

Characterization of the Deformation Behavior of Dynamic Vulcanizates by FTIR Spectroscopy

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ABSTRACT: To clarify the deformation mechanisms and to improve the mechanical properties of dynamic vulcanizates, we studied their deformation behavior by Fourier-transform infrared (FTIR) spectroscopy. It was found that the orientation in the dispersed phase (EPDM phase) is higher than in the matrix (PP phase) upon loading. The orientation of the rubber phase increases continuously. In the thermoplastic phase, a change of the deformation mechanism takes place. With respect to the total strain of the material, the orientation in the thermoplastic phase of the dynamic vulcanizates is lower, and in the elastic phase, it is higher than the corresponding orientation of the pure components. During stress relaxation, there is an increase of the orientation in the crystalline PP phase. Simultaneously, a decrease of the orientation in the EPDM phase is observed. Upon unloading, the orientation recovery in the EPDM phase is always complete, while the orientation recovery in the PP phase is reversible only at low strains. The critical point, where the elastic deformation gets lost, corresponds to the minimum in the orientation function curve. © 2001 John Wiley & Sons, Inc. *J Appl Polym Sci* 80: 148–158, 2001

Key words: dynamic vulcanizates; deformation behavior; FTIR spectroscopy

INTRODUCTION

Thermoplastic elastomers (TPEs) with an intensive growth rate of more than 9% per annum have been one of the most successful developments in the field of polymer technology in the last years.¹ The special feature of TPEs is that they behave like vulcanized rubber at ambient temperature, but at higher temperature, TPEs can be processed like thermoplastics.^{2,3} These materials are phase-separated systems, in which the soft and hard phases are thermodynamically incompatible.⁴

An effective way to produce TPEs is based on the method of dynamic vulcanization. This is the process of vulcanizing a rubber during its melt

mixing with a thermoplastic. Although the content of the rubber usually exceeds that of the thermoplastic, the soft phase is dispersed in the hard matrix. The product is called a dynamic vulcanizate. A schematic representation of the morphology of dynamic vulcanizates is given in Figure 1. Their stress–strain diagrams in comparison to thermoplastics and elastomers are shown in Figure 2. Dynamic vulcanizates exhibit large reversibility and small residual strains. The mechanical properties of dynamic vulcanizates differ significantly from those of the blends with a noncrosslinked rubber phase. The question arises as to why dynamic vulcanizates can recover elastically from highly deformed states, even though the matrix consists of a ductile thermoplastic polymer.

To clarify the deformation mechanism and to improve the mechanical properties of dynamic vulcanizates, we studied their deformation be-

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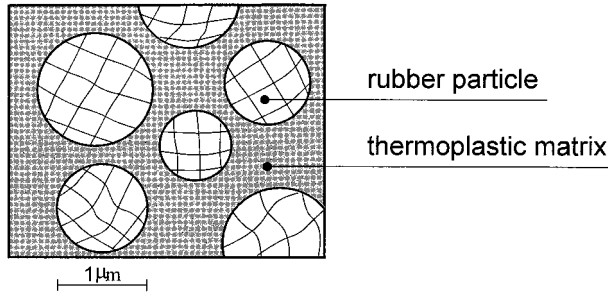


Figure 1 Schematic representation of the structure of dynamic vulcanizates.

havior using Fourier-transform infrared (FTIR) spectroscopy in combination with mechanical tests. This technique is a useful tool to monitor transient changes of particular structural units with respect to the molecular orientation phenomena occurring in different phases of a multiphase polymer during a mechanical treatment and to correlate them with the macroscopic behavior.

FTIR SPECTROSCOPY TO CHARACTERIZE THE ORIENTATION BEHAVIOR

FTIR spectroscopy allows for both qualitative and quantitative interpretation. While the qualitative analysis is used for substance identification, the quantitative analysis is widely applied to basic problems of polymeric structure characterization such as, for example, orientation measurements. The chain orientation is determined because it relates to the amount of local deformation. Owing to the dependence of IR intensities on the change of the dipole moment of the vibrating molecules, structural information may be devised from absolute intensity data. The advantage of infrared spectroscopy is its sensitivity, rapidity, and the ability to investigate the orientational changes not only in separate structural units but also in various phases of multiphase systems.

Using the ratio of the absorbances from beams polarized parallel (A_{\parallel}) and perpendicular (A_{\perp}) to the deformation direction, the dichroic ratio, $R = A_{\parallel}/A_{\perp}$, and the orientation function, f_{IR} , is calculated by

$$f_{\text{IR}} = \frac{R - 1}{R + 2} \times \frac{R_0 + 2}{R_0 - 1} \quad (1)$$

It is differentiated between π -dichroism ($R > 1$), σ -dichroism ($R < 1$), and the absence of dichroism

($R = 1$). $R_0 = 2 \cot^2 \psi$ is the dichroic ratio of perfect aligned chains oriented parallel to the draw direction. ψ is the angle between the direction of the vibrational transition moment and the polymer chain axis, which can be found for selected polymer systems in different publications.^{5,6}

The orientation function f_{IR} is equal to the well-known Herman orientation function f_{H} , which is basically used to describe the segmental orientation in uniaxially oriented samples:

$$f_{\text{H}} = \frac{3\langle \cos^2 \theta \rangle - 1}{2} = f_{\text{IR}} = f \quad (2)$$

where θ is the average angle between the chain axis and the draw direction. A perfect orientation along the draw direction corresponds to $f = 1$, while a perfect perpendicular orientation results in $f = -0.5$. For random orientation or completely unoriented material, one gets $f = 0$.

