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Characterization of Deformation Behavior of Heterogeneous Polymer Systems Using Spectroscopic and Microscopic Methods

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Summary: Rheo-optical Fourier-transform infrared (FTIR) spectroscopy in combination with Atomic Force Microscopy (AFM) was used to clarify the correlation between the morphology and the mechanical properties of two groups of heterogeneous polymers: different styrene-*block*-butadiene-*block*-styrene triblock copolymers and a dynamic vulcanizate based on polypropylene/ethylene-octene-copolymer. In all the polymers investigated the soft phase always oriented more than the hard phase. The degree of orientation in different phases depended on the nature of the phases as well as on the stress distribution in correlation to the morphology and their alignment. The observations at the molecular level corresponded well with the results from morphological studies at the microscopic level, which, in fact, enables an extensive and complex understanding of the structure-properties correlation of these types of polymers.

Introduction

Heterogeneous systems consisting of different polymers often contain two characteristic phases: the soft phase with lower glass transition temperature T_G which is responsible for the low-temperature behavior and the long-time properties of the material and the hard phase with a higher T_G and/or a melting point which determines the short-time properties and the processibility. Heterogeneous polymers can be produced by melt-mixing different homopolymers or by direct synthesis of block or graft copolymers. In this way, some specific synergetic properties can be reached due to a certain degree of incompatibility of the components.

A group of thermoplastic elastomers can be effectively produced by dynamic vulcanization and is called dynamic vulcanizate (DV). Dynamic vulcanization is the process of selective vulcanizing of a rubber during its melt-mixing with a thermoplastic.[1,2] A suitable combination can be selected based on the properties of the individual elastomeric and

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thermoplastic components. The product typically possesses a morphology of vulcanized rubber particles dispersed in the thermoplastic matrix and shows a mechanical behavior similar to vulcanized rubber at ambient temperature and a thermoplastic processibility at higher temperatures.[3,4] In contrast, block copolymers are synthesized in an intentional manner through the variation of the polymerization conditions for example by the control of molecular weight, polydispersity, molecular architecture or phase transition.[5,6] Due to the covalent junctions constituent segments do not segregate at the macroscopic level, but at sufficiently small polydispersity they arrange rather into periodic microscopic domains.[7,8]
The understanding of the correlation between the morphology and the mechanical properties of heterogeneous polymers is still the object of intensive study both from an academic and an industrial point of view. It should be the first relevant stage which enables production of new polymers with specifically selected mechanical properties. Thus, the deformation behavior of these materials has been extensively investigated by means of various methods classified at different levels such as macroscopic, microscopic or molecular (Figure 1). But a more effective way to characterize the deformation mechanisms can be arrived by combining different methods since the results can be completed or be supplementary to each other in conjunction with taking of advantage of the individual methods.

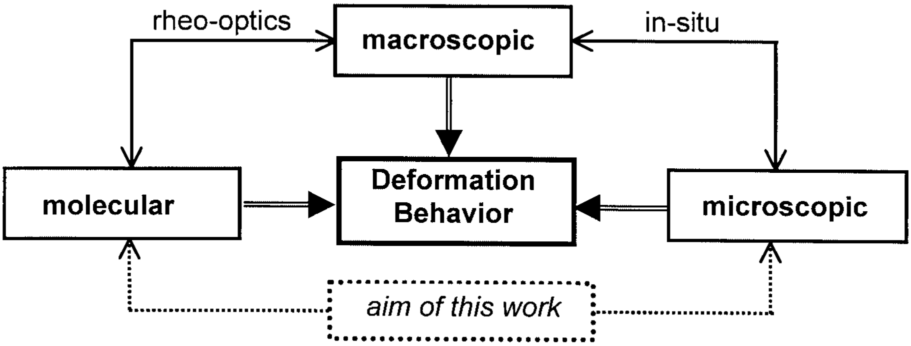


Figure 1. Methods to investigate the deformation behavior of polymers,

Generally, tests at the macroscopic level such as tensile tests, creep tests, relaxation tests or hysteresis tests provide the bulk properties of materials with ultimate characteristic values. At the microscopic level several techniques have been applied to visualize changes of structural details as well as to investigate micromechanical processes. Tests at the molecular level using spectroscopic or scattering methods can be applied to directly obtain data on chain conformations during deformation processes. A combination of molecular and macroscopic investigations by rheo-optical methods, as well as the combination of microscopic and macroscopic investigations in in-situ measurements, have made important progress in polymer research, and are already documented in detail in uncountable publications. In this paper, the methods of investigating the deformation mechanisms in separate phases of selected polymers using the rheo-optical Fourier–transform infrared (FTIR) spectroscopy (molecular method) in combination with the atomic force microscopy (AFM) (microscopic method) will be used. The macroscopic mechanical behavior will firstly be characterized by the use of two standard methods: the tensile test and the loading-unloading cycle test. These combinations enable an extensive and complex understanding of the correlation between the structure and the properties of complicated but useful heterogeneous polymers with different phase characteristies.

Experimental

Materials

To investigate the deformation behavior of heterogeneous polymers three different materials were used. Some important characteristics of the polymers covered in this work are listed in Figure 2. Two poly(styrene-*block*-butadiene-*block*-styrene) triblock copolymers (SBS) with linear molecular architecture were used: SBS1 and SBS2. SBS1 possesses approximately 74 vol. % of polystyrene (PS) and 26% vol. % of polybutadiene (PB), respectively, and has highly asymmetric styrene end blocks with tapered block transition. SBS2 contains 65 vol. % styrene and instead of a butadiene middle block a styrene-butadiene copolymer (SB) was built. However, in this material the outer styrene blocks only amount to 32% volume fraction. The number-average molecular weight M_n for SBS1 and SBS2 is 93000 g/mol and 116000g/mol, respectively, and the polydispersity is 1.13 and 1.20, respectively. The dynamic vulcanizate (DV) was prepared based on polypropylene (PP, Daplen KFC 2008, Borealis AG) and ethylene-octene-copolymer (EOC, Engage 8100, DOW Chemical) containing a thermoplastic/rubber ratio of 30/70 wt%. Cross-linking of the rubber phase was realized by a peroxide. The mixing procedure has been described in detail in the other publication.[9]

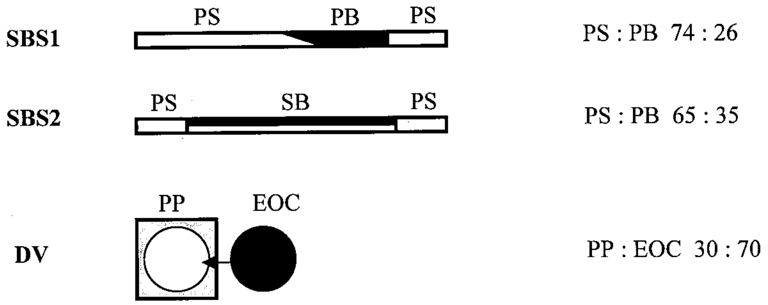


Figure 2. Characteristics of the SBS block copolymers and the dynamic vulcanizate investigated, ▭■ sharp interface, ▭◣■ tapered interface.

