSR. Obviously there is a satisfactory correlation between the reciprocal swell ratio and the temperature coefficient values, which confirms the TSSR method as a suitable tool for the determination of crosslink density. The slopes of the straight lines fitted to the data points are nearly identical for the TPV and thermoset rubber samples, whereas the y-axis intercept of the TPV differs from the thermoset rubber due to the influence of the PP phase on the swelling results.

Conclusions

This paper has introduced a new technique for the determination of the crosslink density of TPV materials. Suitability and reliability of the method have been certified at pure EPDM/PP blends. But more work has to be done on TPV with complex formulation to establish the method also for commercial materials. The values of crosslink density of the investigated TPV, as well as of the thermoset rubber samples, obtained from TSSR measurements are reasonable and are in good agreement with the results of conventional swelling measurements. Beside the determination of crosslink density the TSSR results give additional information about the relaxation behavior of the material. In this case it was concluded from rupture of the samples that degradation of the polypropylene phase occurs if the peroxide content exceeds a value of 1.5 phr.

Acknowledgements: The authors gratefully acknowledge the support of Satchit Srinivasan from Solvay Engineered Polymers, Mansfield, Texas (USA) for providing the opportunity of TEM investigations. We also thank Yi Li and Jeff Day from Solvay for performing the TEM measurements. The assistance of Ramin Djamshidian, Robert Ebermann, Christian Hunnekuhl and Elyes Jendoubi from University of Applied Sciences Osnabrück is also acknowledged.

[1] U. Eisele, *Progr. Colloid & Polymer Sci.*, **1979**, *66*, 59.
[2] M. Garbaraczyk, F. Grinberg, N. Nestle, W. Kuhn, *J.Polym.Sci. Part B: Polym. Phys.* **2001**, *39*, 2207.
[3] G. Holden, Understanding Thermoplastic Elastomers, Carl Hanser, Munich, **2000**.
[4] United States Patent 4,311,628, **1982**.
[5] L. D. Loan, *Rubber Chem. Technol.*, **1967**, *40*, 149.
[6] B. Dickens, *J. Polym. Sci., Polym. Chem. Ed.*, **1982**, *20*, 1065.
[7] W. Hofmann, *Kautsch. Gummi Kunstst.*, **1987**, *40*, 308.
[8] K. Naskar, J. W. M. Nordermeer, *Rubber Chem. Technol.*, **2003**, *76*, 1001.
[9] K. Naskar, J. W. M. Nordermeer, *J. Elastomers and Plastics*, **2006**, *76*, 163.
[10] R. H. Anthony, R. H. Caston, E. J. Guth, *J. Phys. Chem.* **1942**, *46*, 826–840.
[11] P. J. Flory, in: *Principles of Polymer Chemistry*, 14th ed., Cornell University Press, Ithaca, NY, **1990**.
[12] P. J. Flory, *Trans. Farad. Soc.* **1961**, *57*, 829.
[13] J. E. Mark, *Rubber Chem. Techn.* **1973**, *46*, 593.
[14] N. Vennemann, J. Hündorf, C. Kummerlöwe and P. Schulz, *Kautsch. Gummi Kunstst.* **2001**, *54*, 362.
[15] German Patent 10 022 818, **2001**.
[16] N. Vennemann, *Kautsch. Gummi Kunst.* **2003**, *55*, 242.
[17] A. Barbe, K. Bökamp, C. Kummerlöwe, H. Sollmann, N. Vennemann and S. Vinzelberg, *Polym. Eng. and Sci.* **2005**, *45*, 1498.
[18] Ch. G. Reid, K. G. Cai, H. Tran and N. Vennemann, *Kautsch. Gummi Kunstst.* **2004**, *57*, 227.