EXPERIMENTAL

Sample Preparation

The polymers used in this study were polypropylene (PP; Vestolen P7000, Huels AG, Marl, Germany) and EPDM with ethylidene-2-norbornene (Buna AP251, Bayer AG, Ludwigshafen, Germany). We prepared dynamic vulcanizates by melt-mixing both components in a Brabender Plasticoder PL-2100 laboratory mixer in the presence of a crosslinking agent (phenolic resin PA510) and an

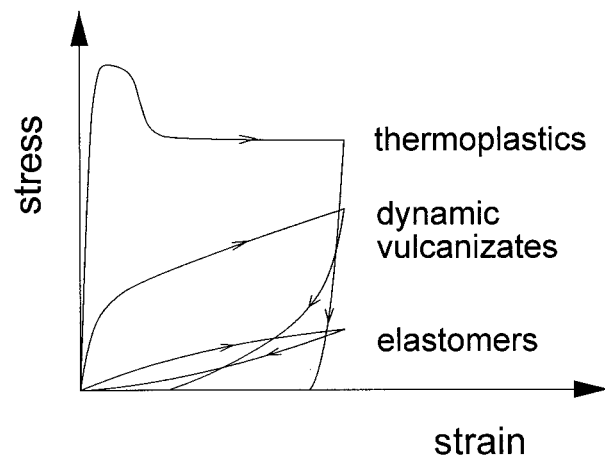


Figure 2 Comparison of the stress-strain behavior of thermoplastics, elastomers, and dynamic vulcanizates (schematic).

Table I Composition of Dynamic Vulcanizates (in Weight Percent)

Sample No.	Rubber EPDM	Thermoplastic PP	Crosslinking Agent PA 510	Activator SnCl ₂
1	70	30	5	0.5
2	60	40	5	0.5
3	50	50	5	0.5
4	70	30	1	0.1
5	70	30	2.5	0.25
6	70	30	5	0.5
7	70	30	10	1
8	70	30	20	2
9	100	0	5	0.5
10	0	100	0	0

activator (SnCl₂). Mixing time and rotor speed were 20 min and 60 min⁻¹, respectively. Mixing temperatures between 160°C (start temperature) and 210°C (end temperature) were used. Mixtures with different rubber/thermoplastic ratios and a constant crosslinking agent content and mixtures with a constant rubber/thermoplastic ratio and different crosslinking agent contents were prepared. An overview of the mixtures is given in Table I. The amount of the crosslinking agent is related to the rubber content. After taking samples from the mixer, they were compression-molded at 180°C. From the molded sheets, samples of the dimension of 20 × 10 × 0.1 mm were cut for FTIR spectroscopy.

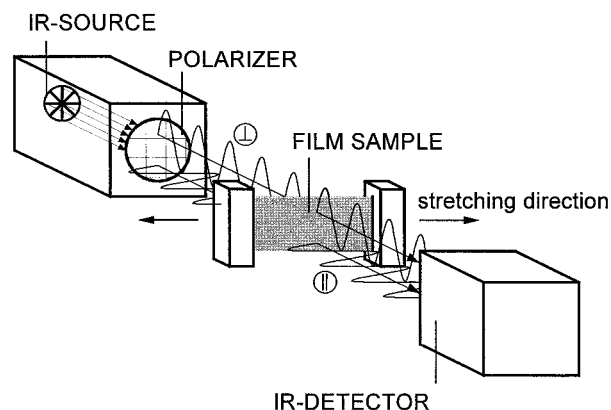
Measurement

FTIR investigations were carried out on a Perkin-Elmer FTIR spectrometer S2000. The spectrum examined covers the range between 700 and 3500 cm⁻¹. Twenty-five scans were added up at 2-cm⁻¹ resolution. The duration of such a measurement was about 30 s. The incident radiation area has a diameter of 5 mm. The experimental setup is illustrated in Figure 3. The measurements were carried out without a polarizer and with the polarizer adjusted alternatively parallel and perpendicular to the draw direction. A stretching machine, which allows for uniaxial stretching, was placed into the sample compartment of the spectrometer. In the tensile test, the extension was carried out incrementally in steps of $\Delta\varepsilon = 5\%$ and $\Delta\varepsilon = 50\%$ at ambient temperature. At the applied strain, the specimen was held for 2 min to relax before IR measurement started. In the strain-recovery test, the reversal points were chosen at the strains of $\varepsilon = 50\%$ and $\varepsilon = 300\%$. In the relaxation test, the changing ori-

entation was investigated at a constant strain of $\varepsilon = 200\%$ over a period of 15 h.

Sample Characterization

Figure 4 shows a general view of infrared spectra of the pure PP, vulcanized EPDM, and a dynamic vulcanizate. The measurement was carried out in the undeformed state with unpolarized IR radiation. For PP, the band at 841 cm⁻¹ is characteristic of the crystalline phase,⁷ and in vulcanized EPDM, the band at 722 cm⁻¹ characterizes ethylene sequences.⁸ The IR spectrum of dynamic vulcanizates can be understood in a first approximation as a superposition of the spectra of PP and vulcanized EPDM. Depending on the composition of dynamic vulcanizates, intermolecular and intramolecular effects influence their vibrational behavior. The wavenumber and the shape of the vibrational bands are stress-dependent. The absorption bands can be deformed asym-