Sample preparation

The block copolymer samples SBS1 and SBS2 were prepared by solution casting. For this purpose, films approximately 50 μm thick were prepared from a 3% solution of the sample in toluene by slowly evaporating the solvent over two weeks followed by vacuum drying. Finally, the samples were annealed for 48 hours at a temperature of 120 °C under reduced pressure. In this way, a well-defined morphology close to equilibrium was expected. The dynamic vulcanizate was firstly manufactured by a twin-screw extruder in form of pellets which were then compression-molded at 180 °C for 3 min using a laboratory compression molding device (Perkin Elmer). Films with the thickness of about 50 μm were produced and then air-cooled. Samples with dimensions 20 mm × 10 mm × 0.05 mm were cut for FTIR spectroscopy from the molded sheets and solution cast films.

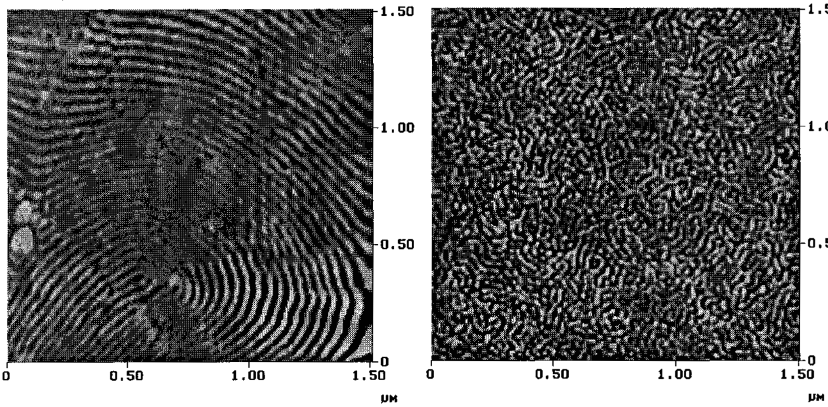
Measurement

FTIR investigations were carried out on a Bruker IFS 88 FTIR spectrometer. The spectrum examined covered the range from 4000 to 600 cm^{-1}. A total of 10 scans per second were recorded at 4 cm^{-1} resolution. A stretching machine developed by Siesler[10] was placed into the sample compartment of the spectrometer. During the mechanical treatment, interferograms were taken at small time/strain intervals with radiation polarized alternatively parallel and then perpendicular to the draw direction. The interferograms were transformed to conventional data upon completion of the experiment. Two modes were employed in the rheo-optical experiments. In the tensile tests, the samples were uniaxially stretched at constant strain rate ($\dot{\varepsilon} = 0.115\ s^{-1}$) at room temperature up to breaking point. In the cycle tests, the reversal points were chosen at strains of ε = 20%, 40%, 60 %, 80%, 100%, 150 %, 200% and 250%. The polymer film under investigation was stretched at a constant strain rate to predetermined strains fixed at the outset of the experiments, returned to the original position (i.e. the bottom reversal points) and then stretched again to the upper reversal points, returned again and so on.

Morphological investigations were carried out by means of an AFM (Multimode atomic force microscope, Digital Instruments Inc.). The AFM investigations were operated in tapping mode (phase signals) using silicon cantilevers with a resonant frequency of about 300 kHz and a spring constant 15N/m. Height and phase data were collected simultaneously. For the micromechanical investigations, the samples were first stretched outside the microscope and then mounted onto the sample holder of the microscope.

Sample characterization

The morphologies of the SBS block copolymers and dynamic vulcanizate investigated are shown in Figures 3 and 4. Under moderate and hard tapping forces the soft and hard domains appear dark and bright, respectively, in the AFM images. Thus, in these figures the bright domains reveal the PS phase in SBS block copolymers and the PP phase in DV, respectively; and the dark domains reveal the PB phase in SBS block copolymers and the EOC phase in DV, respectively.



a) SBS1 b) SBS2

Figure 3. Morphology of the block copolymers investigated, dark: soft phase (PB), bright: hard phase (PS).

In spite of similar chemical composition (approximately 70 vol % PS), a significantly different morphology can be observed among the SBS block copolymers. While SBS1 possesses an alternating PS/PB lamellar structure with a lamellar thickness being approximately 20 nm (Fig. 3a), SBS2 shows a complex morphology with disordered hard domains (cylindrical or spherical) in the soft matrix (Fig. 3b, domain periodicity is about 37 nm). It was found that the morphology of these SBS triblock copolymers does not match the classical phase diagram of SB diblock copolymers[5,11] according to Leibler's theory of microphase separation in block copolymers.[12] Hence, the phase diagram of SBS block copolymers can be strongly influenced by the modification of the interfacial structure and the molecular architecture.[13,14] The hard/soft volume ratio in SBS triblock copolymers can be adjusted by interfacial or architecture modification which, in turn, results in different morphologies.

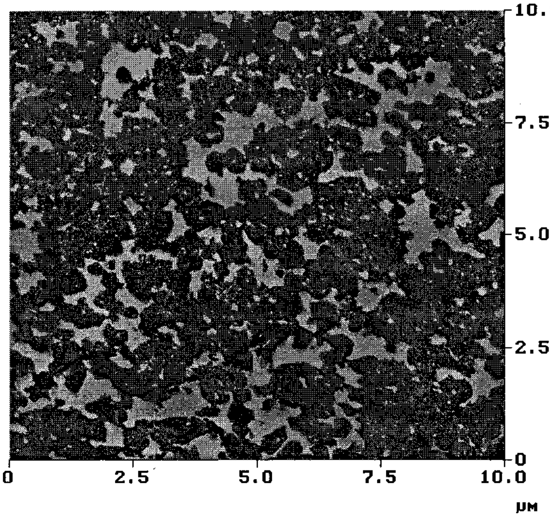


Figure 4. Morphology of the dynamic vulcanizate, dark: soft phase (EOC), bright: hard phase (PP).

Although the rubber content exceeds that of the thermoplastic, in the dynamic vulcanizate a morphology of EOC particles with an average diameter of under 1 μm can be clearly seen finely distributed in the PP matrix in Figure 4. The distance between the particles was very small compared to the particle size. Furthermore, in the rubber particles a few thermoplastic domains could be detected which are intended to act as reinforcing fillers to improve the mechanical behavior of this phase compared to common vulcanized elastomers. This peculiar morphology of DV is caused by the in situ dynamic vulcanization of the rubber phase during the mixing process, leading to a drastic increase in its viscosity. The high shear and elongational forces and temperature conditions also cause the vulcanized rubber phase to break into small particles.[3,15] This means that a co-continuous morphology is transformed into a particle-matrix structure resulting from the physical blending of the rubber and the thermoplastic in conjunction with chemical cross-linking.

By FTIR investigations, using the ratio of the absorbances from beams polarized parallel ($A_{//}$) and perpendicular ($A_{\perp}$) to the deformation direction (draw direction), the dichroic ratio $R = A_{//}/A_{\perp}$ and the degree of orientation *f* is calculated by :

$$f = \frac{R-1}{R+2} \cdot \frac{R_0+2}{R_0-1} \qquad (1)$$

where $R_0 = 2\cot^2\psi$ is the dichroic ratio for perfectly aligned chains oriented parallel to the deformation direction and ψ is the angle between the direction of the vibrational transition moment and the polymer chain axis. Thus, if the transition moment angle is known the degree of orientation may be easily quantified.

For the quantitative characterization of chain alignment during the deformation process the bands at 1493 cm^{-1} and 966 cm^{-1} were selected for the PS phase and the PB phase, respectively, in the SBS block copolymers. The band at 1493 cm^{-1} was assigned to an in-plane phenyl ring deformation mode ν_{19A},[16] its transition moment angle was observed to be perpendicular to the chain axis.[17] The band at 966 cm^{-1} was assigned to an out-of-plane CH bending mode in *trans*-1,4-butadiene,[18] its transition moment angle was also observed to be roughly perpendicular to the chain axis.[19] For the dynamic vulcanizate the band at 841 cm^{-1} for the PP phase and the band at 722 cm^{-1} for the EOC phase were selected. The corresponding transition moment angles were 0° and 90°, respectively.[20,21] The 841 cm^{-1} band was variously assigned to C-C stretching, to C-CH_3 stretching and to CH_2 rocking in the crystalline phase of PP.[22] The 722 cm^{-1} band was assigned to CH_2 rocking in the ethylene segments of EOC.[18]

Results and discussion

In Figure 5 the deformation behavior obtained from the rheo-optical FTIR spectroscopy of SBS1 is shown in full. The orientation effects for both the phases (PS and PB) can be detected separately by using this technique. The stress-strain diagram provides information about the macroscopic deformation. In this case, because of the necking process occurring during the stretching of the specimen the stress-strain curve does not exactly correspond to the orientation-strain curve since the degree of orientation investigated represents only the average values. However, the deformation is in no way homogeneous and the necking zone can be localized either from inside or outside or from both inside and outside the measurement windows (i.e. the IR radiation flow).

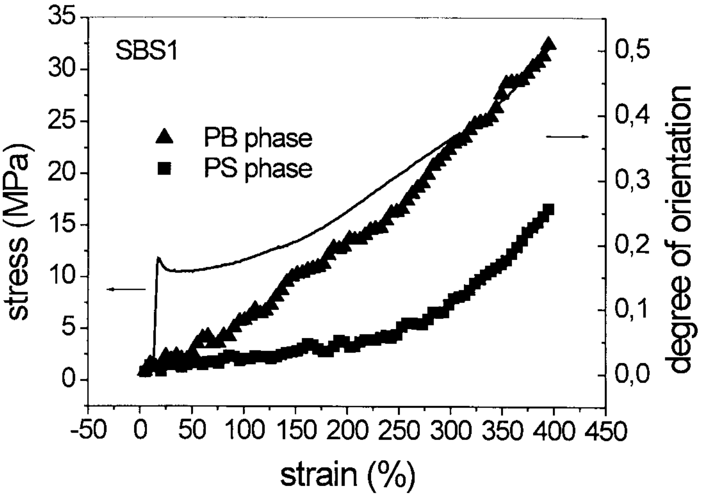


Figure 5. The deformation behavior of SBS1 observed at the macroscopic and molecular levels.

It is obvious that in this block copolymer the soft phase orients more than the hard phase. This is caused by the lower Young's modulus of the PB phase compared to the PS phase by appropriate stress distribution within the specimen during deformation. Usually, in SBS 1 the lamellar structure at first enables an equivalent stress distribution in both the PS and PB phases. But due to its lower Young's modulus the soft phase can respond to the macroscopic load earlier and therefore the PB chains orient more quickly and to a greater extent than the PS chains. In the hard phase, the PS chains remain unoriented at first. Only once about 100% applied strain is reached, the PS chains orient significantly with increasing strains.

Figure 6 reveals the orientation behavior of SBS2. The graph is plotted in half logarithms in order to observe the more important behavior in the individual phases at small deformation. In agreement with the graph in Fig. 5, the higher orientation in the PB phase compared to that of the PS phase can be confirmed. In SBS2 the soft phase forms the matrix and in addition to the effect of its lower Young's modulus it promotes the reception of the given stress in this phase. Consequently, the PB chains already show a remarkably high degree of orientation at small strains. In contrast, PS chains exhibit only very low orientation during the whole deformation process (see the insert plotted in the other logarithmical scale). It is interesting to mention that the matrix of SBS2 contains not only butadiene sequences but also styrene sequences (see Fig. 2) which are miscible in the soft phase. Monnerie and coworkers[23,24] investigated intensively the orientation behavior of individual phases in a series of miscible polymer blends. Their results pointed out that in spite of the compatible nature of these blends, chains in individual phases can still orient in a different way. Thus, the degree of orientation of the PS phase estimated quantitatively is actually the average values of both the PS chains in the pure PS domains and the PS chains in the SB soft phase. One possibility to discriminate the orientation behavior of these types of PS chains may be realized by the deuteration of the PS end blocks, which will lead to a shifting of some of the characteristic frequency of their absorption bands compared to that of the undeuterated ones.