**Figure 3** Experimental setup.

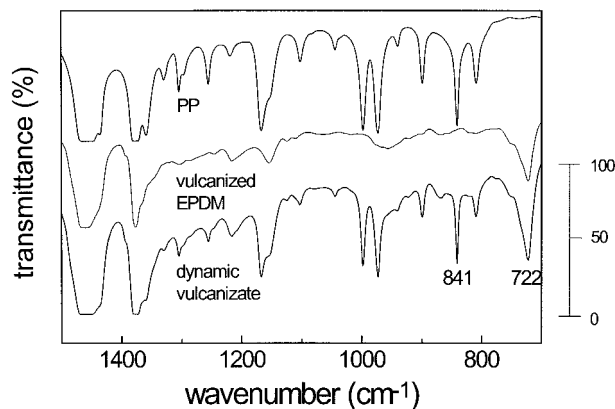


Figure 4 IR spectra of PP, vulcanized EPDM, and dynamic vulcanizates.

metrically or shifted slightly to another wavenumber.⁹

A difficulty of FTIR spectroscopy is to find suitable bands for quantitative orientation measurements. These bands have to meet the following requirements:

- strong dependence on polarization direction
- well-known transition moment angle
- clear assignment to a separate phase
- separate band position
- sufficient band intensity.

The peculiarity of the system EPDM/PP is the similarity of the chain structure of both components. For instance, bands originating from propylene segments in amorphous parts can be found in both the thermoplastic and the rubber. Therefore, the absorption bands, which characterize the oscillation in crystalline parts of PP and ethylene bands of the EPDM, were used for investigation. Finally, the band at 841 cm^{-1} for the PP phase and the band 722 cm^{-1} for the EPDM phase were selected. The transition moment angle was taken from the literature. For vibrations at 841 cm^{-1} , $\psi = 0^\circ$ and for 722 cm^{-1} , $\psi = 90^\circ$ were used.^{5,6} The 841-cm^{-1} band was variously assigned to C—C stretching, to C—CH₃ stretching, and to CH₂ rocking in the crystalline phase of PP.⁷ The 722-cm^{-1} band was assigned to CH₂ rocking in the ethylene segments of EPDM.⁸ With regard to eq. (1), the orientation function of both phases was calculated by

$$f_{\text{PP}} = \frac{(R_{841} - 1)}{(R_{841} + 2)} \quad (3)$$

and

$$f_{\text{EPDM}} = (-2) \times \frac{(R_{722} - 1)}{(R_{722} + 2)} \quad (4)$$

For the quantitative analysis, either the absorbance at the peak maximum or the integral absorbance applying an appropriate baseline is determined. Different baseline constructions were given in the literature.^{8,10} In our investigations, we used a baseline connecting the intensities at two fixed wavenumbers on both sides of the peak maximum. For the 841-cm^{-1} band and the 722-cm^{-1} band, 845 and 835 cm^{-1} and 730 and 715 cm^{-1} were chosen, respectively.

Figure 5 depicts the change of the absorption peak at 841 cm^{-1} for the dynamic vulcanizate 1 as a function of polarization direction and strain. At the undeformed state ($\varepsilon = 0\%$), the parallel and perpendicular absorbances exhibit no difference, indicating an unoriented material. At high deformation ($\varepsilon = 400\%$), however, significant differences of the absorbance parallel and perpendicular to the draw direction arise. In general, the absorbance decreases by stretching because of the film thickness reduction.

Figure 6 presents the strain dependence of the orientation function f_{722} of the dynamic vulcanizate 7 determined at three different samples. As shown in this figure, the reproducibility of the results is excellent.

RESULTS AND DISCUSSION

FTIR Characterization of the Basic Components

Prior to the investigation of dynamic vulcanizates, the basic components of the system, that is,

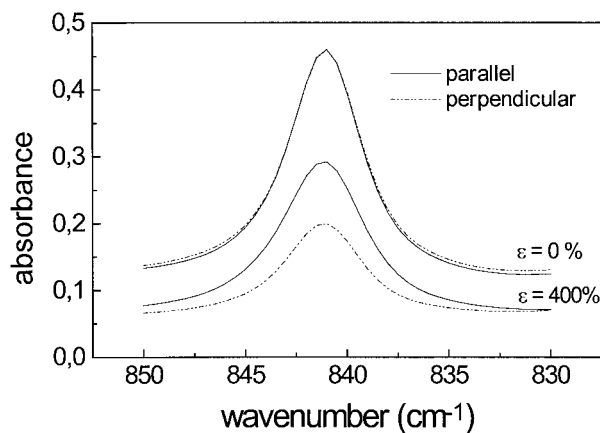


Figure 5 The 841-cm^{-1} band of the dynamic vulcanizate 1 in dependence on the polarization direction and strain.

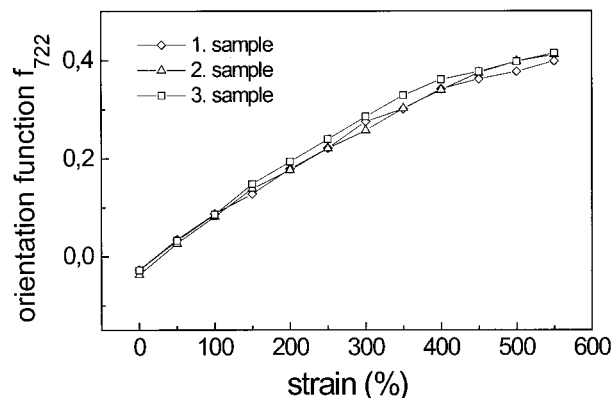


Figure 6 Reproducibility of the orientation function f_{722} (measured at the dynamic vulcanizate 7).

the pure PP and the vulcanized EPDM, were characterized under uniaxial deformation. Figure 7 shows the change of the orientation function f_{841} of the crystalline phase of PP during tensile loading. The stress-strain diagram provides information about the macroscopic deformation. Up to the yield point, a slight decrease of the orientation function f_{841} toward negative values was found. This means an increase of the transverse orientation. In the following necking zone, an abrupt increase to a steady value takes place. The strain, at which the rapid increase in orientation function occurs, may shift more or less on the strain scale because it depends on the position of the necking zone relative to the sampling area.^{9,11} Immediately before the break, the alignment of the PP molecules in the crystalline region is nearly perfect. The orientation function reaches a very high value of $f = 0.9$.