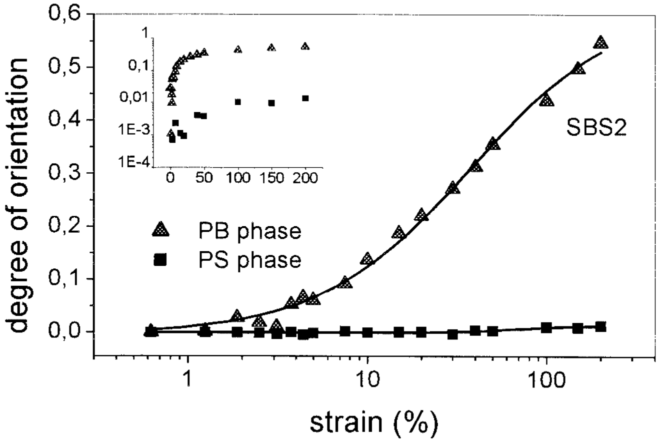


Figure 6. The orientation behavior of SBS2.

Furthermore, at the reference temperature (room temperature) the PB chains are in the entropy elastic state and can relax very well during the stretching process whereas the PS chains are expected to remain inflexible, because they still remain in the glassy state. Recently, it was established by 2D-IR spectroscopy, for example, that in ABS materials the PB chains can relax entirely independently from the SAN matrix.[25] Hence, it would be expected that if the time resolution is minimized the orientation in the PB phase would be differentiated to a greater extent than that of the PS phase.

The higher orientation of the PB phase compared to the PS phase can be illustrated by the morphological investigations. In the SBS block copolymers with lamellar structure it was shown that the deformation of the lamellae strongly depended on the alignment of the lamellae relative to the stretching direction[11,26] as well as on the thickness of the lamellae.[27] The morphology of the SBS1 sample deformed in the tensile test is shown in Figures 7 to 9 each showing the different lamellar alignment. The sample was stretched well above the yield point before being imaged, i.e. the sample underwent plastic deformation. In the pictures the stretching direction is indicated by the arrow and some interesting locations are marked with white ellipses.

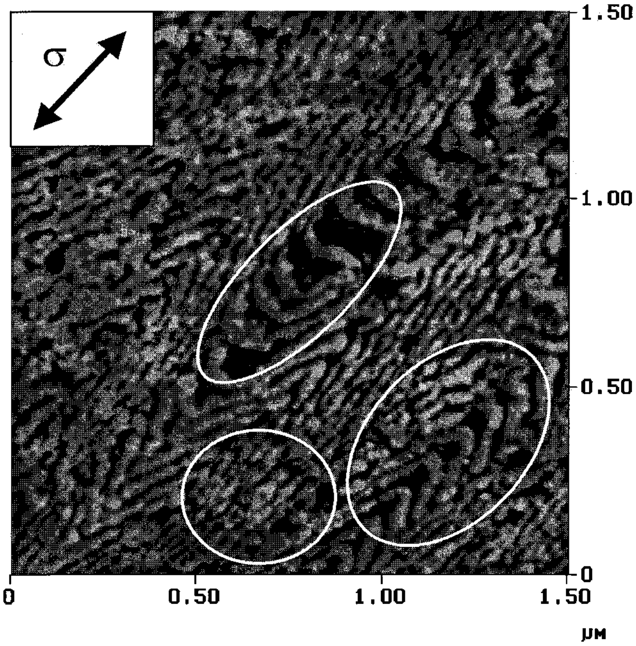


Figure 7. Micromechanical deformation of lamellae in SBS1 randomly aligned to the draw direction.

For the most randomly aligned lamellae in SBS1, at high deformation a chevron fold-like morphology can be seen in Figure 7. The deformation mechanism has already been theoretically and experimentally interpreted in different block copolymers[28] having lamellar or (rigid) cylindrical morphology[29] using different investigation methods such as TEM or SAXS. As shown in this figure, the deformed lamellae have been aligned strongly in the deformation direction indicating the rotation of the lamellae towards the draw direction. Disruptions in the PS lamellae can be detected in some places. Furthermore, the widening of the PB layers observed in other places indicates dilation due to tensile stress which results in higher orientation of the PB phase.

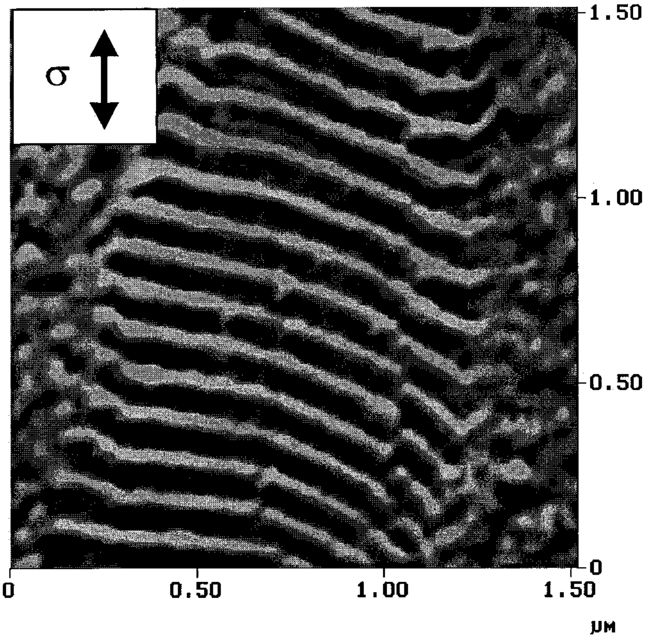


Figure 8. Micromechanical deformation of lamellae in SBS1 aligned perpendicular to the draw direction.

The phenomena of widening of the PB phase can be explicitly explained if the lamellae lie perpendicular to the draw direction as shown in Figure 8. This situation provides a favorable stress field for the orientation of the chains occurring across the lamellae, i.e. parallel to the draw direction. It is obvious that the thickness of the PB lamellae exceeds that of the PS lamellae indicating a higher local deformation of the PB phase compared to the PS phase corresponding well with the results of FTIR investigations. In this context the PB chains revealed very extensive elongation as a result of their high extensibility between a network of rigid PS junctions. Assuming a linear correlation between degree of orientation and strain in the rubber network[30] of some heterogeneous polymers, for example dynamical vulcanizes, the average internal strain in the soft phase can exceed the applied strain, which leads to a higher degree of orientation in this phase compared to that in the pure rubber with equivalent macroscopic strains.[31]

In the case of the lamellae aligned parallel to the draw direction, assuming the same thickness for PS and PB lamellae in an undeformed state (see Fig. 3a), we can see a distinct difference in the deformed state as shown in Fig. 9. This can be explained by a new deformation mechanism called “hard layer slipping”.[32] According to this mechanism, in the initial state of deformation the PS lamellae can slightly slip towards each other without significant distortion at the expense of the high extensibility of the PB lamellae. Owing to the higher Poisson’s ratio of the soft phase compared to that of the hard phase, the PB layers appear clearly thinner than the PS layers. Moreover, at higher deformation the PS lamellae are fragmented into smaller domains, which are ordered in series to give a lamellar structure again. This kind of plastic deformations of the hard phase provides an explanation for the extensive stress softening of the block copolymer connected with the neck formation and drawing of the specimens.