The orientation of PP molecules in the crystalline phase is characterized by the alignment of lamellae occurring in a spherulitic structure. The minimum in the orientation function of the crystalline phase has been explained by the existence of different deformation mechanisms. According to Samuels¹³ and Peterlin,¹² below the yield point, an affine deformation of the spherulitic structure takes place by interlamellar shear. During this process, the chains in the crystalline lamellae orient predominantly perpendicular to the draw direction as shown in Figure 8 schematically. In the necking zone, a transformation from a spherulitic structure into a fibrillar structure takes place.¹⁴ The spherulites are deformed irreversibly. Chains can unfold by intralamellar shear or melt locally. Consequently, they orient along the draw direction. That leads to a very strong alignment of the PP molecules and a dras-

tic increase of the orientation function. The above-mentioned structural transformation is restricted to the necking region. Further stretching causes a further perfection of the fibrillar structure. In this stage, only slight changes of the orientation function can be detected spectroscopically.

The vulcanized EPDM rubber shows a completely different deformation behavior in Figure 9. In contrast to the PP, a continuous growth of the orientation function is obtained. Shortly before fracture at strains of about $\epsilon = 250\%$, the EPDM chains reach the orientation function of $f = 0.15$, which is very low compared to the orientation of PP. This is caused by the rubber network structure. For this network, due to the permanent junction points and the critical junction distance, respectively, the network chains cannot orient freely in the draw direction.

By means of the network theory of Kuhn and Gruen, the orientation function in a rubber network can be calculated by¹⁵

$$f = \frac{1}{k_k N} (\lambda - \lambda^{-2}) \quad (5)$$

where λ is the stretch ratio. N is the number of Kuhn segments between two junction points of the network and k_k is constant. N and k_k have to be determined.

A determination of N is difficult because EPDM is a statistic copolymer. Assuming that this vulcanized EPDM is an exact alternating copolymer, meaning that the constitution corresponds to $[-(\text{CH}_2-\text{CH}_2)-(\text{CH}_2-\text{CHCH}_3)-]_x$, the value of N can be calculated from the number

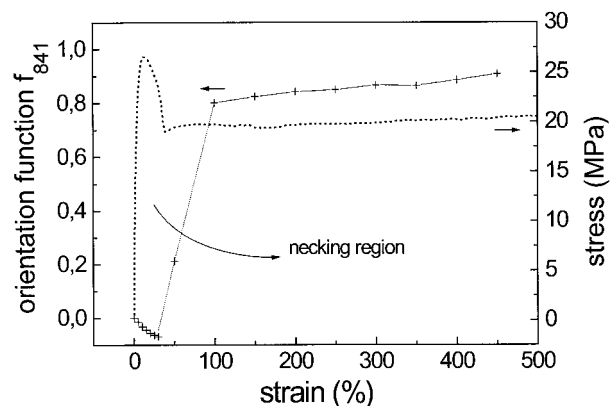


Figure 7 Deformation behavior of the PP in uniaxial loading.

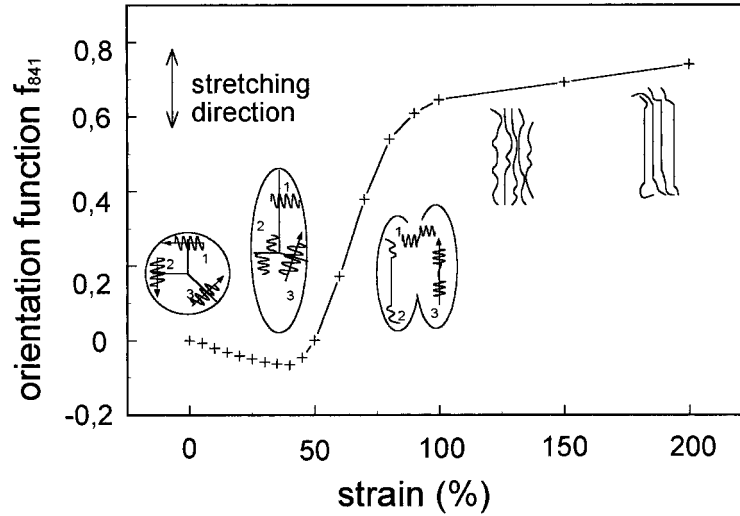


Figure 8 Orientation behavior of lamellae within PP spherulites.

of monomer units between two junction points x by

$$x = \frac{M_{c(\text{EPDM})}}{M_{\text{PE}} + M_{\text{PP}}} \quad (6)$$

Here, M_c is the average molecular weight between entanglements. M_{PE} and M_{PP} are the molecular mass of PE and PP units in EPDM. From the swelling experiments, M_c was calculated to be $M_c = 4232.29 \text{ g mol}^{-1}$ and, consequently, $x = 57$. Because each EPDM monomer unit consists of four successive C—C bonds, the number of the C—C bonds per network chain is $z = x \cdot 4 = 228$. Assuming the number of C—C bonds per Kuhn segment to be six for EPDM, the number of Kuhn

segments per network chain N is as given by eq. (7)¹⁵:

$$N = \frac{z}{6} = 38 \quad (7)$$

With $N = 38$, the constant k was determined by adaptation of eq. (5) to the experimental data. In our case, a value of $k = 0.5$ was determined. This value corresponds to other experimental data from the literature.¹⁶ However, it is an order of magnitude smaller than is the original value $k = 5$ of Kuhn and Gruen, based on theoretical considerations of the network theory. Equation (5) was developed originally for freely joined chains without mutual interaction. Moreover, this model is valid only for an affine network without network defects.

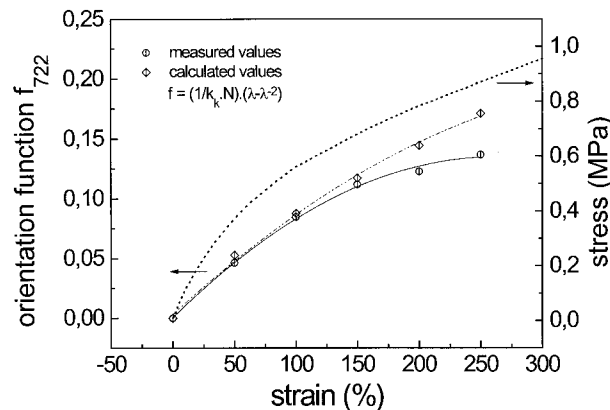


Figure 9 Deformation behavior of the vulcanized EPDM in uniaxial loading.

Deformation Behavior of Dynamic Vulcanizates

Stress–Strain Behavior

Taking an example, the deformation behavior of the dynamic vulcanizate 1 in uniaxial loading is shown in Figure 10. Owing to the absence of a necking region, an abrupt change in the orientation function was not observed. The orientation in the PP phase begins to increase continuously above a strain of $\varepsilon = 100\%$. At an applied strain of $\varepsilon = 400\%$, the orientation function in the crystalline PP phase reaches a relatively low value of $f = 0.15$. From these, it follows that here a structural change such as the transition from a lamel-

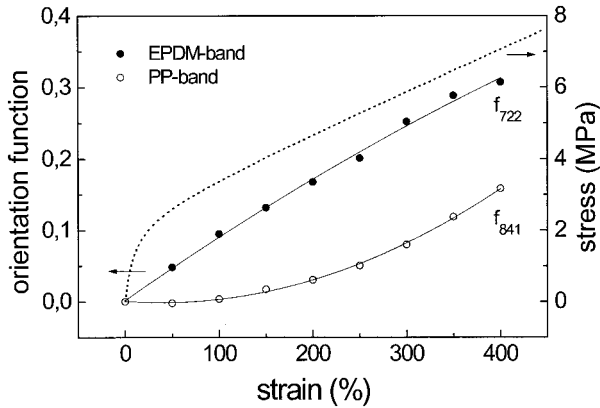


Figure 10 Deformation behavior of the dynamic vulcanizate 1 in uniaxial loading.

lar to a fibrillar structure as observed in pure PP does not take place.

The orientation function of the EPDM phase increases continuously and immediately upon loading. Interesting to note that in dynamic vulcanizates the orientation of the dispersed phase (EPDM) is stronger than is the orientation of the matrix (PP). This is caused by a heterogeneous deformation in the thermoplastic phase due to local stress differences. A plastic deformation takes place when the local stress exceeds the yield stress. According to calculations in the literature,¹⁷ the stress concentration in the thermoplastic phase reaches its maximum at the equatorial zones of the elastic particles, and, therefore, in this region, the plastic deformation starts first. At the polar regions, a compressive stress is predominant in the matrix, which prevents plastic

deformation. With increasing strain, the plastic deformation zone spreads out from the equatorial to the polar regions and the orientation function of the PP phase increases.

Note that the orientation in the PP phase of dynamic vulcanizates is smaller than in the pure PP at the same elongation. Contrary to that, in dynamic vulcanizates, the orientation function of the rubber phase is larger than in static vulcanizates crosslinked with the same amount of a vulcanizing agent. This results from stiffness differences in both components, leading to local strain differences in the heterogeneous material.

It had been shown that the mechanical properties of dynamic vulcanizates are strongly dependent on the composition of the material.¹⁸ In particular, the content of thermoplastic and vulcanizing agents determine properties like reversibility and stiffness. The influence of the composition on the local deformation behavior of the dynamic vulcanizates is discussed in the following.