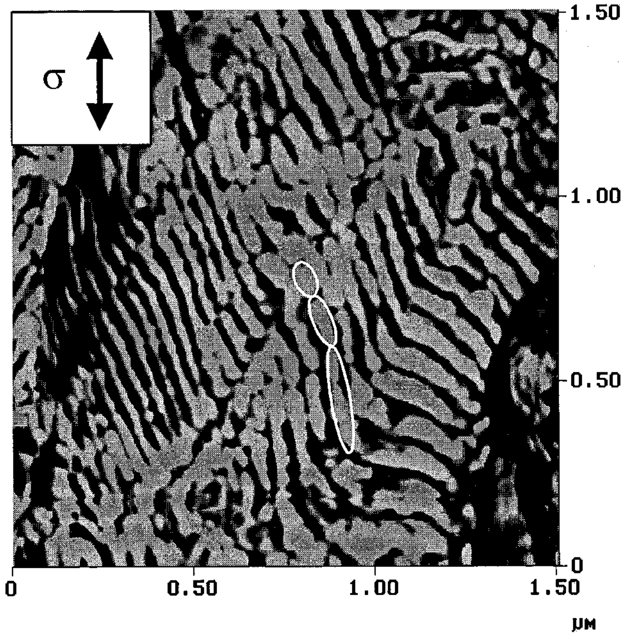


Figure 9. Micromechanical deformation of lamellae in SBS1 aligned parallel to the draw direction.

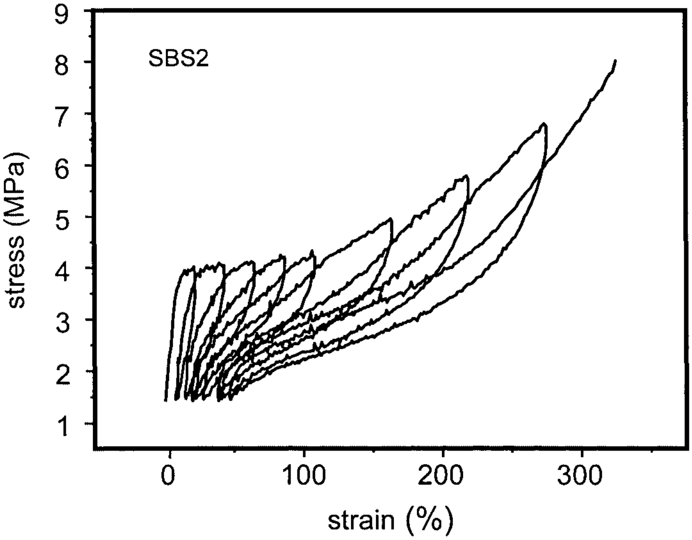


Figure 10. Stress-strain diagram taken during loading-unloading cycles of SBS2.

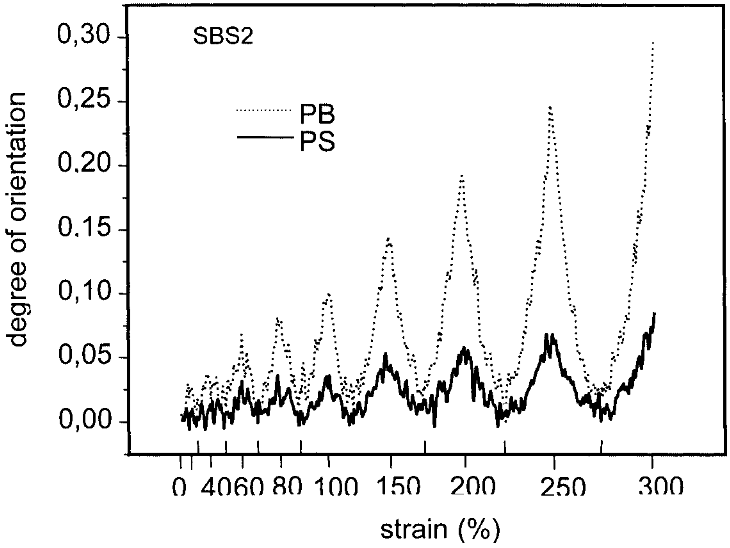


Figure 11. Orientation-strain diagram for the hard and soft segments of SBS2 in the loading-unloading test.

Generally, the structural changes taking place in any stretching process (for example, the conformational changes of chains or morphological changes) can be effectively represented by hysteresis experiments because phenomena in the unloading part reflect what actually happened in the loaded state. Therefore, in our stepped cycle test we did not need to change the specimen. Different levels of deformation including strain-recovery were detected, leading to a clear view of the deformation processes. Figure 10 shows the stress-strain diagrams for successive loading-unloading cycles for SBS2. The orientation-strain plot recorded during the rheo-optical tests corresponding to this mechanical treatment is shown in Figure 11. Obviously both Figures 10 and 11 demonstrate the very good reversibility of this block copolymer. Here, the low residual strains observed in the macroscopic scale can be explained by the reversible orientation in both the hard and soft phase in the molecular scale.

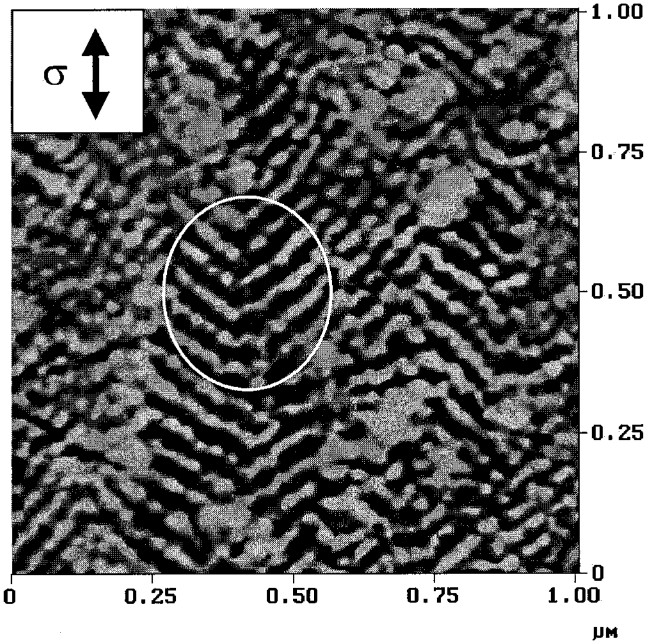


Figure 12. Morphology of SBS2 at high deformation with part chevron structure.