The change of the orientation of the thermoplastic phase of dynamic vulcanizates with varying PP content is shown in Figure 11. With an increasing thermoplastic content, the participation of the PP phase in the deformation processes increases. Thus, the dynamic vulcanizate EPDM/PP 50/50 exhibits the highest orientation. As in the pure PP in dynamic vulcanizates, the orientation function is negative at small strains. With further deformation, it turns to positive values. In dynamic vulcanizates, the PP molecules in the crystalline phase are arranged in stacks of lamellae. At lower strains, the orientation of crystals takes place by interlamellar shear processes. Lamellae, as the primary deforma-

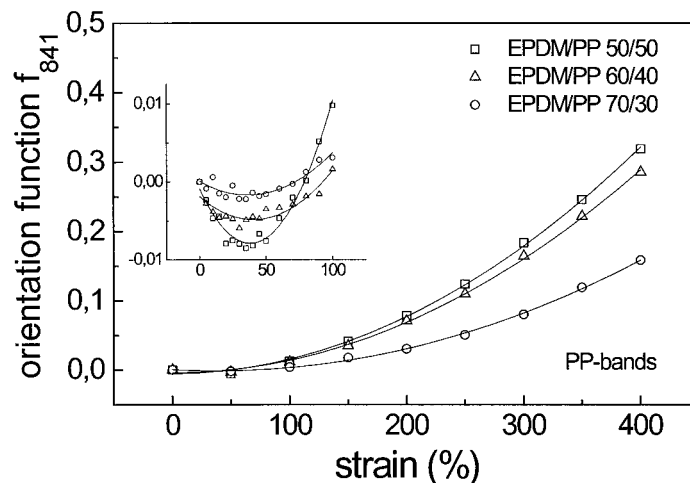


Figure 11 Influence of thermoplastic content in dynamic vulcanizates EPDM/PP on the orientation behavior of the PP phase.

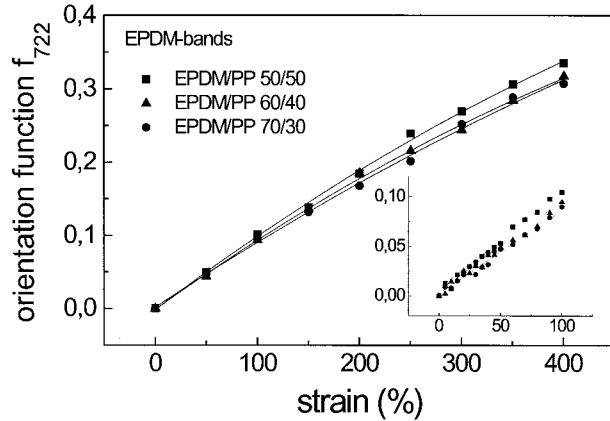


Figure 12 Influence of thermoplastic content in dynamic vulcanizates EPDM/PP on the orientation behavior of the EPDM phase.

tion unit, turn gradually into the draw direction. By passing the minimum point, the deformation mechanism converts from a predominantly reversible interlamellar slip to an irreversible intralamellar slip (chain slip). The minimum in the orientation curves corresponds to the yield strain of the dynamic vulcanizates.

In contrast to the thermoplastic phase, the orientation behavior of the rubber phase of dynamic vulcanizates is not significantly influenced by the thermoplastic concentration. Figure 12 shows that the orientation function of the EPDM phase depends on the strain, but not on the PP content. The shape of the curves corresponds to the theoretical prediction of Kuhn and Gruen.¹⁵

Figures 13 and 14 present the influence of the crosslinking agent concentration on the strain dependence of the orientation function of thermo-

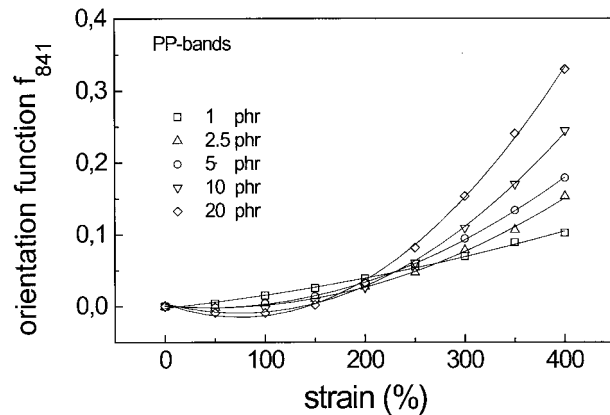


Figure 13 Influence of curative concentration in dynamic vulcanizates on the orientation behavior of the PP phase.

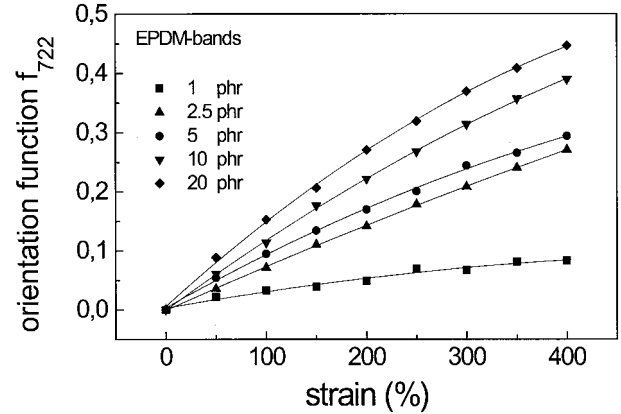


Figure 14 Influence of curative concentration in dynamic vulcanizates on the orientation behavior of the EPDM phase.

plastic and rubber phase. The increasing crosslinking agent concentration causes an increase of the network density of the rubber phase and, accordingly, of the elastic modulus. As shown in Figure 13, in the PP phase, the orientation increases with increasing crosslinking agent content. This results from the reduced difference of the moduli of both phases. Also, in the EPDM phase, a stronger orientation with an increasing curing agent content was observed. This behavior corresponds to the network theory of Kuhn and Gruen. According to eq. (5), the orientation function rises with increasing network density and decreasing number of Kuhn segments between the junction points, respectively.

Relaxation Behavior

Because dynamic vulcanizates are viscoelastic materials, their deformation behavior is time-dependent. Moreover, the material consists of different phases with different relaxation time spectra, so that the relaxation behavior in both phases differs from each other. The investigation of the relaxation of orientation during stress relaxation gives instructive information about the changes of local deformation processes at a constant applied strain.

Figure 15 shows the relaxation curve of three different dynamic vulcanizates. For comparison, the stress $\sigma(t)$ was normalized with respect to the initial stress σ_0 . From a formal point of view, the relaxation behavior of dynamic vulcanizates is similar to the relaxation behavior of other polymers.¹⁹ At short times, an exponential decay of stress is observed. After that, a power law behavior describes the relaxation function. The thermo-

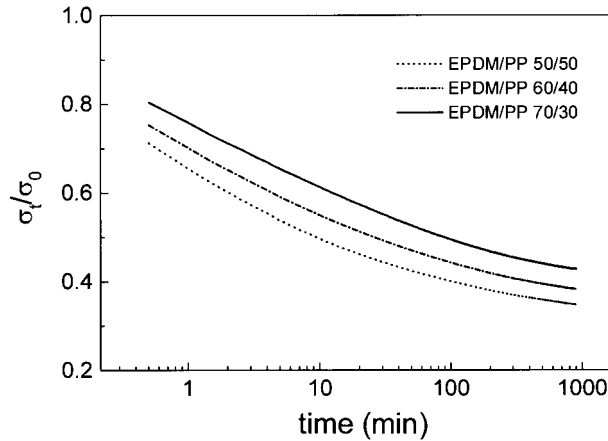


Figure 15 Influence of the thermoplastic content on the relaxation behavior of dynamic vulcanizates EPDM/PP; $\epsilon_0 = 200\%$.

plastic content has no significant influence on the relaxation time spectrum. With an increasing amount of PP in the mixture, the relaxation curve shifts to higher normalized stresses. Stress relaxation as observed in Figure 15 results from local plastic deformation processes in the material and, correspondingly, from a change of local orientation. The results of our FTIR experiments on materials of different thermoplastic content are given in Figure 16. The orientation function is strictly linear on a logarithmic time scale. Interesting to note that the slope of the straight lines is different in sign for both the thermoplastic and rubber phase. While the orientation of the EPDM phase decreases with the relaxation time, it increases in the PP phase. This leads to the conclu-

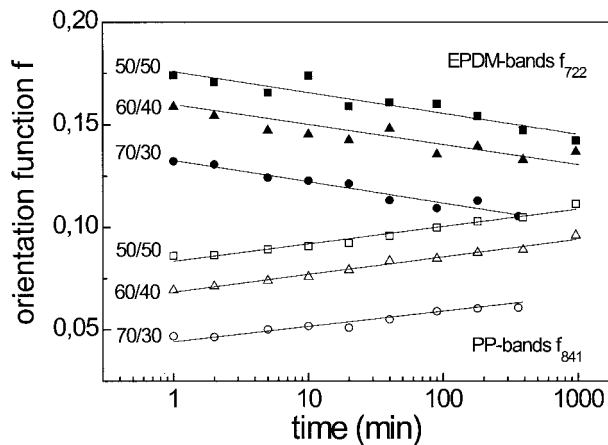


Figure 16 Orientation behavior of both phases of dynamic vulcanizates EPDM/PP in relaxation test for different thermoplastic contents; $\epsilon_0 = 200\%$.

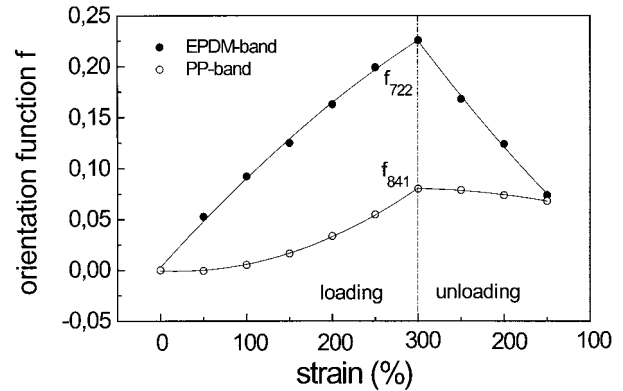


Figure 17 Orientation behavior of the dynamic vulcanizate 1 in cyclic test at high deformation.

sion that during stress relaxation plastic deformation processes in the thermoplastic matrix dissipate the elastically stored energy in the rubber phase.

Loading and Unloading Behavior

Reversibility is a property of high practical importance for dynamic vulcanizates. To quantify this quality, cyclic loading and unloading tests are often used. The study of the change of the orientation function may give essential information about the origin of the reversibility in dynamic vulcanizates.

Figure 17 reveals the orientation behavior of the dynamic vulcanizate EPDM/PP 70/30 in a loading/unloading cycle, where the unloading starts at a strain of 300%. In the loading process, the same phenomena are observed as in the tensile test discussed above. Upon unloading, the orientation function of the rubber phase decreases instantaneously with reversing deformation, while the orientation function of the thermoplastic phase remains nearly constant. After unloading has finished, the orientation of both phases is nearly the same, but the value is higher than is the initial one.

It has already been pointed out that the orientation behavior of the PP phase in tensile loading does not proceed continuously. Above and below the yield point, the orientation obviously takes place in a different manner. The orientation behavior of the dynamic vulcanizate EPDM/PP 70/30 at a low applied strain of 50% is given in Figure 18. Immediately after unloading, a reversing orientation in both phases is observed. In the PP matrix, the orientation function increases while it decreases in the dispersed rubber phase.