In SBS2 the rubbery matrix gives the elastic behavior, while the PS phase functions both as physical crosslinks and reinforcing fillers. This morphology consequently enables only a small change in the PS phase with respect to the molecular orientation. Nevertheless, careful

AFM investigation reveals the distortion of the original domain structure of SBS2 at high deformation with about 100% strain (Figure 12). The image was collected as the sample was fixed in the strained state. The cylinder-like domains are partly broken down and partly organized in a chevron-like fashion. With increasing strain, however, the population of chevron morphology was found to decrease which is connected to the fragmentation of cylinders with higher deformation.[33]

On unloading the sample, however, the morphology is almost completely restored as shown clearly in Figure 13 as the result of the high reversibility of this material with only local plastic deformation in the dispersed domains (fragmentation of glassy cylinders). That means, in the unloaded state the rubber network-like structure can be rapidly and effectively healed up by low distortion of the structure especially in the matrix.

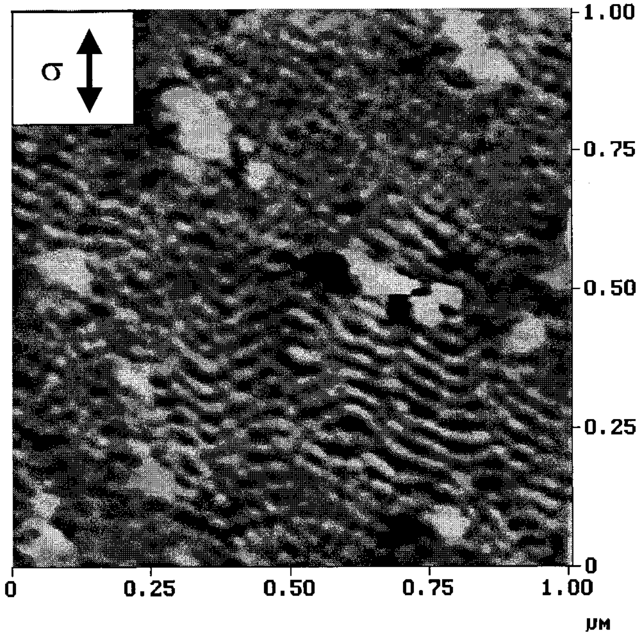


Figure 13. The morphology of SBS2 after deformation in the unloaded state.

In Figure 14 the stress-strain curve of the dynamic vulcanizate is demonstrated. Although the matrix consisted of a ductile thermoplastic polymer (PP) the dynamic vulcanizate exhibits large reversibility and small residual strain. To clarify the elastic behavior of this thermoplastic elastomer several models have been suggested in literature.[34-37] In general, the strain recovery of dynamic vulcanizates may originate, on the one hand, partly from the altered structure of the thermoplastic matrix. For example, PP itself in DV is expected to be less ductile and more elastomeric than pure PP due to the rather fragmented crystallites caused by the presence of rubber domains embedded in the PP phase during the dynamic vulcanization. On the other hand the low stress evolved in the ductile matrix, especially in the ligament matrix between rubber particles in the stretching direction, is preserved locally within an elastic limit and it acts as an adhesive formed during the deformation for interconnecting the rubber particles. Again, the volumetric strain of rubber particles with high Poisson's ratio provides the contracting stress to heal up the plastically deformed thermoplastic phase outside the ligament matrix.

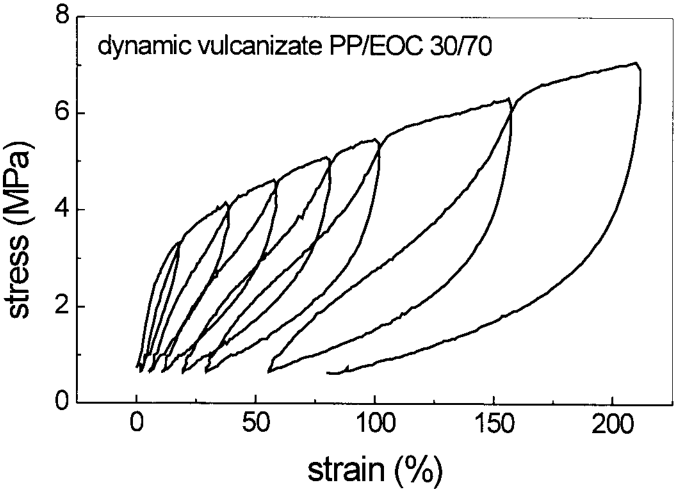


Figure 14. Stress-strain diagram taken during loading-unloading cycles of the dynamic vulcanizate.

Figure 15 reveals the orientation-strain diagram of the DV investigated in the stepped cycle test. Like the results for both the SBS block copolymers discussed above, the higher orientation of the soft phase compared to the hard phase can be clearly seen. The peculiarity in this case is, however, that the orientation of the dispersed phase (EOC) is stronger than that of the matrix (PP). This is caused by a heterogeneous deformation in the thermoplastic phase due to local stress differences. According to the calculations reported in the literature,[34-36, 38] the stress concentration in the thermoplastic phase reaches its maximum at the equatorial zones of the rubber particle leading to plastic deformation in these regions during the first state of deformation. In contrast, in the polar regions the compressive stress is predominant in the matrix and the PP phase still remains within its elastic limit corresponding to the schematic plot in Figure 16. Thus, the plastic deformation in the thermoplastic matrix occurs only locally and it dominates the deformation profile if the specimen is stretched above its yield point. Therefore, after straining the sample beyond its yield point (about 50%) the orientation of both phases by unloading becomes significantly higher and the material becomes more irreversible. In a recent publication[39] it has been shown that the irreversibility of dynamic vulcanizates is caused by the plastic deformation of the matrix indicating a high degree of orientation in both hard and soft phases in the unloaded state.

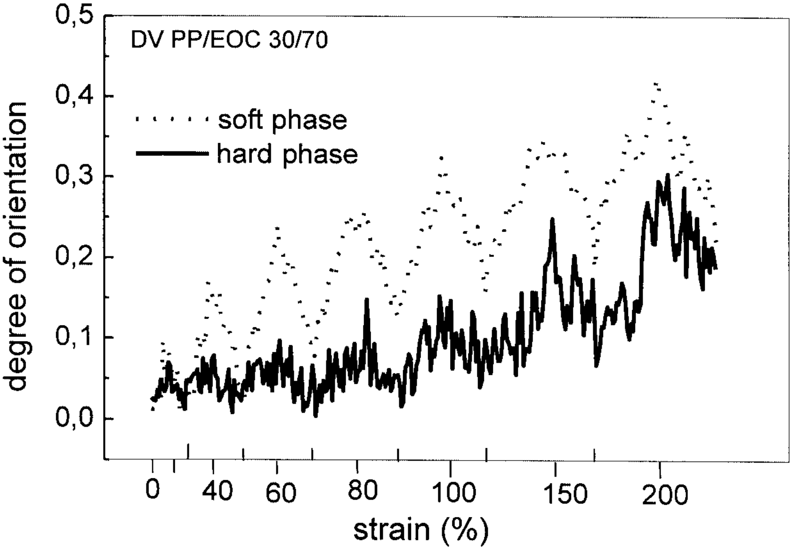


Figure 15. Orientation-strain diagram for the hard and the soft phase of DV in the loading-unloading test.

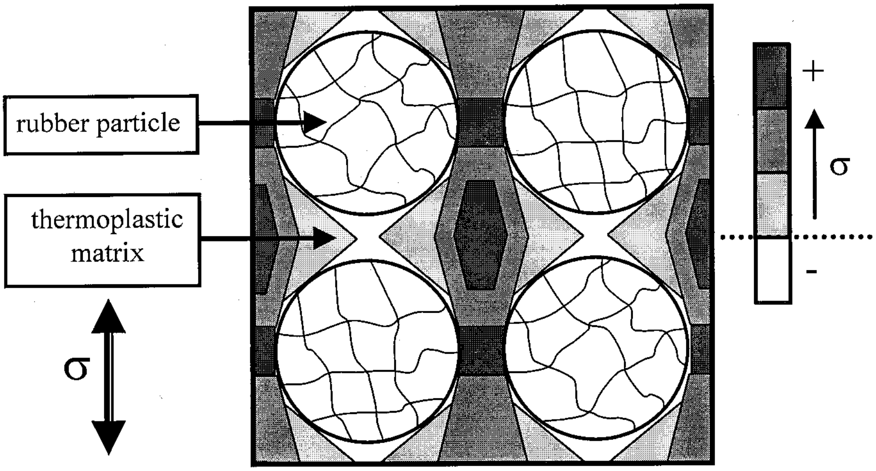


Figure 16. Contour plot of the stress distribution in the matrix of DV calculated by FEM method (schematic).

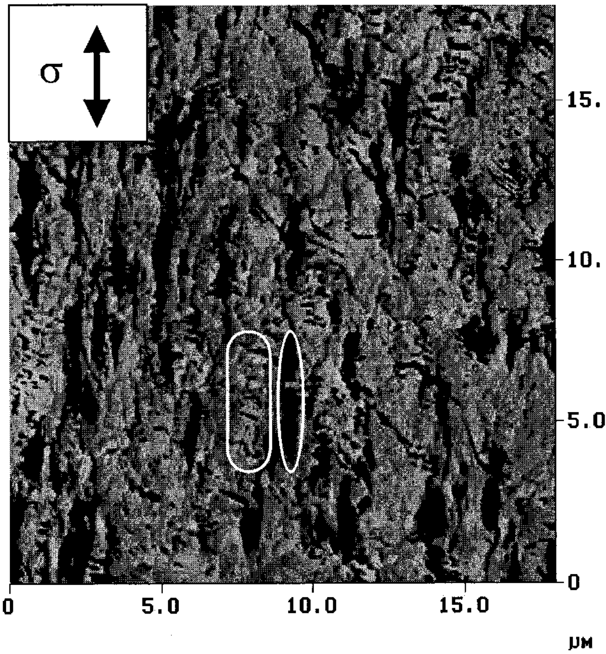


Figure 17. The morphology of the DV after deformation in the unloaded state.

To explain the irreversibility of the dynamic vulcanizate, we investigated its morphology after high deformation (about 300%) following a relaxation process removing the load. The morphology is shown in Figure 17. On loading the sample the rubber particles were elongated along the stretching direction. It is obvious that these elongated particles kept their shape even after removal of load. In the thermoplastic matrix several damaged zones could be imaged by the AFM, which, in fact, limit the elastic recovery of the soft phase as well as of the entire material. Hence, the topology changes caused by the stretching procedure could be healed up, but in this case the original structure could not be maintained because of the long relaxation time of the thermoplastic at room temperature which reduces the reversibility of this material. After relaxation for a long time (e.g. several months at room temperature) without stress dynamic vulcanizates can be healed up and show behavior comparable to that of undeformed DV.[40]

Conclusions

The heterogeneous polymers investigated (SBS block copolymers and dynamic vulcanizate) reveal different mechanical behavior depending on their morphology. Independent of the morphology of these materials the soft phase always orients more than the hard phase because of its lower Young's modulus. Thus, the external stress is first localized in the rubbery phase leading to a higher internal strain in this phase and as a result a higher degree of orientation can be observed. Unlike the soft phase, the hard phase responds less sensitively towards strain resulting in a lower degree of orientation on average. This is attributed on the one hand to the ductile nature of the thermoplastic and, on the other hand, to the heterogeneous stress distribution with local stress concentration.

Among the block copolymers SBS1 with the alternating PB and PS lamellae structure shows a stress-strain diagram with a pronounced necking zone caused by plastic deformation including the fragmentation of PS lamellae, especially those aligned parallel to the draw direction. Furthermore, for this type of morphology the deformation mechanism is locally different and depends on the alignment of the lamellae relative to the draw direction. Owing to the matrix role in the SBS2 the PB phase can deform very strongly in conjunction with a slow deformation of the PS domains, which in turn gives the SBS2 a very good reversibility.