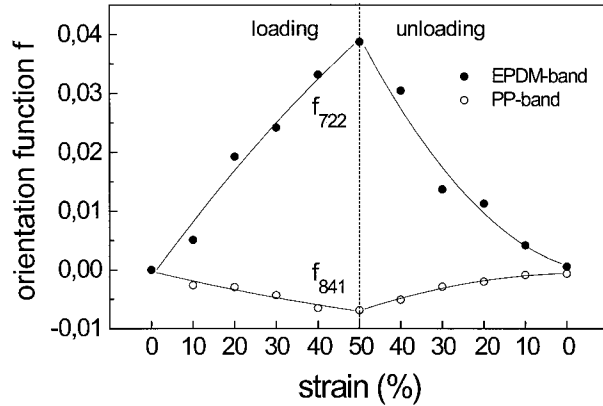


Figure 18 Orientation behavior of the dynamic vulcanizate 1 in cyclic test at low deformation.

Finally, the orientation function arrives at its initial value ($f \approx 0$). The orientation of both phases is completely reversible.

The orientation behavior reflects mainly the mechanical behavior of the pure components of the mixture. An improvement of the reversibility of dynamic vulcanizates would be possible, if the elastically stored energy of the rubber phase could be used to reverse the orientation in the thermoplastic matrix. Basic requirements therefore are an intensive phase coupling and an optimized morphology.

MODEL OF THE DEFORMATION BEHAVIOR OF DYNAMIC VULCANIZATES

A simple mechanical model to explain the deformation behavior of dynamic vulcanizates based on the Takayanagi model is illustrated in Figure 19.²⁰ Because the tensile stress concentration in the PP phase near the equator of the EPDM particles is significantly higher than at the poles, the fraction of the plastically deformed PP in the ligament perpendicular to the draw direction is significantly smaller than is the fraction in the ligament parallel to the draw direction. These proportions are represented by the size of PP boxes 1 and 2 in Figure 19, respectively. At low applied strains ($\epsilon \leq 50\%$), the deformation behavior is determined predominantly by the parallel model in Figure 19(a). The deformation of the PP phase is characterized by a reversible deformation of box 2, while box 1 does not contribute to the total deformation of the matrix. The orientation occurring by the deformation process in both phases is recovered completely upon unloading. At higher

applied strains, the series model in Figure 19(b) becomes predominant. With nearly the same stress in both phases, the deformation concentrates mainly on the EPDM phase owing to its lower Young's modulus. Therefore, in comparison to the pure components in dynamic vulcanizates, the orientation function in the PP phase is lower, and in the EPDM phase, it is higher. A plastic deformation in the PP phase takes place in box 2, whereas in box 1 a reversible deformation still occurs. Upon unloading, the deformation of box 2 prevents a recovery of the PP phase, which limits the recovery of dynamic vulcanizates. By means of the series model, the relaxation behavior of dynamic vulcanizates can be explained successfully. The decreasing orientation in the EPDM phase by a constant applied strain corresponds to the increasing orientation in the PP phase due to plastic deformation processes.

CONCLUSIONS

The deformation behavior of dynamic vulcanizates is the result of the phenomena in the thermoplastic and the rubber phase. The FTIR spectroscopy investigations showed the significant difference in the orientation behavior of the PP and the EPDM phase. In the rubber phase, an elastic deformation process takes place. Thus, the orientation function increases and decreases continuously with the applied strain. In the thermoplastic phase, the deformation process is characterized by two different deformation mechanisms. At strains below the yield point, a reversible interla-

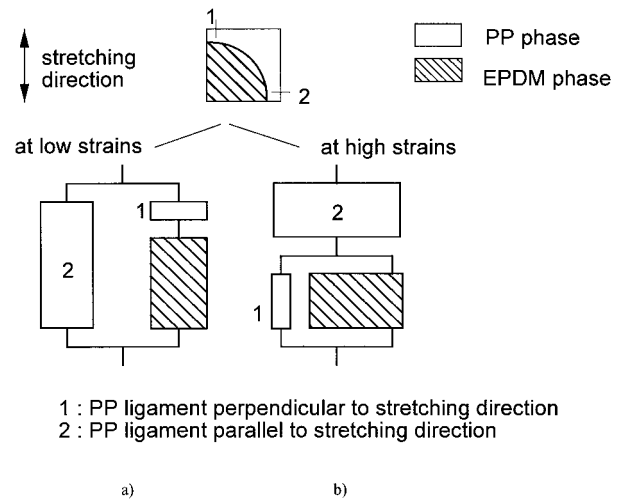


Figure 19 Analytical model to describe the deformation behavior of dynamic vulcanizates.

mellar shear process predominant. The lamellae constituting the deformation units rotate reversibly around their axis and align parallel to the draw direction. It leads to a decrease of the orientation function with increasing strain. Above the yield point, an intralamellar deformation process predominates. Single chains as deformation units slip past each other and orient irreversibly parallel to the draw direction, so that the orientation function increases. The change of the deformation mechanism in the thermoplastic phase from lamella to chain slip is characterized by a minimum in the orientation function curve.

At low strains ($\epsilon \leq 50\%$), the deformation behavior of dynamic vulcanizates may be described preferably by the parallel rule like the model in Figure 19(a), which explains a rubberlike reversibility. At high strains, the series rule according to the model in Figure 19(b) becomes predominant, and because of the plastic deformation of the matrix, the reversibility of dynamic vulcanizates decreases. The change from the parallel to the series model does not require the exchange of the morphology; it arises from the increasing plastic deformation of the thermoplastic phase.

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