In the dynamic vulcanizate the different local deformation level in the different phases leads to a significantly lower degree of orientation in the PP phase compared to that in the EOC phase. The plastic deformation of the thermoplastic matrix especially with high deformation is the reason for the irreversible deformation of this material and for it showing an increase in degree of orientation in both phases at the unloading stages. The hard phase is destroyed during the stretching process and does not heal up in a short time leading to decreased reversibility (e.g. increased residual strain) in this material.

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References

[1] A. Y. Coran, R. P. Patel, in: "*Thermoplastic Elastomers*", 2nd ed., G. Holden, N. R. Legge, R. Quirk, H. E. Schroeder, Eds., Carl Hanser Verlag, Munich; Vienna; New York 1996, Chapter 7, p. 153-190.
[2] A. M. Gessler. US Patent 3.037.954 (June 5, 1962).
[3] H.-J. Radusch, T. Pham. *Kautschuk+Gummi Kunststoffe* **1996**, 49, p. 249.
[4] S. Abdou-Sabet, R. C. Puydak, C. P. Rader. *Rubber Chem. Technol.* **1996**, 69, p. 476.
[5] K. Knoll, N. Nießner. *Macromol. Symp.* **1998**, 132, p. 231.
[6] A. J. Ryan, I. W. Hamley, in: "*The Physics of Glassy Polymers*", R. N. Haward, R. J. Young, Eds., Chapman & Hall, London 1997, Chapter 10, p. 451-497.
[7] T. Hashimoto, in "*Thermoplastic Elastomers*", 2nd ed., G. Holden, N.R. Legge, R. Quirk, H.E Schroeder Eds., Carl Hanser Verlag, Munich; Viena; New York 1996, Chapter 15A, p. 429-464.
[8] A. E. Woodward, "*Atlas of Polymer Morphology*", Hanser Publishes, Munich; Vienna; New York 1988.
[9] T. Pham, in: "Polymers in the Third Millennium", Montpellier, September 2001.
[10] H. W. Siesler, Makromol. Chem., Macromol. Symp. **1992**, 53, p. 89
[11] R. Adhikari, PhD Thesis, Martin Luther University Halle-Wittenberg, 2001.
[12] L. Leibler, *Macromolecules* **1980**, 13, p. 1602.
[13] T. A. Huy, L. H. Hai, R. Adhikari, G. H. Michler, in: "Trends und Entwicklungen auf dem Gebiet der Polymerblends", Merseburg, March 2001, Conference Papers, p. 60.
[14] R. Adhikari, G. H. Michler, E. Ivankova, S. Goerlitz, R. Weidisch, R. Godehard, K. Knoll, in: "Trends und Entwicklungen auf dem Gebiet der Polymerblends", Merseburg, March 2001, Conference Papers, p. 43.
[15] T. Pham, PhD Thesis, Martin Luther University Halle-Wittenberg, 1996.
[16] C. Y. Liang, S. Krimm, *J. Polym. Sci.* **1958**, 27, p. 241.

[17] P. C. Painter, S. L. Koenig, *J. Polym. Sci., Polym. Phys. Ed.* **1977**, 15, p. 1885.

[18] J. Dechant, "*Ultrarotspektroskopische Untersuchungen an Polymeren*", Akademie Verlag, Berlin 1972.

[19] S. Sakurai, J. Sakamoto, M. Shibayama, S. Nomura, *Macromolecules* **1993**, 26, p. 3351.

[20] M. Houska, M. Brumell, *Polym. Eng. Sci.* **1987**, 27, p. 917.

[21] S. Onogi, T. Asada, A. Tanaka, *J. Polym. Sci.* **1969**, Part A-2, 7, p. 171.

[22] J. M. Chalmers, M. W. Mackenzie, H. A. Willis, *Spectrochim. Acta* **1991**, A47, p. 1677.

[23] D. Lefebvre, B. Jasse, L. Monnerie, *Polymer* **1984**, 25, p. 318.

[24] J. P. Faivre, B. Jasse, L. Monnerie, *Polymer* **1985**, 26, p. 879.

[25] P. A. M. Steeman, R. J. Meier, A. Simon, J. Gast, *Polymer* **1997**, 38, p. 5455.

[26] I. Yamaoka, M. Kimura, *Polymer* **1993**, 34, p. 4399.

[27] R. Adhikari, G. H. Michler, W. Lebek, S. Goerlitz, R. Weidisch, K. Knoll, *J. Appl. Polym. Sci.* in Press.

[28] Y. Cohen, R. J. Albalak, B. J. Dair, M. S. Capel, E. L. Thomas, *Macromolecules* **2000**, 33, p. 6502.

[29] T. Pakula, K. Saijo, H. Kawai, T. Hashimoto, *Macromolecules* **1985**, 18, p. 1294.

[30] I. Bahar, B.Erman, in: "*Oriented Polymer Materials*", S. Fakirov, Ed., Hüthig & Werf Verlag, Zug Heidelberg Oxford 1996, Chapter 16, p. 467– 482.

[31] T. A. Huy, "*Rheo-optische Charakterisierung des Deformationsverhaltens Dynamischer Vulkanisate*", Shaker Verlag, Aachen 1999.

[32] T. A. Huy, R. Adhikari, G. H. Michler, "Deformation behavior of styrene-block-butadiene-block-styrene triblock copolymers having different morphologies", to be published in *Polymer.*

[33] R. Adhikari, G. H. Michler, T. A. Huy, R. Godehard, "On the deformation behavior of block copolymers with glassy cylinders", to be published in *Colloid Polym. Sci.*

[34] Y. Yang. T. Chiba, H. Saito, T. Inoue, *Polymer* **1998**, 39, p. 3365.

[35] Y. Kikuchi, T. Fukui, T. Okada, T. Inoue, *J. Appl. Polym. Sci., Appl. Polym. Symp.* **1992**, 50, p. 261.

[36] T. Aoyama, A. J. Carlos, H. Saito, T. Inoue, Y. Niitsu, *Polymer* **1999**, 40, 3657.

[37] L. D'Orazio, C. Mancarella, E. Martuscelli, G. Sticotti, R. Ghisellini, *J. Appl. Polym. Sci.* **1994**, 53, p. 387.

[38] G. H. Michler, "*Kunststoff-Mikromechanik*", Carl Hanser Verlag, München; Wien 1992.

[39] T. A. Huy, Th. Lüpke, H.-J. Radusch, *J. Appl. Polym. Sci.* **2001**, 80, p. 148.

[40] T. A. Huy, Th. Lüpke, H.-J. Radusch, *Kautschuk+Gummi Kunststoffe* **2000**, 53, p. 656.